EXTENDED STUDIES OF THE PHOTOCHEMICAL 4,4-DIPHENYL-2-CYCLOHEXEN-1-ONE REARRANGEMENT

By

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REARRANGEMENT

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PREFACE

The synthesis and photochemistry of four cyclic unsaturated systems, structurally related to 4,4-diphenyl-2-cyclohexen-1-one (**1**) is described. These include the 4,4-diphenylcyclohexenone analogs, 10,10-dimethylspiro[anthracene-9(10*H*),1'-[2]cyclohexen]-4'-one (**14**) , 10',11'-dihydrospiro[2-cyclohexene-1,5'-[5*H*]dibenzo[*a*,*d*]cyclohepten]-4-one (**18**), 4,4a,5,6-tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**4**), and *cis*-4,4-diphenyl-2-cyclohepten-1-one (**11**). Spirocyclohexenones **14** and **18** were studied to evaluate the possibility of altering the stereochemical outcome of the photochemical 4,4-diphenyl-2-cyclohexen-1-one rearrangement. The naphthalenone **4** and cycloheptenone **11** were investigated to determine if an extended π-system or a medium ring enone would exhibit similar reactivity to that observed for the parent compound **1**. These studies have provided additional information regarding the mechanism, energetics and general requirements for photochemical aryl migration.

ACKNOWLEDGEMENTS

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Special thanks are due to the bag lady (TWH) for helping me to never lose sight of my priorities. To Craig Jones, who has been my constant source of motivation and emotional support, I give him my love and appreciation. Most importantly, I thank the dear Lord, for providing the strength to endure and the ability to succeed.

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Finally, I wish to dedicate this thesis to my family, my parents Freddie and Gwendola Taylor, and my sisters, Pamela Hamons and Lisa Willis. Their unconditional love, encouragement, and support was essential in attaining this goal.

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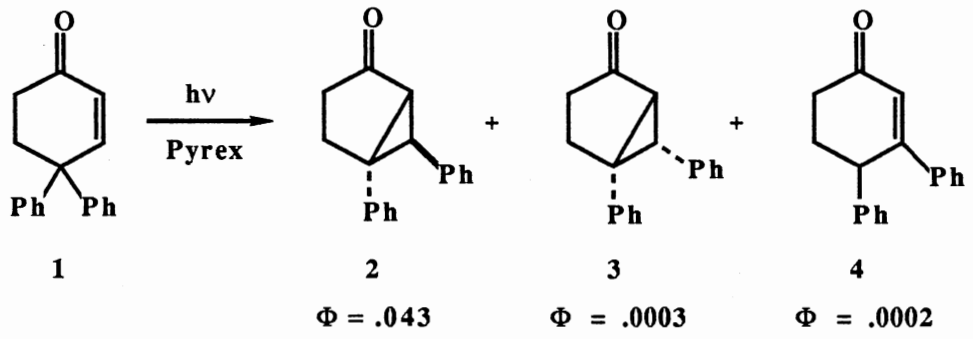
HISTORICAL BACKGROUND: α,β-ENONE PHOTOREARRANGEMENTS

Introduction

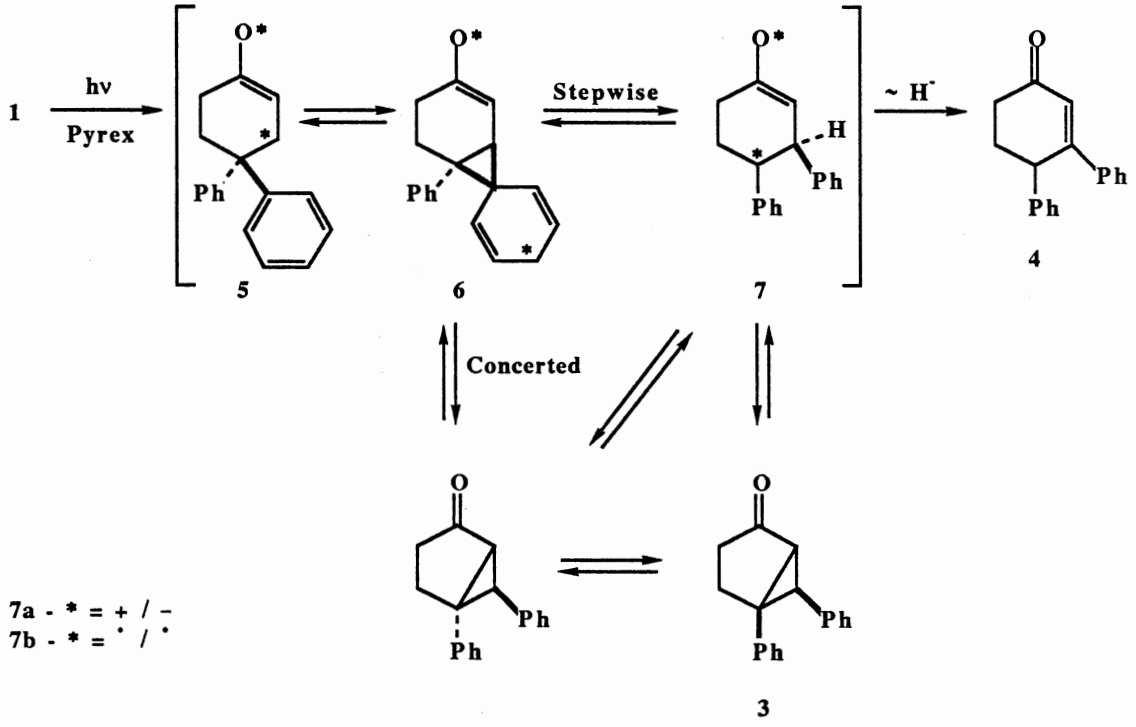
This chapter presents an overview of the photochemical behavior of cyclic α,β-unsaturated ketones. Attention has been focused on the unimolecular rearrangements of five, six, and seven-membered cyclic 4,4-disubstituted α,β-unsaturated enones and linearly conjugated dienone systems. Common rearrangements (aryl migration and Type A) as well as competing photoreactions (inter- and intramolecular cycloadditions, reduction, deconjugation, and [1,3]-sigmatropic shifts) have been discussed in terms of mechanism, reaction efficiency and electronics. Specific examples have been included to illustrate these processes.

Aryl Migration

Photorearrangements of 4,4-diarylcyclohexenones to bicyclo[3.1.0]hexanones have been studied extensively.[1-16] One of the first reported examples of the aryl migration reaction was that of Zimmerman and coworkers on 4,4-diphenyl-2-cyclohexen-1-one (**1**).[1] Irradiation of **1** resulted in the formation of three photoproducts, *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexanone (**2**) and (**3**), and 3,4-diphenyl-2-cyclohexen-1-one (**4**). The formation of the bicyclohexenones was kinetically stereoselective, the trans isomer **2** was formed in preference to the cis isomer **3**, in a ratio of 140:1 at low conversions. The mechanism proposed for the transformation has received much



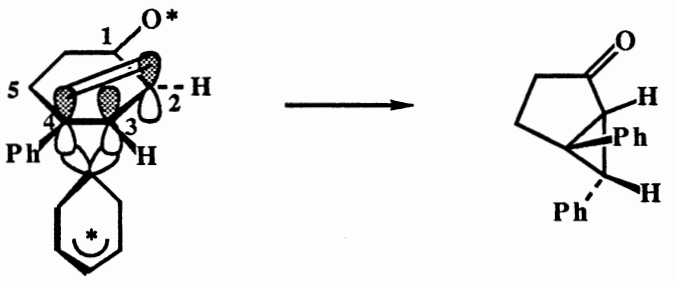
attention and is relatively well understood [1,2] Triplet sensitization and quenching studies indicate the aryl migration reaction proceeds through a n-π^* triplet state (69 kcal/mol). The enone undergoes initial (n-π^*) electronic excitation and intersystem crossing to the triplet. A C-4 aryl group then migrates to the odd electron center at the β-carbon of the excited enone. It has been suggested that it is the pseudo axial phenyl that migrates since its π system is in the proper orientation for overlap with the enone π system. Electron



demotion and three ring formation by either a concerted or stepwise process then generates the bicyclohexenones. Demotion to the ground state prior to complete migration has been suggested by analogy with the nonphotochemically generated zwitterion intermediate observed for related dienone and bicyclic ketone rearrangements.[17,18] Formation of the enone **4** results from hydride migration from C-3 to C-4 in species **7a**.

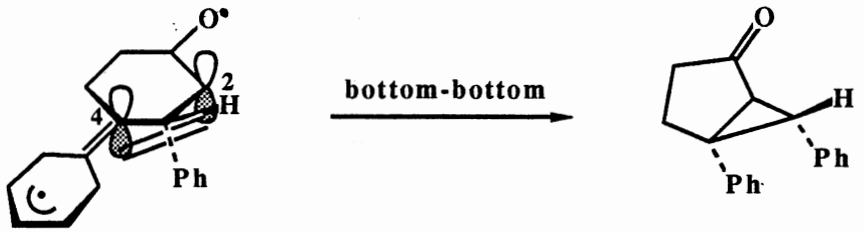
The nature of the excited state species (radical or dipolar) and the sequence in which demotion and migration occurred for the enone system has spawned much discussion.[1,2] Chapman proposed a "polar state concept" to describe the mechanisms of enone photorearrangements.[19] He suggested the involvement of a dipolar species **7a**, without specifying whether the proposed dipolar intermediate was an excited state or a ground state species distinct from starting material. To test the "polar state concept" in the aryl migration mechanism, migratory studies of 4-*p*-cyanophenyl-4-phenyl- and 4-*p*-methoxyphenyl-4-phenylcyclohexenones were carried out by Zimmerman and coworkers.[3,4] These studies revealed a preference for cyanophenyl and anisyl group migration over phenyl migration. This suggested that a dipolar intermediate was not a good representation of the excited state intermediate but that the β-carbon of the excited state exhibited odd electron character. This study also indicated that demotion to ground state could not precede the rate limiting stage of the reaction because a dipolar intermediate would be generated upon demotion and reversal in the selectivity would result.

Preference for the trans diphenyl isomer was originally ascribed to a concerted process with inversion of configuration at C-4 of the enone.[2] This concerted process is illustrated below. When the C-4 phenyl migrates to C-3, an incipient orbital is developed at C-4. Rotation about the C-4-C-5 and C-1-C-2 bonds of the bridged intermediate in a distotatory fashion, allows cyclopropyl bond formation between this incipent orbital at C-4 and the C-2 orbital. This concerted orbital interaction leads exclusively to the trans product. The diradical stepwise process is thought to lead to the cis isomer. Recently, an



2

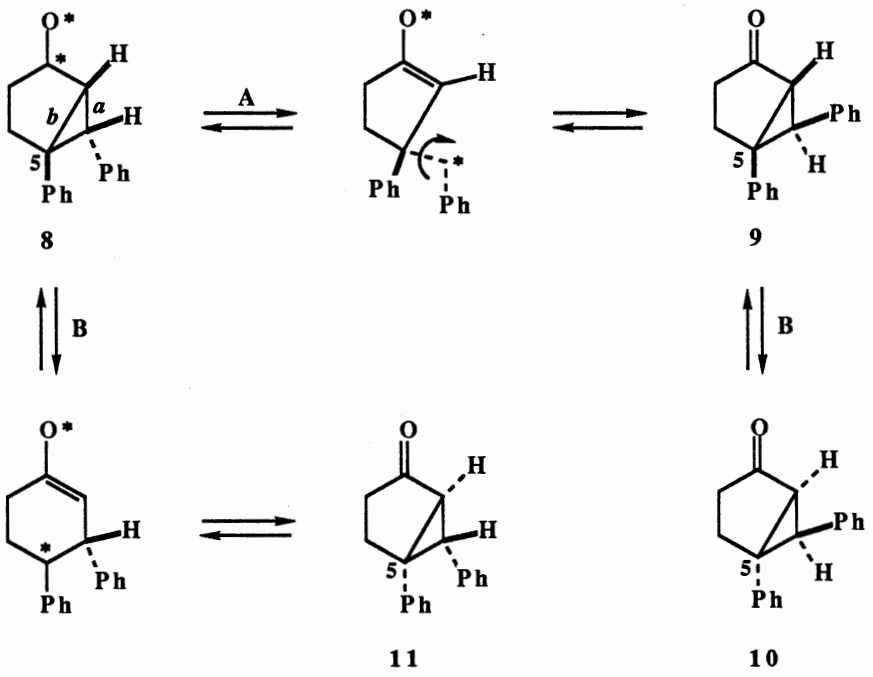
alternative rationale for the trans stereoselectivity was proposed involving preferential closure of the diradical species **7b**.[5-11] The open diradical resulting after migration can form a three-membered ring by overlap of either the bottom-bottom C-2-C-4 orbitals to form the cis isomer **3** or top-top C-2-C-4 orbital overlap to form the trans isomer **2**. The bottom-bottom overlap is thought to be energetically unfavorable since the migrated phenyl at C-3 is in an incipient transoid conformation and must twist past the delocalized and thus fixed phenyl at C-4 to form the cis product.



7b 3

Extended irradiation of 4,4-diphenylcyclohexenone afforded a 43:57 photostationary mixture of the trans:cis isomers.[2] Independent irradiations of the photoproducts **2** and **3**, revealed a photochemical trans to cis interconversion. This accounted for the increasing proportion of the cis isomer seen upon extended irradiation of **1**.[9,10] Two different mechanisms were envisaged for the isomerization, pathway A

and pathway B. In pathway A, fission of the external three ring bond *a* of the trans isomer, followed by rotation and reclosure would give the cis isomer. Alternatively, in pathway B, the internal three ring bond *b* is cleaved, followed by reclosure of the bottom-bottom C-2-C-4 orbitals to generate the cis isomer. Both pathways (A and B) were mechanistically reasonable in that the n-π^* excited state would expect to weaken an adjacent bond. Since the two pathways have different stereochemical implications, differentiation of the two pathways was easily accomplished. By starting with one



enantiomer of the trans bicyclohexanone, two cis enantiomers of product were possible. Depending on which cis enantiomer was produced, one could tell which pathway was followed. Irradiation of the optically active trans-bicyclic ketone **8** gave the cis bicyclic ketone **9**, in which the C-5 configuration was retained. Additionally, no loss of optical activity was observed for recovered **8**. Therefore it was concluded that the trans to cis

conversion proceeded exclusively by pathway A. Irradiation of the cis isomer **9** resulted in 86% conversion to trans ketone **8** by pathway A, in which the configuration at C-5 was retained, and 14% inversion of stereochemistry at C-5 to give **10** by pathway B. This preference for pathway A was attributed to the near parallel alignment of the antibonding carbonyl π orbital and the sigma orbitals of bond *a*.

Further mechanistic studies of 4,4-diphenylcyclohexenone **1** were completed by Zimmerman and coworkers[11,12] to determine if any activation barriers existed in the aryl migration reaction. In order to determine if any did exist, it was necessary to first determine if there was a wavelength or temperature dependence on the reaction. From these studies, it was concluded that the reaction was not wavelength dependent but a temperature dependence was observed. A 50°C temperature increase led to a 16-fold increase in the rate of rearrangement and a 2-fold increase in the triplet decay rate. From these results it was concluded that there was a small energy barrier (*ca.* 10 kcal/mol) that must be overcome for rearrangement. This requirement was reasonable due to the fact that the electronics of the migrating phenyl ring are disrupted. Therefore, despite the fact the reaction occurs from an excited state, there is loss of energy which occurs upon phenyl bridging. Results of the temperature experiment were applied to the Eyring equation, and this indicated that the production of the trans isomer was not only energetically preferred but also entropically favored (Table 1). The author reasoned that the less positive activation entropy for formation of the cis isomer was due to the fact that it derived from an open diradical while the trans proceeded from the concerted pathway. In the open diradical, the odd electron at C-4 would be stabilized by the C-4 phenyl group, therefore conformationally restricting this group and making ΔS more negative.

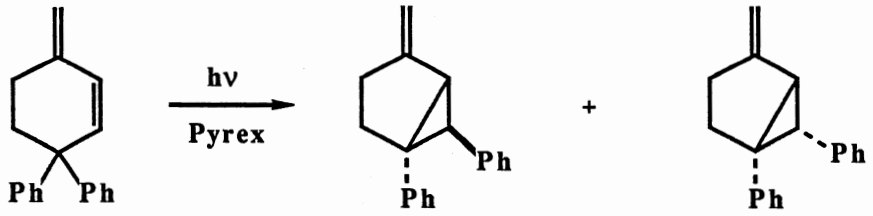
The photochemical aryl migration reaction is thought to be totally analogous to the di-π-methane rearrangement, except that the enone rearrangements proceed in the n-π^* state, while for the hydrocarbon systems, the π-π^* state is utilized.[13] It is interesting to note that the photorearrangement of the hydrocarbon analog **12**, which proceeds

TABLE 1

ACTIVATION ENERGIES, ENTHALPIES AND ENTROPIES[a]

Compound	ΔE_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Trans - (2)	10.53	9.86	6.95
Cis - (3)	11.27	10.70	-0.65

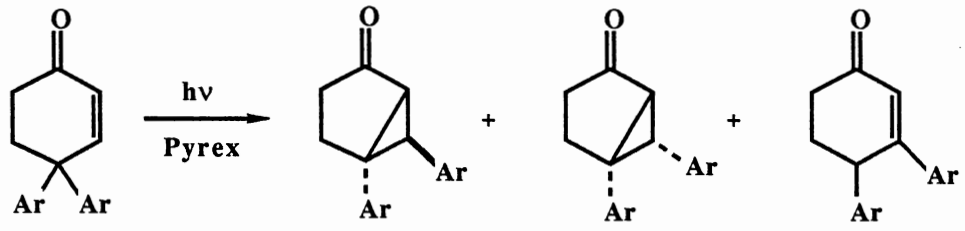
[a]Results from two temperatures only



12 13 major 14 minor

through a di-π-methane reaction also yields predominantly the trans diphenyl product over the cis product even though this is a singlet (concerted) and not a triplet reaction.

The photochemistry of a number of other 4,4-diarylcyclohexenones were studied by Zimmerman and coworkers.[14,15] It was of interest to investigate 4,4-dibiphenyl- (**15**), 4,4-di(α-naphthyl)- (**19**) and 4,4-di(β-naphthyl)-2-cyclohexen-1-one (**22**) in order to determine the effect of having a chromophore at C-4 that had a triplet energy approximately equal to or lower than that of the enone chromophore (69 kcal/mol).[14,15] 4,4-Di(α-naphthyl) and 4,4-di(β-naphthyl) substituents had triplet energies of approximately 60 kcal/mol and therefore could conceivably act as triplet quenchers. The biphenyl substituent had a triplet energy of approximately 69 kcal/mol and could act only as a weak quencher. Photolysis studies of these system indicated that the aryl migration

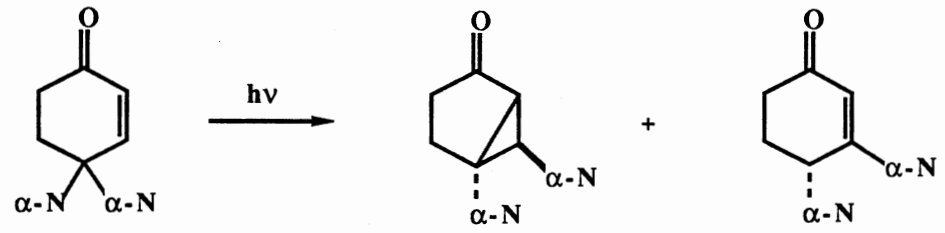


15 **16** **17** **18**

Φ = .26 **Φ = .024** **Φ = .02**

Ar = *p*-biphenyl

reaction was not inhibited by the presence of biphenyl, or naphthyl substituents. Irradiation of the 4,4-dibiphenyl system **15** yielded *trans*- and *cis*-5,6-dibiphenylbicyclo-[3.1.0]hexanones (**16**) and (**17**), and 3,4-dibiphenylcyclohexen-1-one (**18**). Direct irradiation of 4,4-di(α-naphthyl)cyclohexen-1-one (**19**) led to two products, *trans*-5,6-di(α-naphthyl)bicyclo[3.1.0]hexanone (**20**) and 3,4-di(α-naphthyl)-2-cyclohexen-1-one

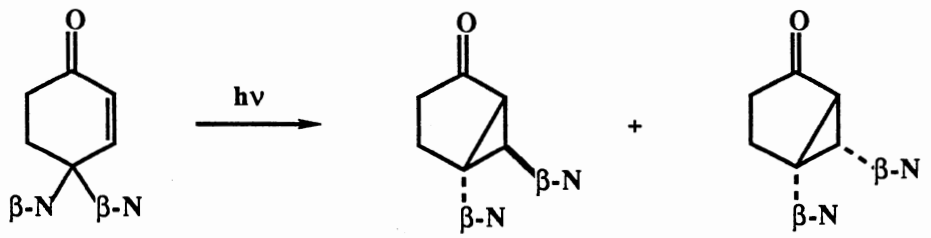


19 **20** **21**

Φ = .46 **Φ = .54**

α-N = α-naphthyl

(**21**). Photolysis of 4,4-di(β-naphthyl)-2-cyclohexen-1-one (**22**) also led to two photoproducts, *trans*- and *cis*-5,6-biphenylbicyclo[3.1.0]hexanones (**23**) and (**24**). As in the previously reported 4,4-diphenylcyclohexanone studies, the trans isomer was kinetically preferred over the cis and enone photoproducts. The absence of the cis product in the α-naphthyl photolysis was thought to be due to the severe naphthyl-



22 **23** **24**

Φ = .38 **Φ = .02**

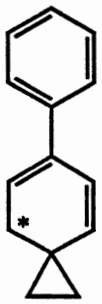
β-N = β-naphthyl

naphthyl steric interactions encountered in the intermediate diradical and not due to the small steric differences seen between the cis and trans products. During the migration one α-naphthyl group must twist past the rotationally fixed C-4 α-naphthyl for bottom-bottom C-2-C-4 overlap and cis product formation. This aryl-aryl interaction is magnified in the α-naphthyl case and, thus, the rearrangement becomes very stereoselective. With the β-naphthyl substituents, the rings are angled away from each other, in the half-migrated species and, thus, the interaction is not as severe.

The observed aryl rearrangements of **15**, **19**, and **22** are thought to proceed by initial excitation localized in the enone end of the molecule. This is due to the high singlet energies, 90-99 kcal/mol, for the biphenyl and naphthyl substituents as compared with 74 kcal/mol for the enone moiety.[14,15] Intersystem crossing to the enone triplet would then be followed by rapid energy transfer to the naphthyl chromophore (exothermic energy transfer, E_T (enone) = 69 kcal/mol, E_T (naphthyl) = 60 kcal/mol). This is also supported by sensitization and quenching studies. These reactions of biphenyl- and naphthyl-substituted enones are, therefore, better described as di-π-methane reactions since the reaction involves the C=C π bond of the enone moiety and the π system of a C-4 aryl group.

Quantum efficiencies for the 4,4-disubstituted α- and β-naphthyl and biphenyl reactions were found to be 11, 8 and 8 times more efficient then the parent 4,4-diphenyl-

cyclohexenone reaction with the rate of radiationless decay being 2 times slower. This increase in efficiency was attributed to the increase in conjugating ability of the aromatic group at C-4. Delocalization of the odd electron density in the bridged species should be best for a migrating α-naphthyl substituent and worst for a phenyl. The facility of aryl group migrations follows in the order of α-naphthyl > β-naphthyl- biphenyl > phenyl. This increase in conjugating ability is reasonable on the basis of the bridged structures **25**, **26** and **27**, by either counting resonance structures or by simple Hückel MO calculations.



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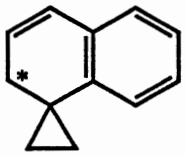

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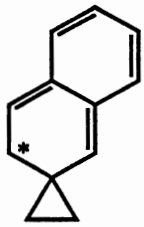
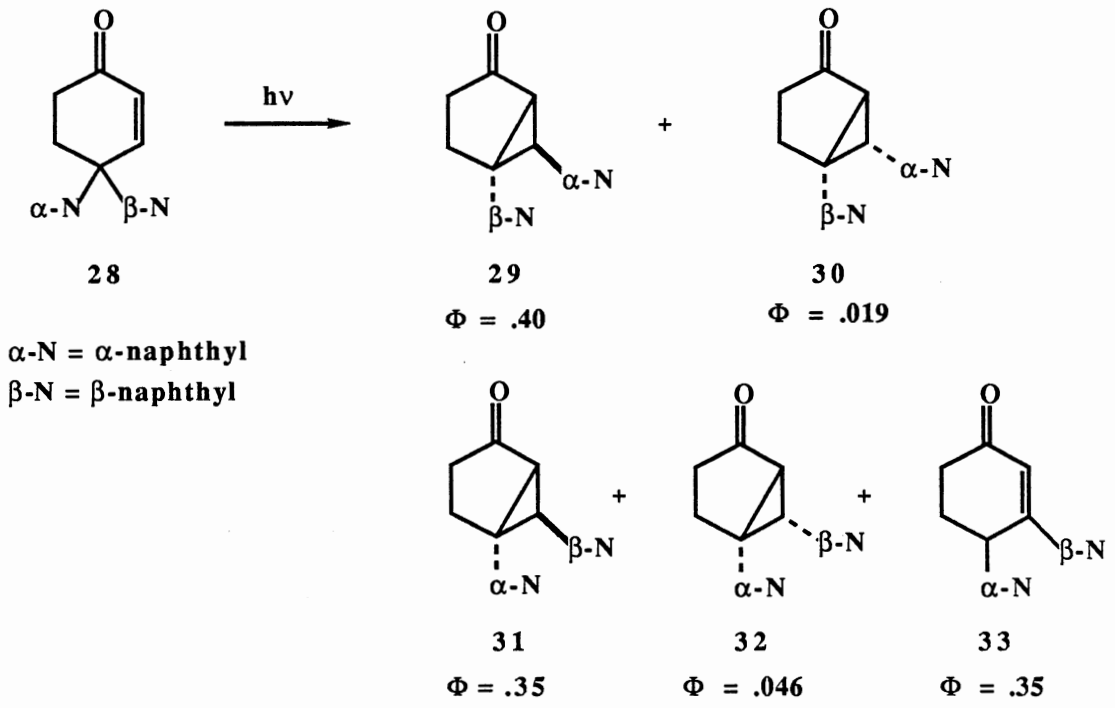


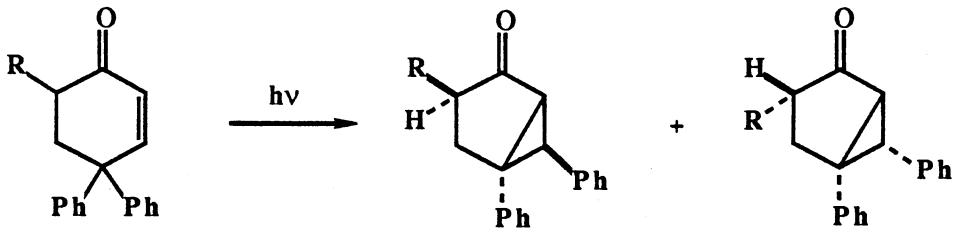
27

Intramolecular migratory aptitudes in the aryl migration reaction have also been explored.[6] The photochemistry of 4-α-naphthyl-4-β-naphthyl-2-cyclohexen-1-one (**28**) was studied and found to afford trans and cis isomers of 5-α-6-β- and 5-β-6-α-naphthylbicyclo[3.1.0]hexanone (**29-32**) as well as 3-β-naphthyl-4-α-naphthyl-2-cyclohexen-1-one (**33**). The trans isomers were preferred for both the 6-α- and 6-β-naphthyl cases over the cis and enone systems. It was surprising to find that intramolecular competition between the α- and β-naphthyl groups led to a ratio of 48:52 slightly in favor of the β-naphthyl migration, since the α-naphthyl substituent should



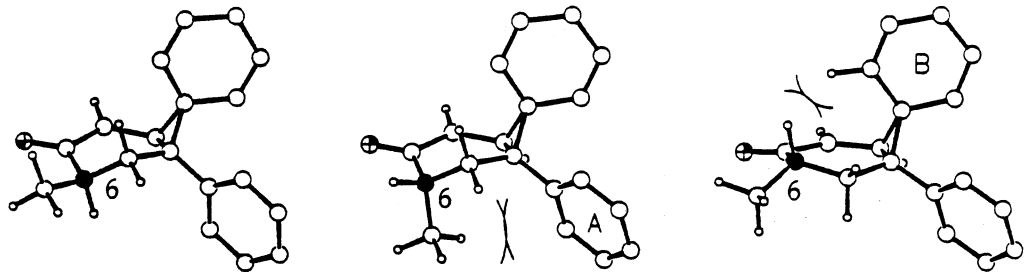
better stabilize the odd electron density at C-3. The slight preference for β-naphthyl migration was thought to derive from conformational effects.

Zimmerman and coworkers[7] have also studied the photochemistry of 4,4-diphenylcyclohexenones bearing a C-6 substituent in order to evaluate the effect of having a substituent at the end of a chain capable of quenching the enone rearrangement. It was thought that the quencher side chain might also intercept triplet energy from an external sensitizer. The C-6 substiuents under study were β-naphthylbutyl, β-naphthylmethyl and *p*-biphenylmethyl groups. Also 4,4-diphenylcyclohexenones having C-6 methyl and propyl substituents were used as controls. Irradiation of the enones **34-38** led to the formation of two photoproducts in each case, corresponding to C-3 epimers of *trans*-5,6-diphenylbicyclo[3.1.0]hexanones **39-48**. In all of these systems, the 3-endo product was formed in kinetic preference to the 3-exo isomer. This observed stereoselectivity was rationalized on the basis of steric interactions in the bridged phenyl intermediate. There are two basic conformations possible for each exo and endo C-6 substituted



			endo:exo ratio
34 R = β-naphthylbutyl	**39**	**44**	**1.7**
35 R = β-naphthylmthyl	**40**	**45**	**1.8**
36 R = *p*-biphenylylmethyl	**41**	**46**	**1.4**
37 R = methyl	**42**	**47**	**3.8**
38 R = propyl	**43**	**48**	**1.6**

diradical. Steric interactions between the migrating phenyl and the C-6 substituent in the exo precursors, **49** and **50**, are unfavorable. The half-migrated endo conformer **51**, however, has the C-6 substituent placed away from the phenyl rings and is therefore energetically preferred. Exclusive endo isomer production also indicated that the rate determining stage of the rearrangement must come near or prior to half migration since the less stable endo isomer is formed preferentially.



19-Endo

19-Exo

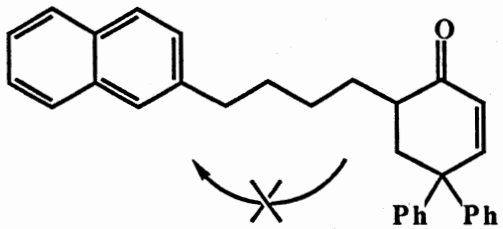
(Oxygen = ⊕)

19-Exo'

49 **50** **51**

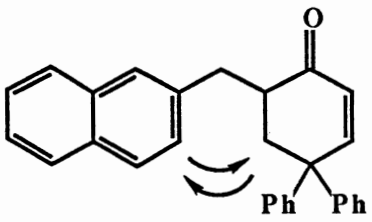
Quantum yields for C-6-substituted 4,4-diphenylcyclohexenones were found to be dependent on the separation between the naphthyl chromophore and the enone moiety.

naphthylbutyl enone had direct quantum yields within experimental error of those reported for the unsubstituted 4,4-diphenylcyclohexenone while the β-naphthylmethyl enone reaction efficiency was quite depressed ($\Phi_{naphthylmethyl}$ = .0059 *vs* Φ_{phenyl} = .043). This markedly diminished quantum yield was thought to be due to the short-range exchange mechanism necessary for triplet energy transfer. The naphthylmethyl substituent is close enough to the enone moiety to quench the excited triplet and, thus, lower the quantum yield. The β-naphthylbutyl substituent is too far away from the enone moiety for short-range transfer to occur and therefore, no effect on quantum yield was observed. The biphenylmethyl substituent, despite being within range to quench the enone triplet, has a triplet energy very near that of the enone moiety and, thus, acted only as a very weak quencher ($\Phi_{biphenylmethyl}$ = .033 *vs* Φphenyl = .043). Both of the



energy transfer

34



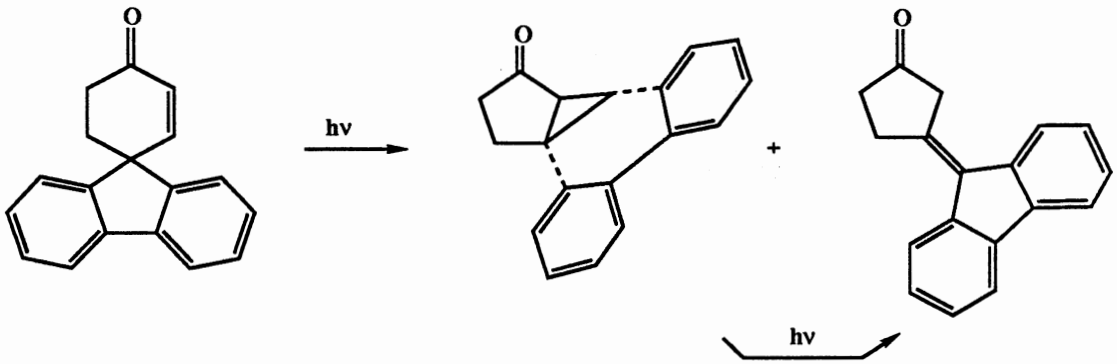
energy transfer

35

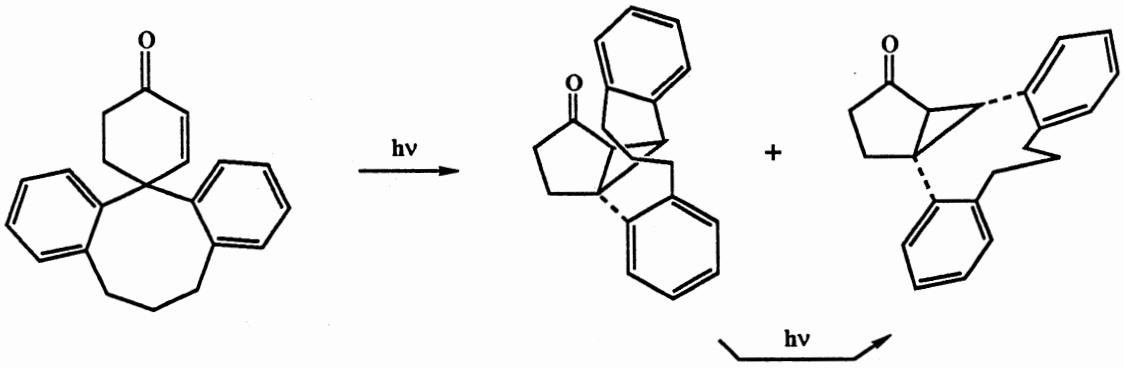
naphthyl substituted enones were found to intercept and quench external sensitizer triplets. The β-naphthylmethyl system intercepted ≥ 75% of the sensitizer triplets while the β-naphthylbutyl system quenched only 50% of the external triplets. This indicated that in the β-naphthylbutyl system there was equal probability that the sensitizer triplet would collide with the β-naphthylbutyl chromophore as it would the enone system. In the β-naphthylmethyl case, where the separation between the chromophore and the enone is smaller, it was difficult for sensitizer triplets to approach the enone without also being

near the naphthyl group as well. Therefore, a larger number of triplet sensitizers were quenched for **35**.

A recent study was initiated to explore the possibility of altering the stereochemical outcome of the aryl migration reaction seen in 4,4-diphenylcyclohexenone.[16] It was thought that by placing a carbon-carbon bridge between the ortho positions of the two C-4 phenyl groups which migrate apart during trans isomer formation, the stereochemistry could be controlled by varying the length of the bridge. Two systems were studied - spirofluorenyl cyclohexenone **52** and spirodibenzocyclooctenyl cyclohexenone **55** - corresponding to systems with a zero and a three-carbon bridge. Irradiation of **52** resulted in the formation of the cis diphenyl bridged system **53** and the β,γ-unsaturated enone **54**. Extended irradiation showed that **53** rearranges to **54** which was photostable. Irradiation of **55** showed normal aryl migration, yielding the kinetically preferred trans diphenyl system **56** and the cis isomer **57**. Upon extended irradiation, it was noted that the cis isomer was formed at the expense of the trans isomer. The diversion from the normal migration course seen in the irradiation of **52** has been attributed to the fact that the zero-carbon bridge is too short to span the distance between the two ortho positions in the trans system, therefore yielding the cis bicyclic and the β,γ-enone products instead. The length and flexibility of the three-carbon bridged system allows formation of the trans and cis isomers.

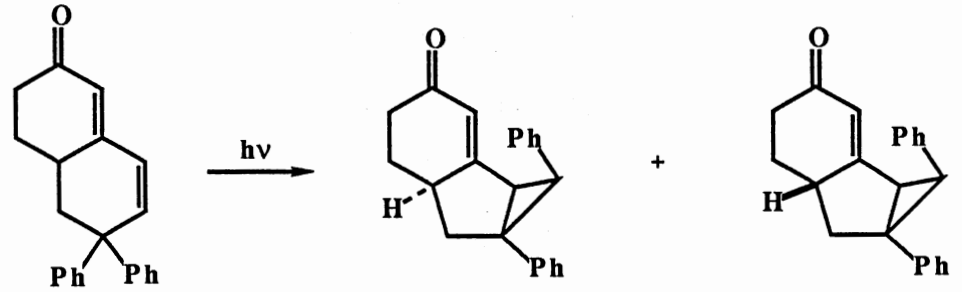


52 **53** **54**

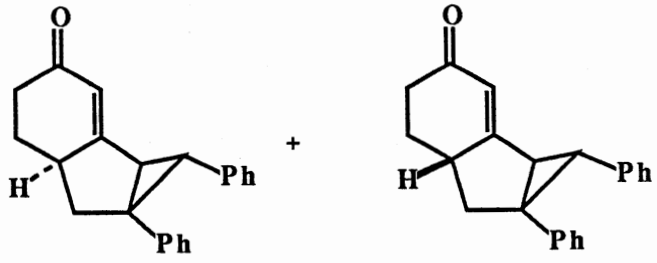


55 56 57

Aryl migration reaction studies have recently been reported for the linearly conjugated enone **58** and trienone analog **63**.[8] Low conversion irradiation of **58** resulted in the production of two tricyclic photoproducts **59** and **60** with products **61** and **62** formed as secondary products and seen only at higher conversion irradiations. The

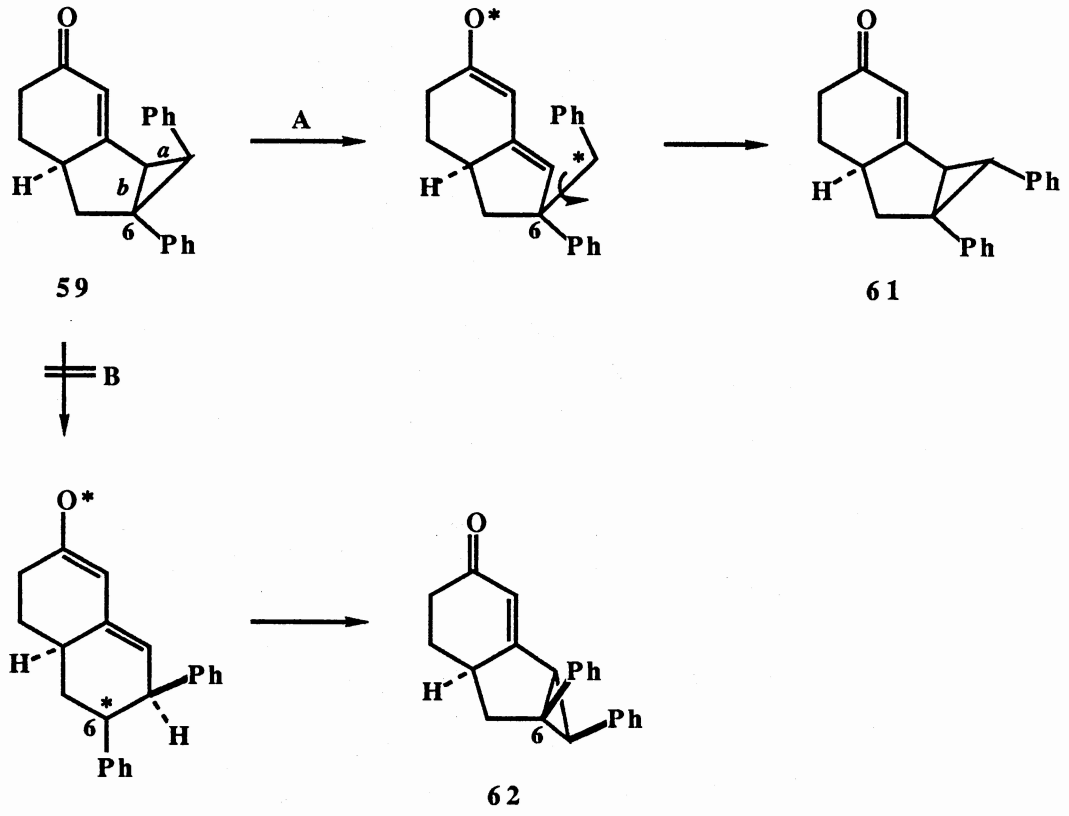


58 **59** (27%) **60** (16%)

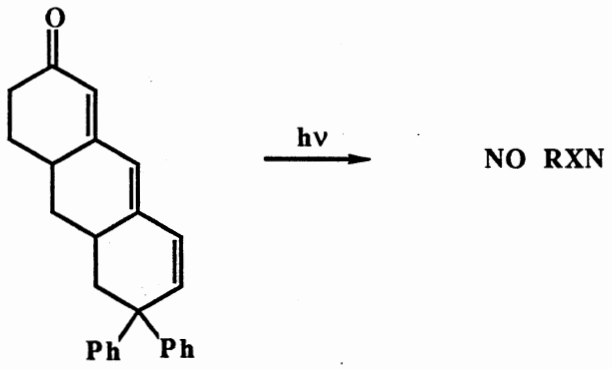


61 (37%) **62** (13%)

observed kinetic stereoselectivity favoring the anti conformation with respect to the angular C-4a hydrogen and the cyclopropyl ring in **59** is due to the steric hindrance encountered in the bridged intermediate. Steric interactions are greater when the phenyl bridge is syn to the angular C-4a hydrogen than when the phenyl bridge is syn to the C-5 endo methylene group, thus leading to the kinetically preferred product **59**. Independent irradiation of the primary photoproducts **59** and **60** resulted in photoisomerization of the trans isomer **59** to only **61** and trans isomer **60** to only **62**. This indicated that only pathway A was followed since the stereochemistry about C-6 would not be retained if pathway B was followed.

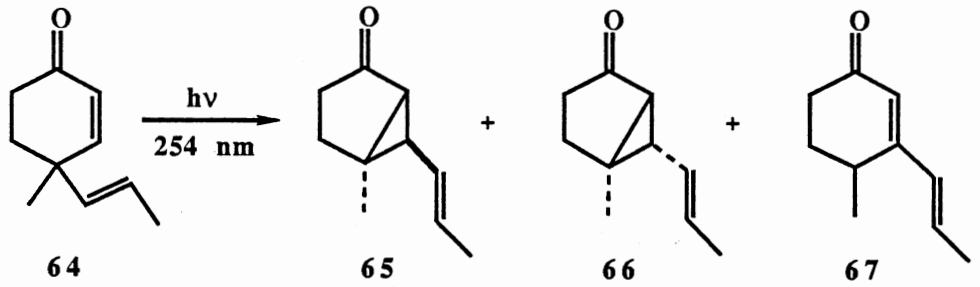


The trienone **63** was found to be stable upon direct and sensitized irradiation.[8] The lack of reactivity is thought to derive from an excess in phenyl bridging energy (provided by MNDO-CI calculations) which is not compensated by the slightly longer triplet lifetime. Therefore, two factors are competing -- the rate of phenyl migration and the rate of radiationless decay, the latter prevailing. Additionally, the energy of the trienone triplet is lower as a result of the extended π system. Therefore the energy required to disturb the phenyl aromaticity upon bridging may not be as readily available as in the higher energy triplets of the monocyclic enone and bicyclic dienone systems.

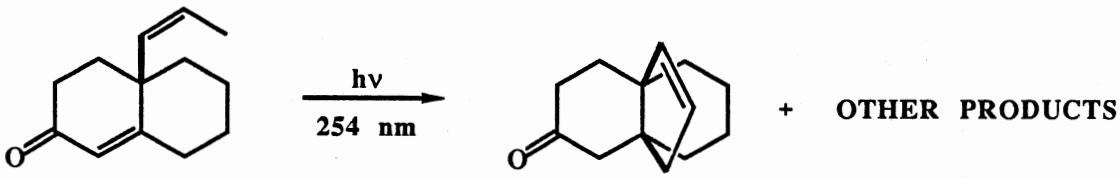


63

A mechanistically analogous rearrangement to the aryl migration reaction was **64** (λ = 254 nm) in dioxane to 50% conversion gave a mixture of the 6-*endo* propenyl ketone **65** (major product), the 6-*exo* propenyl ketone **66** and the dienone **67**. Cis-trans isomerization of the starting material was found to compete with the rearrangement. A cyclization reaction similar to that reported for **68** was not observed for **64**.[20] The fact that the propenyl group points away from the enone system in **64** is thought to contribute to the lack of hydrogen abstraction and cyclization.



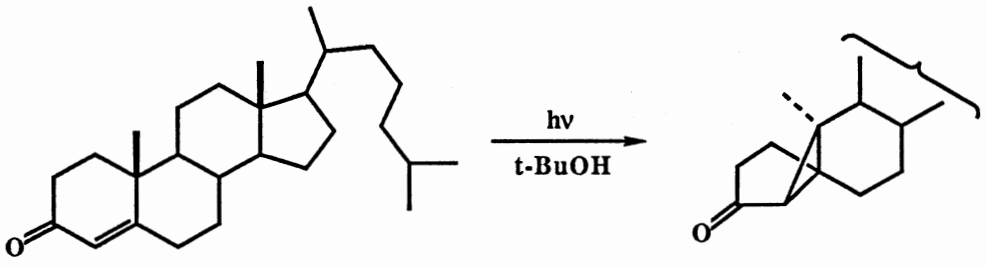
64 65 66 67



68 69

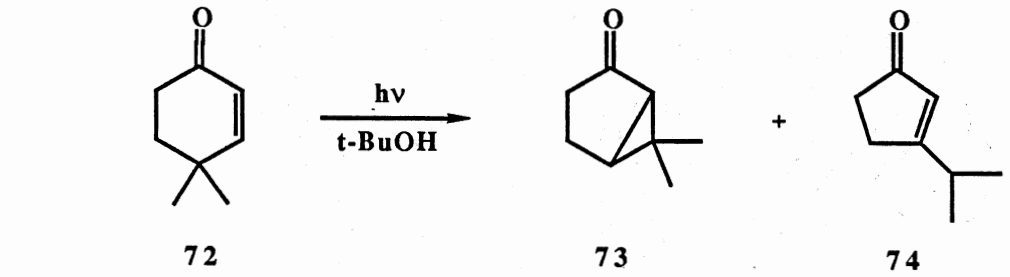
Type A Rearrangements

4,4-Dialkylated cyclohexenones have been reported to undergo photorearrangements to 6,6-disubstituted bicyclo[3.1.0]hexanones (lumiketones). This subject has been reviewed extensively.[13] One of the first examples of this type of photorearrangement was reported by Gardner, in which 4-cholesten-3-one (**70**) stereospecifically photoisomerizes to the lumiketone **71**.[21] Shortly thereafter, Chapman reported the photochemical rearrangement of 4,4-dimethylcyclohexenone **72** and testosterone derivatives **75-78** in *tert*-butanol to the lumiketones **76-79** and ring contracted

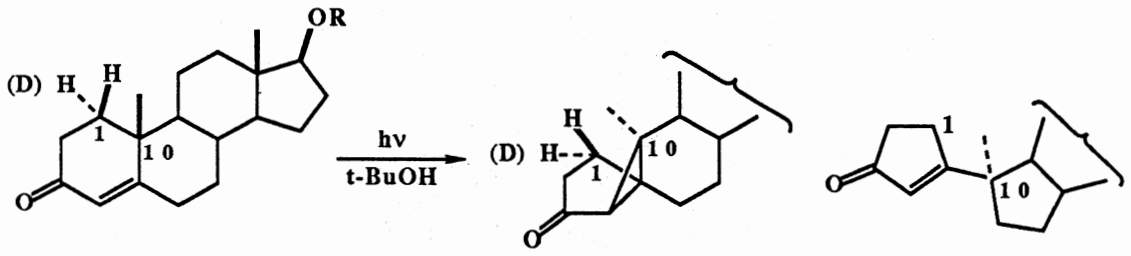


70 71

3-substituted cyclopentenones **77-80**.[22] From these pioneering studies, the photochemistry of a number of 4,4-dialkylated enones were investigated in order to obtain additional information regarding the lumiketone rearrangement.



72 **73** **74**



75 - R = OAc
78 - R = H
81 - R = OAc
H = (D)

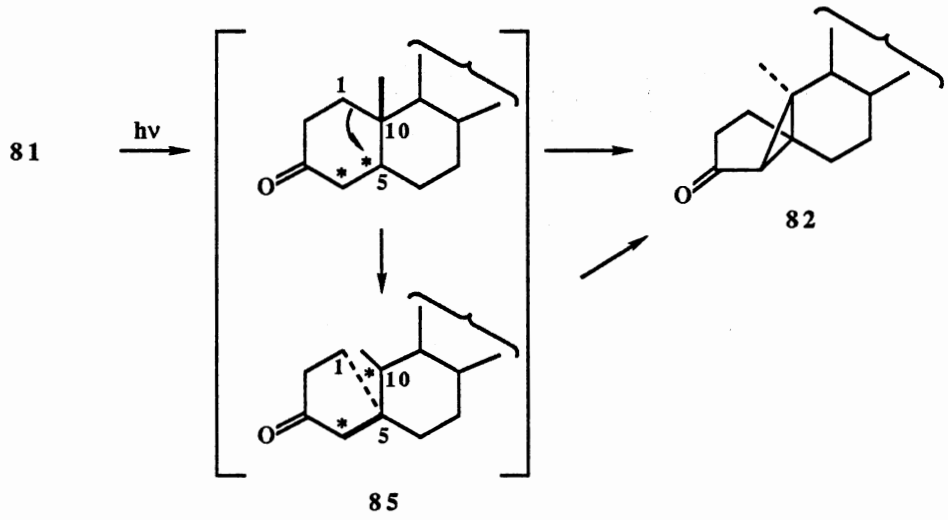
76 **79** **82**

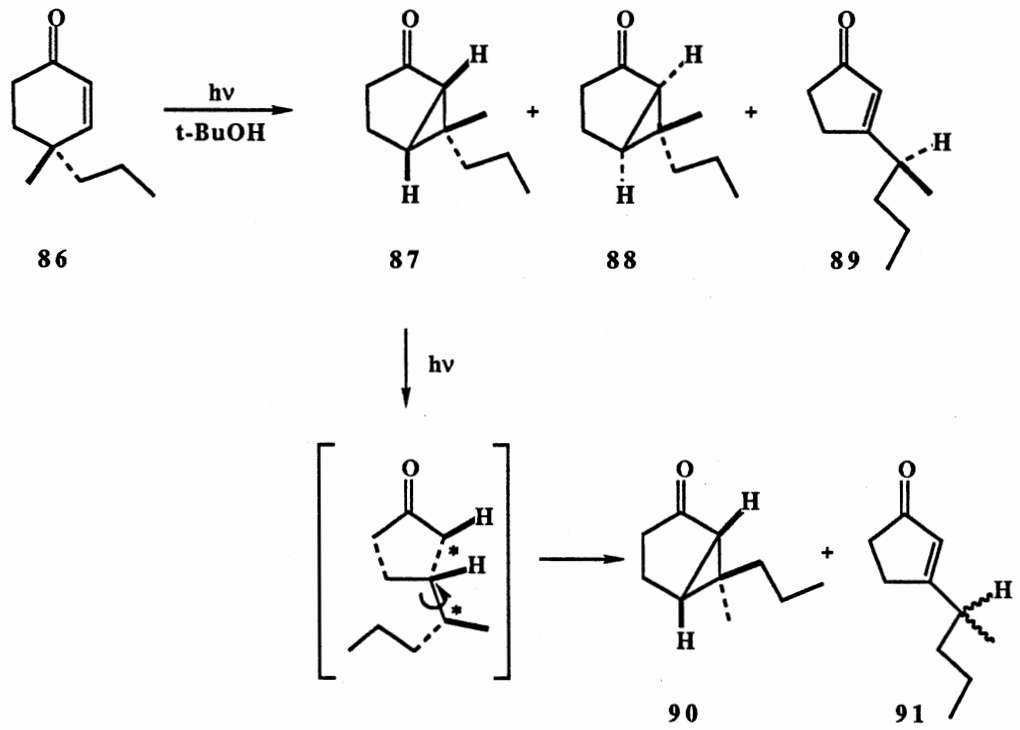
77 **80** **83**

Initially it was concluded that aryl or dialkyl substitution at the C-4 position of cyclohexenones was a necessary but not a sufficient structural condition for occurrence of the lumiketone rearrangement since 2,4,4-trimethyl- and 3,4,4-trimethylcyclohexenones did not afford lumiketones upon irradiation.[13,23] Later studies by Schuster and coworkers[24] determined that both enones indeed produced lumiketones upon irradiation. These results indicated that alkyl substitution on the enone double bond did not inhibit the rearrangement but only lowered the quantum yields relative to those reported for 4,4-dimethylcyclohexenone. The failure of the earlier report to detect rearrangement was

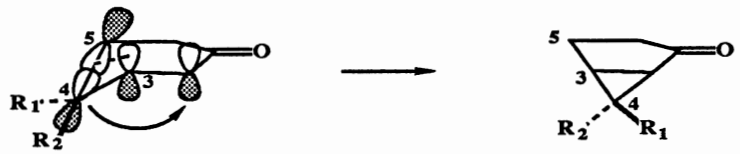
attributed to the poor analytical techniques available. In *tert*-butanol the most common photoreaction observed for cyclic α,β-unsaturated ketones lacking the 4,4-dialkylation is dimerization.[13]

In general, the lumiketone rearrangement has been found to be a very stereospecific reaction. For example, the photorearrangement of both deuterotestosterone acetate **81** and phenanthrenone **84** occurred with inversion of configuration at the C-10 center (steroid numbering) to afford only the lumiketone stereoisomers.[25,26] These results ruled out the possibility of a planar achiral intermediate since this would lead to racemization. It was felt that steric constraints imposed by the A-B ring fusion in steroidal systems would direct the stereochemical course of the reaction. The angular C-10 methyl would direct C-1-C-5 bonding to the rear face since it would be energetically unfavorable for the C-1 containing chain to pass the methyl substituent for front face bonding. Whether the stereospecific rearrangement proceeded by a concerted or stepwise mechanism was not clear since the imposing steric constraints would allow a stepwise mechanism via **85** to be feasible. Therefore, the optically active monocyclic 4,4-disubstituted cyclohexenone **86** was studied in order to determine the stereochemical





course of the reaction since steric constraints were minimized in this system.[27] Irradiation of **86** led to the formation of the lumiketones **87** and **88**. These lumiketones were formed stereospecifically with inversion of configuration at C-4; no isomerization of recovered starting enone was observed. From these results, a diradical intermediate analogous to **85** was excluded and a concerted mechanism was proposed.[27,28] The lumiketone reaction can be described as a [$\pi 2_a + \sigma 2_a$] cycloaddition. The C-3-C-5 bond is formed by antarafacial overlap of the excited π system and the back lobe of the C-4-C-5 σ bond. This occurs simultaneously with C-2-C-4 bond formation to give the inverted center at C-4.

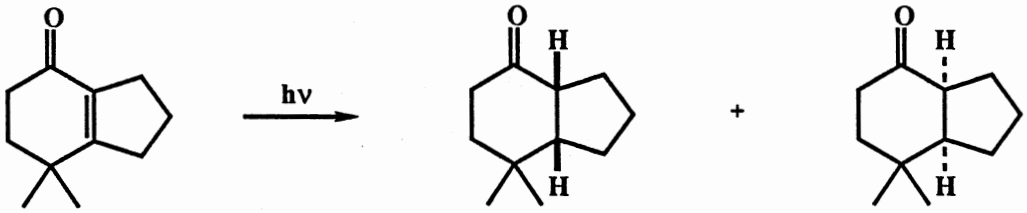


The production of optically active cyclopentenone **89** is consistent with the concerted mechanism, i.e. simultaneous ring contraction and migration of a hydrogen atom from C-3 to C-4, leading to inversion of configuration at C-4. Control irradiation of **87** was found to produce **90** and racemic **91**. A stepwise process is thought to intervene in the production of secondary photoproducts. This racemization occurs by C-1-C-6 bond cleavage, followed by either rotation and reclosure to give **90** or rotation and hydrogen atom migration to give **91**.

The 4,4-disubstituted cyclohexenone lumiketone rearrangement is analogous to the photorearrangement reported by Zimmerman on 4,4-diphenyl-2,5-cyclohexadienone **92**.[29] Sensitization and quenching studies indicated that both the enone and dienone rearrangements (known as Type A rearrangements) proceeded from the triplet excited state.[13,29] The configuration of the excited state is still a matter of some controversy but has been reported to proceed via the π-π^* triplet state in polar solvents.[24] The major differences between the enone and dienone Type A rearrangements is the efficiency of the reaction. The dienone rearrangements have been found to proceed with quantum efficiencies ranging from 0.8-1.0 while the 4,4-dialkylated enones have quantum efficiencies of only 0.0065-0.0077.[2,13] Involvement of the second double bond is thought to be the reason for the high quantum efficiencies reported for the 2,5-dienone system.[2] The second double bond provides additional stabilization to the excited system by π overlap with the β carbon radical center. Type A rearrangements of dialkylated cyclohexenones are also less efficient than aryl migration reactions of 4,4-diarylcyclo-hexenones. The qualitative order of reaction efficiencies is therefore Type A dienone > aryl migration > Type A enone rearrangement.[2]

The low quantum yields observed for Type A enone rearrangements have been rationalized by competitive pathways available to the twisted cyclohexenone triplet.[13,30-32] Until recently, the reactive excited state species for α,β-unsaturated cyclohexenones was described as a planar enone triplet generated by intersystem crossing of the singlet

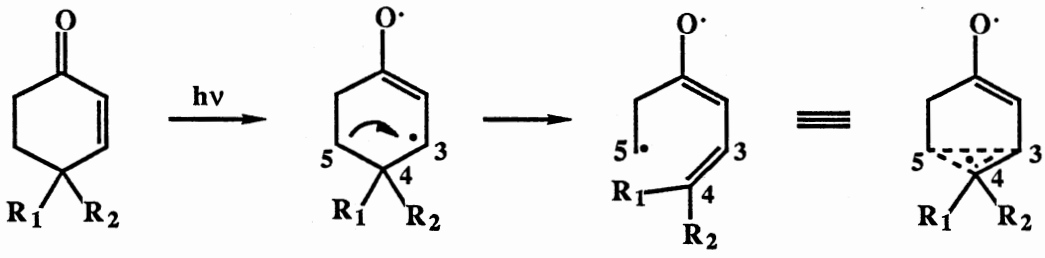
with unit efficiency ($\Phi_{direct} = \Phi_{sensitized}$).[13] Recently, it has been suggested that the planar enone triplet relaxes around the enone double bond to give a twisted enone triplet.[30-32] A transient observed in direct laser enone photolysis studies has been assigned to a twisted enone triplet.[13,30-32] This triplet has the ideal geometry for radiationless decay from T_1 directly to S_0.[13,33-34] Therefore, in the Type A enone reaction, return to starting material is the major reaction pathway while lumiketone formation is a minor pathway, thus accounting for the low quantum yields observed. Schuster[35] believes the twisted triplet is essential for Type A rearrangements and feels this is evidenced by the lack of lumiketone rearrangement in **93** and lower quantum yields seen for other C=C substituted enones. In **93**, the constrained C=C system inhibits twisting of the enone triplet and, thus, photoreduction occurs instead.



93 **94** **95**

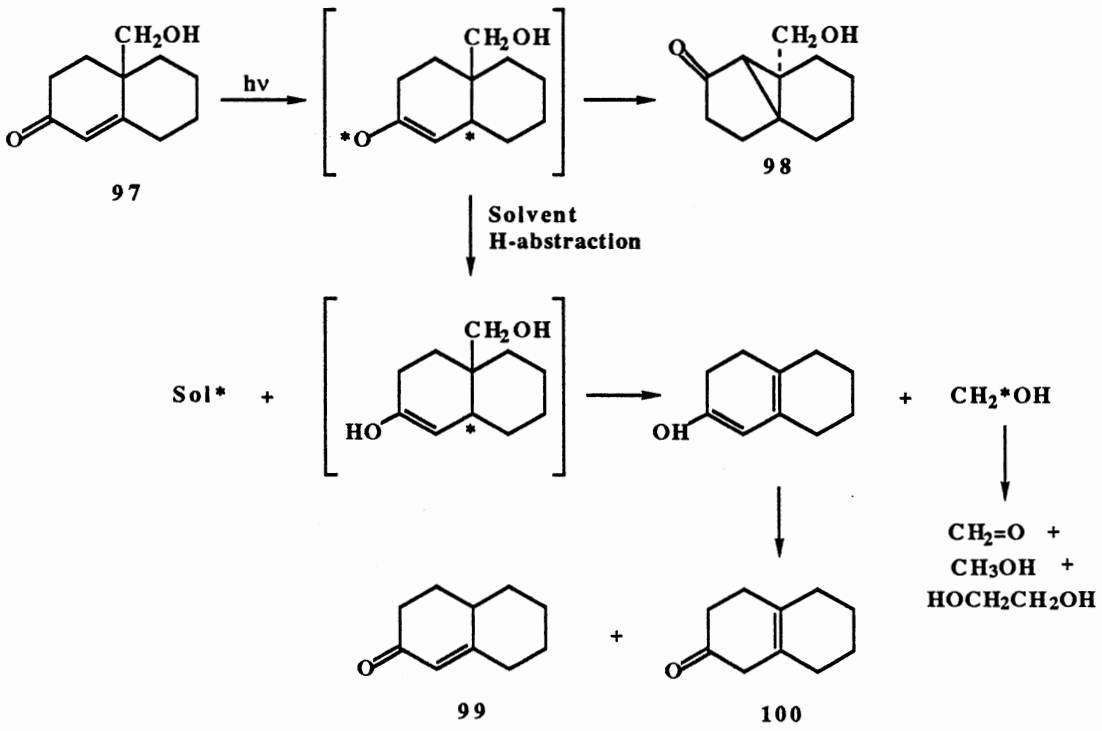
Pienta[32] and Schuster[30,31] have found that the twisted triplet transients, detected by laser flash photolysis of a series of enones, were not quenched by cyclohexadiene. This would suggest that this triplet is not responsible for aryl migration rearrangements since these diaryl systems are quenched by cyclohexadiene. The short lifetime of the twisted triplet may account for the lack of triplet quenching.

Zimmerman proposed a stereospecific diradical mechanism for the Type A enone rearrangement.[30] Scission of the C-4-C-5 bond is envisioned to give the diradical species **96** in which the radical center at C-5 does not become completely free but rather remains associated with the developing ethylenic group at C-3-C-4. Since neither C-4 nor C-5 achieves a flat geometry and rotation around C-5-C-6 as well as C-3-C-4 is restricted, a stereospecific rearrangement can occur.



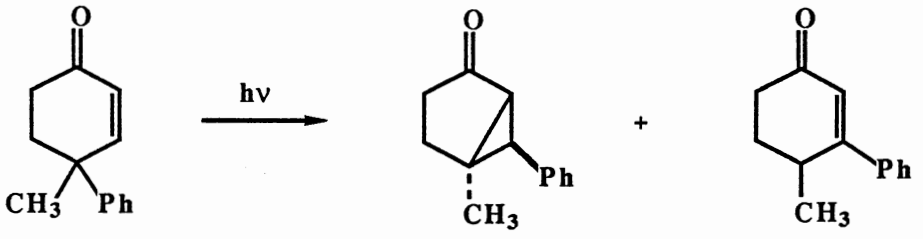
96

Chapman suggested a dipolar intermediate versus a diradical species for the Type A enone photorearrangement, could account for both the lumiketone and the 3-cyclopentenone photoproducts.[19] Schuster and Brizzolara tested this "polar state concept" versus a diradical process by studying the photochemistry of 10-hydroxyoctalone **97**.[35] They felt that if any diradical species were involved, they would see some explusion of the hydroxymethyl radical and, thus, competition between radical fragmentation and rearrangement. Irradiation of **97** in chloroform, toluene or cumene afforded the lumiketone **98** along with ketones **99** and **100**, generated from a competing radical fragmentation pathway. The formation of formaldehyde, methanol and ethylene glycol by solvent H-abstraction and coupling indicated the intermediacy of a diradical species and not a dipolar intermediate. Later studies suggested that these products might have derived from an excited state protonated enone species.[36]



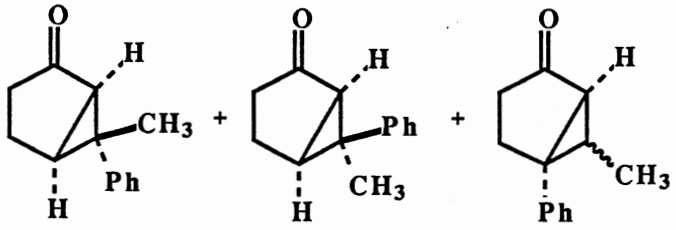
Aryl Migration *vs.* Type A

Intramolecular competition between the aryl migration and the Type A enone rearrangement was presented in the photochemical study of 4-phenyl-4-methylcyclohexen-1-one (**101**).[37] In aprotic, nonpolar solvents, irradiation of **101** yielded 5-methyl-*endo*-6-phenylbicyclo[3.1.0]hexan-2-one (**102**) and 4-methyl-3-phenylcyclohexen-1-one (**103**). Both photoproducts derived from the aryl migration reaction. In protic polar solvents, irradiation of **101** afforded predominantly Type A rearrangement products **104** and **105**, as well as photoproducts **102, 103** and **106**. The observed solvent dependence on reaction pathway was rationalized by a change in the character of the lowest-lying triplet (n-π^* or π-π^*).[13,38] The aryl migration reaction is thought to proceed via the n-π^* triplet while Type A enone rearrangements occur from the π-π^* triplet state. It has been reported that the n-π^* and π-π^* triplet levels of cyclohexenones are close together and a change in solvent may bring about inversion of these two states. Increasing the solvent polarity and hydrogen bonding ability may result in stabilization of



101 102 103

in nonpolar solvents - 102-103
in polar solvents - 102-106



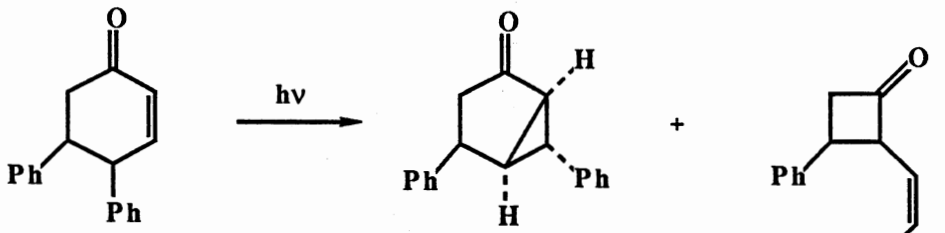
104 105 106

the π-π* state versus the n-π* state, thus lowering its energy. Therefore in protic polar solvents, products from the π-π* state (Type A) are produced at the expense of the products from the n-π* state (aryl migration). Additionally, quenching experiments have shown that photoproducts **102** and **104** are quenched differently by naphthalene suggesting these products arise by two non-equilibrating triplets, i.e. π-π* and n-π*.

Solvent effects have also been reported in a number of Type A enone and aryl migration rearrangements.[2,13] The yields of lumiketone in the Type A enone rearrangement are usually optimized in *tert*-butanol with side reactions (dimerizations, reduction and deconjugation) enhanced in 2-propanol, toluene, pyridine and benzene. Zimmerman reported a 16-fold increase in the production of 3,4-diphenylcyclohexenone **4** upon irradiation of 4,4-diphenylcyclohexenone **1** in *tert*-butanol versus benzene.[2] This effect has been attributed to either inversion of two close-lying triplets or to the possibility of hydrogen bonding at the enone oxygen in the excited state, enhancing hydride migration over cyclopropyl formation.

The absence of any Type A rearrangement products from 4,4-diphenylcyclo-

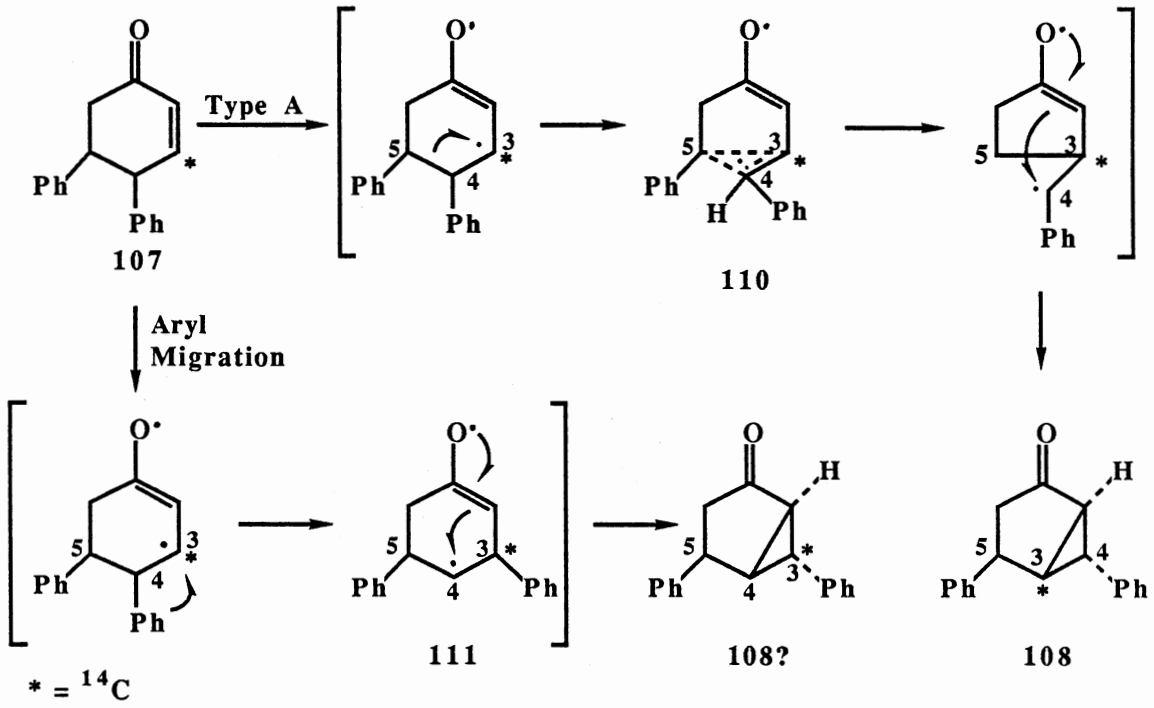
hexenone provoked interest in a more thorough study of 4-phenyl substituted enones.[39,40] The photochemistry of 4,5-diphenyl-2-cyclohexen-1-one (**107**) was studied since both aryl migration and Type A enone rearrangements were possible.[39] It was thought that the 5-phenyl substituent would enhance the Type A rearrangement by facilitating breakage of the C-4-C-5 σ bond due to its ability to stabilize the odd electron density at C-5 of species **110**. Photolysis of **107** in 95% ethanol led to a single stereoisomer **108**. Irradiation of **107** in *tert*-butanol also afforded **108** along with a minor product, 2-(*cis*-styryl)-3-phenylcyclobutanone **109**. It was not initially apparent whether **108** derived from aryl migration or from Type A rearrangement since both



107 **108** **109**

in 95% ethanol - 108
in t-BuOH - 108-109

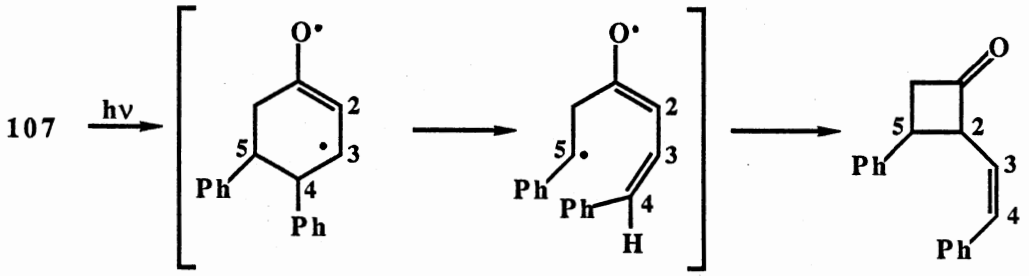
pathways led to the same product. However, the skeletal changes (interchange of C-3 and C-4) that occur only in the Type A enone rearrangement did permit determination of the reaction pathway. ^{13}C labeling of C-3 in **107**, followed by irradiation, degradation of photoproduct **108** and assay of the degradation fragments revealed that the Type A rearrangement predominated over the aryl migration reaction by 70:1. Several reasons are advanced to explain the preference for Type A rearrangement in 4,5-diphenylcyclohexenone **107** while 4,4-diphenylcyclohexenone **1** chooses the aryl migration pathway:



1) In the aryl migration reaction, once phenyl migration occurs, an odd electron center is generated at C-4. This center is localized in **111** while it is delocalized by the non-migrating phenyl in **1**.
2) If you assume there is a greater van der Waals phenyl-phenyl interaction between geminal phenyls than vicinal ones, there would be a greater relief of this interaction in the phenyl migration of **1** than in **107**.
3) It has been suggested that the axial phenyl migrates (better orbital overlap with enone system) in the the aryl migration reaction. In the 4,5 diphenyl system **107**, the phenyls are most certainly trans equatorial and in poor alignment for migration. In **1,** one phenyl is necessarily axial and can easily migrate.
4) Phenyl delocalization of the odd-electron center at C-5 generated in the Type A reaction is possible in **107** and not in **1**.

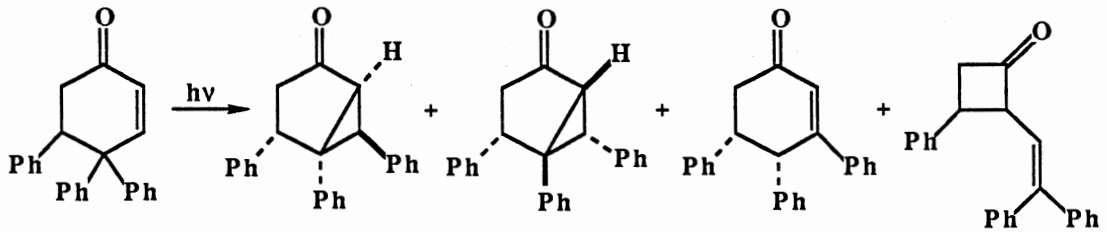
The formation of **109** is thought to proceed by homolytic fission of the C-4-C-5 bond of **107** followed by cyclobutane ring formation. It is possible that the odd electron

at C-5 is not completely free but "bicycles" from C-4 to C-3 to C-2 and then bonds. Cyclobutanone photoproducts of this type have not been reported in Type A rearrangements of 4,4-dialkylcyclohexenones.



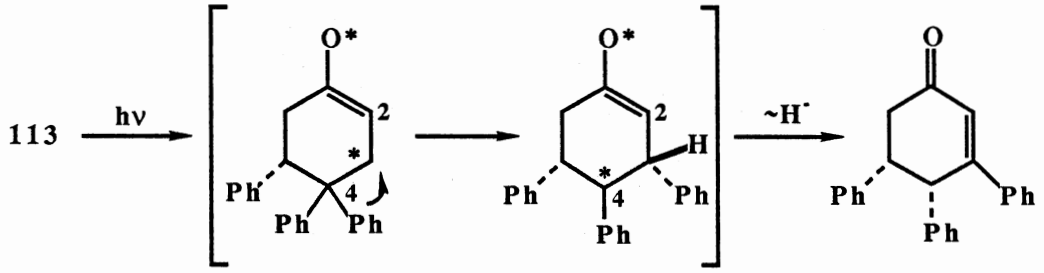
112 109

The photochemistry of 4,4,5-triphenyl-2-cyclohexen-1-one (**113**) was studied to gain further insight into the differences in photoreactivity between 4,4- and 4,5- diphenyl-cyclohexenones.[41] The triphenyl system had features that enhanced both the Type A and aryl migration reaction. Irradiation of **113** in *tert*-butanol resulted in the formation of four photoproducts, three derived from aryl migration **114-116**, and one **117**, by a mechanism involving C-4-C-5 bond fission. The lack of cis diphenyl photoproducts supports Zimmerman's earliest theory of C-2-C-4 bonding concerted with aryl migration, resulting in production of only the trans diphenyl isomers. The formation of only the cis-

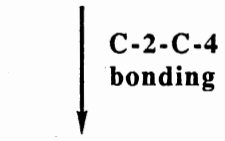


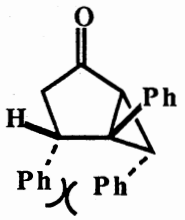
113 114 115 116 117

3,4,5-triphenyl enone system **116** is thought to be a result of incomplete C-2-C-4 bonding in **118** since this bonding leads to a strained trans-trans system **119** in which the C-4-C-6 phenyls are forced together. It was concluded that because the aryl migration route was preferred for **113**, the enone **107** may not have undergone the aryl migration reaction because of lack of C-4 stabilization in the migrated diradical **111.**



118 **117**

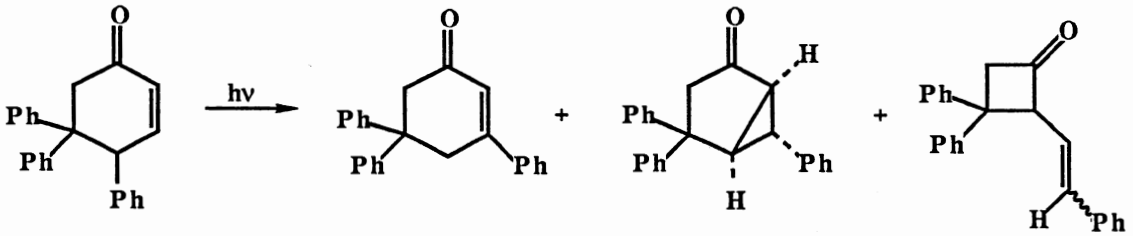




119

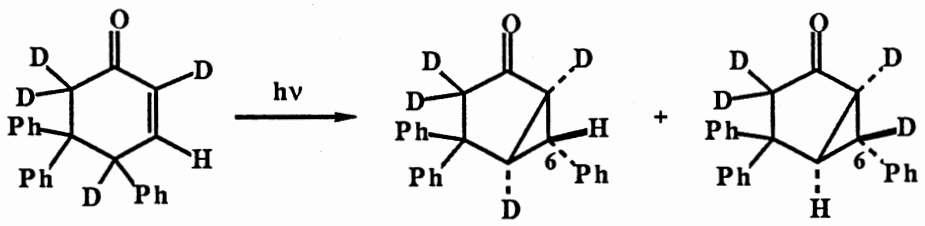
The vinylcyclobutanones isolated as minor photoproducts in the photolysis of **107** and **113** sparked an investigation into the photochemistry of two other 5-aryl substituted cyclohexenones, 4,5,5-triphenyl-2-cyclohexen-1-one (**120**) and 4-methyl-5,5-diphenyl-2-cyclohexen-1-one (**129**).[5] The 5,5-diphenyl substituents were expected to further stabilize the radical center generated upon homolytic fission of the C-4-C-5

bond such that cyclobutane formation would be enhanced. Direct irradiation of **120** led to the formation of four photoproducts, 3,5,5-triphenyl-2-cyclohexen-1-one (**121**), *exo*-4,4,6-triphenylbicyclo[3.1.0]hexanone (**122**), and the cis and trans-2-styryl cyclobutanones (**123**) and (**124**). Labeling studies were completed in order to determine



120 **121** **122** **123-124**

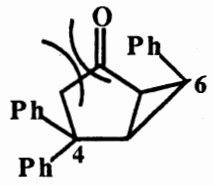
which pathway, Type A or aryl migration led to **123**. Irradiation of deuterium labeled 4,5,5-triphenylcyclohexenone **125** led to the formation of bicyclic ketone **126**, in which the C-6 bore only hydrogen, this product resulting from a phenyl migration pathway. It was of special interest to note that in the 4,5,5-triphenylcyclohexenone photolysis, none of the endo phenyl products were observed but instead the exo isomer was produced. In all previously reported cases of the aryl migration reaction, preference for the endo isomer was observed. This exception has been rationalized by the severe C-4-C-6 phenyl-phenyl



125 **126** **127**

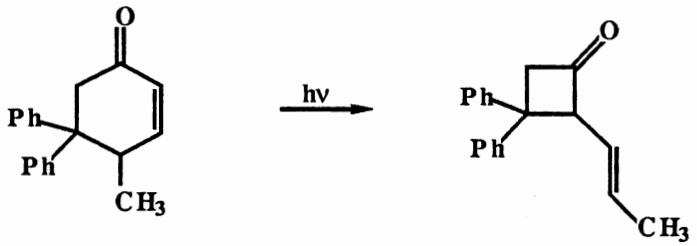
if aryl migration **if Type A**

steric interaction that would be seen in the endo product **128.**



128

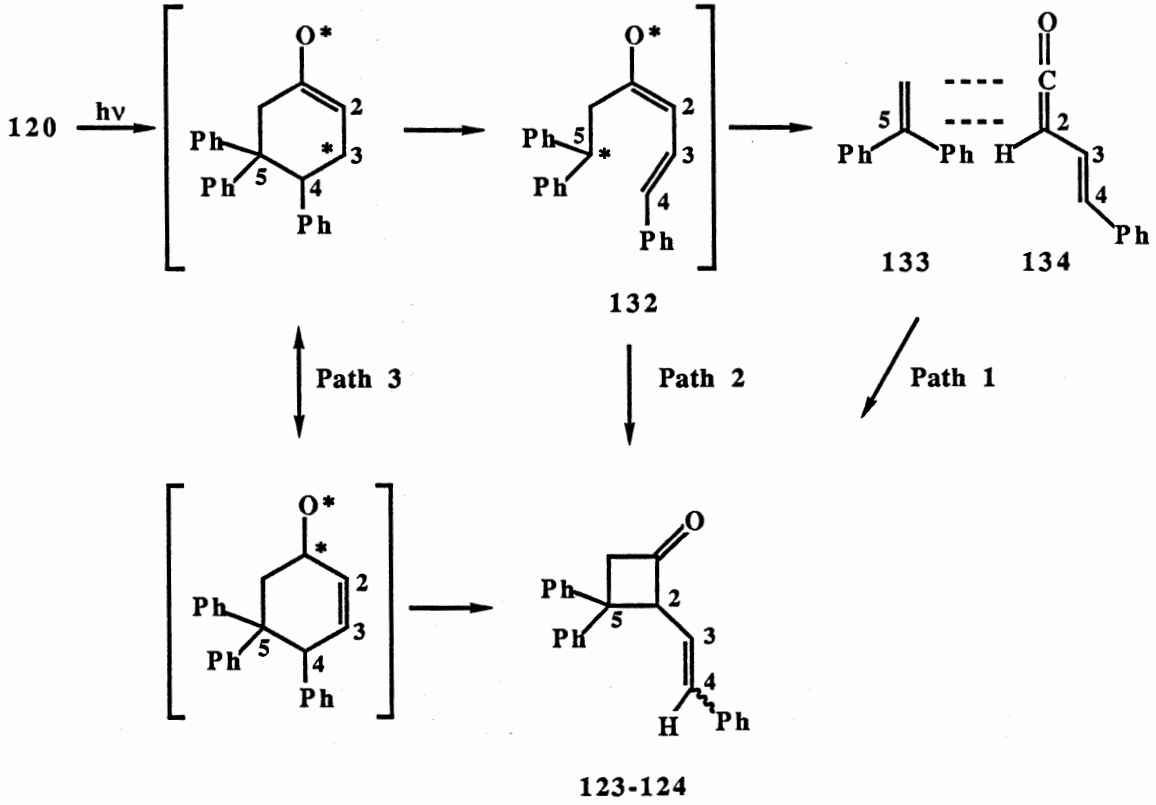
Irradiation of **129** afforded only *trans*-propenylcyclobutanone **130** in excellent yield (93-97%). The spectral data suggested the cyclobutanone **130** -- this structure was later confirmed by degradation to the known 3,3-diphenylcyclobutan-1-one **131.** The degradation sequence involved ozonolysis of **130** to generate the β-ketoaldehyde, followed by oxidation to the acid and then loss of carbon dioxide to give 3,3-diphenylcyclobutanone **131.**



129 **130**

Three possible mechanisms were reasonable for the cyclobutane formation seen in irradiations of **120** and **129.** Path 1 involves fission of the C-4-C-5 bond to generate a 1,4 diradical that undergoes a C-1-C-6 bond fragmentation to give the ketene intermediate and 1,1-diphenylethylene, followed by [2+2] cycloaddition. Path 2 involves fission of

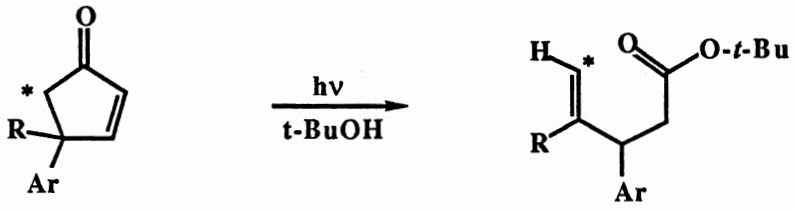
the C-4-C-5 bond followed by attack of the diphenyl radical center on C-2. Path 3 involves a concerted [1,3]-sigmatropic rearrangement. Trapping experiments irradiating in ethanol or benzene containing cyclohexylamine failed to yield esters or amides and, thus, ruled out the ketene mechanism. A concerted [1,3]-sigmatropic rearrangement was ruled out when the photolysis of optically active **129** led to a completely racemic mixture of cyclobutanone **130**. Therefore, path 2, appears to be the process responsible for cyclobutanone formation.



In the photolysis of the 5-phenyl substituted enones **107**, **113** and **120**, the yield of cyclobutanone formation reached only as high as 0.3, 10 and 20%. The low yields observed were attributed to the tendency for the C-4 aryl group to migrate in preference to cyclobutanone formation. Additionally, cyclobutanone formation appears to occur only

in those cases where the ethylvinyloxy diradical is sufficiently stabilized. Despite the lower cyclobutanone yield obtained for **120** relative to **129**, the rate of cyclobutanone formation was faster in the triphenyl system than in the methyldiphenyl system. This rate increase was thought to be due to either the relief of vicinal phenyl-phenyl steric repulsions upon scission of the C-4-C-5 bond or to the available C-4 phenyl conjugation of the π system in **132** derived from **120**.

Interest in 4,4-disubstituted cyclohexanone photorearrangements led to investigations into the photochemistry of 4,4-disubstituted cyclopentenones.[42-43] The photochemistry of 4,4-diphenyl- and 4-methyl-4-phenyl-2-cyclopenten-1-ones (**135** and **137**, respectively) were studied.[42] Direct irradiation of both systems in *tert*-butanol, led to the almost quantitative production of the 3,4-disubstituted pentenoic esters **136** and **138**. It was suggested that the rearrangement of **135** and **137** involved a ketene

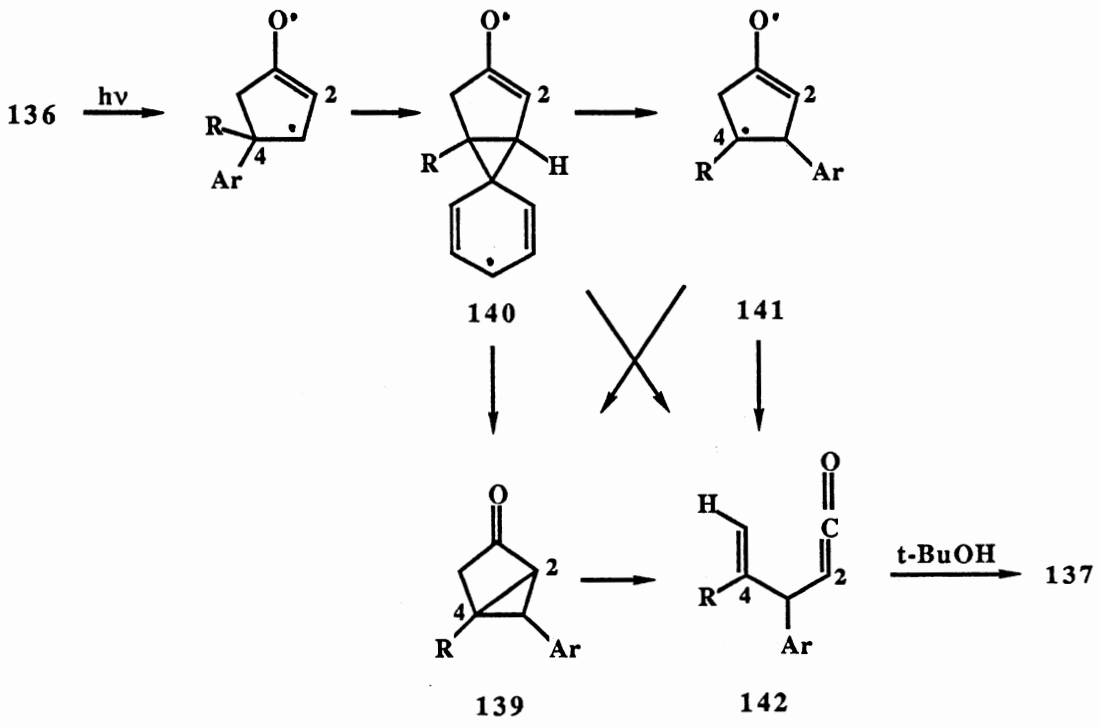


135 - R = Ph, Ar = Ph
137 - R = Me, Ar = Ph
143 - R = Me, Ar = *p*-anisyl, * = ^{14}C

136 - R = Ph, Ar = Ph
138 - R = Me, Ar = Ph
144 - R = Me, Ar = *p*-anisyl, * = ^{14}C

intermediate based on the products derived from reactions run in alcohol solvents and its observed IR absorption. The proposed mechanism involved migration of a C-4 phenyl to the C-3 electron center of the excited enone. Concerted or stepwise C-1-C-5 bond opening generated the ketene intermediate, which underwent addition of alcohol solvents to afford the esters **136** and **138**. The possibility for production of the ketene

intermediate via the housone **139** was considered, despite the fact that this intermediate could not be detected during room temperature irradiations. Low temperature (-140°C) irradiations were completed on both **135** and **137** in an attempt to determine if initial aryl migration occurred to generate the strained housone intermediate **139**. The housone system could be produced by C-2-C-4 bonding in either **140** or **141**. Ring opening of the housone would then generate the ketene and alcohol addition would afford the esters **136** and **138**. IR monitoring of the low temperature photolysis indicated a reaction intermediate that was tentively assigned to a housone structure **139**. Despite this observation, evidence for the completed aryl migration mechanism prior to fragmentation for room temperature irradiations is still in question. Direct fragmentation of the bridged or diradical species **140** or **141** to generate the ketene may also intervene at low

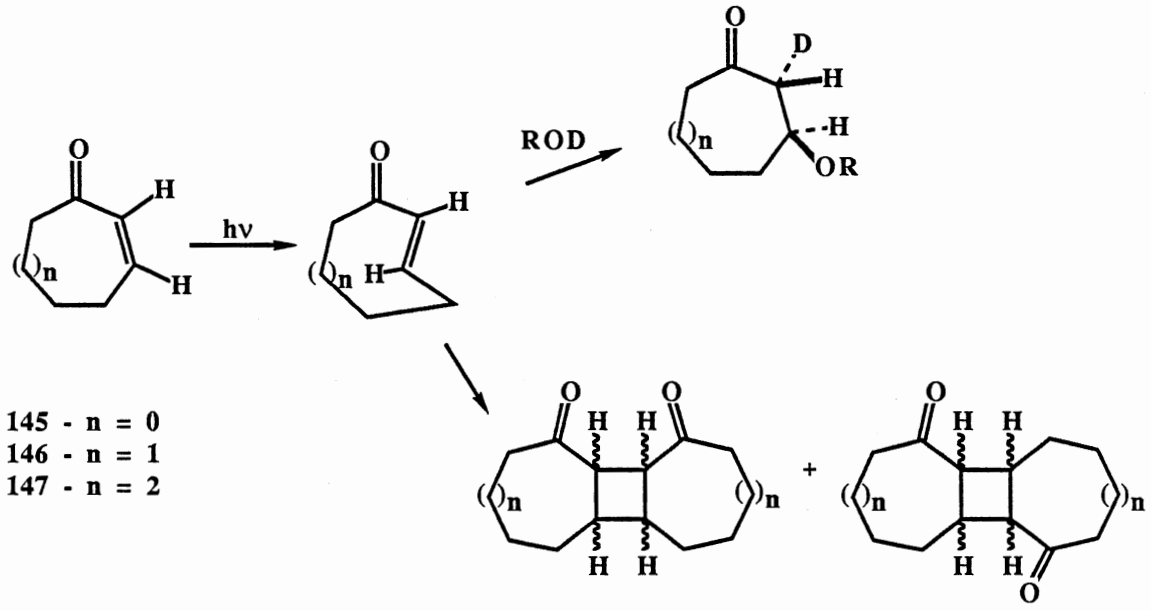


temperature. Attempts to independently synthesize the housone system nonphotochemically were unsuccessful, leading only to production of the ester photoproducts.

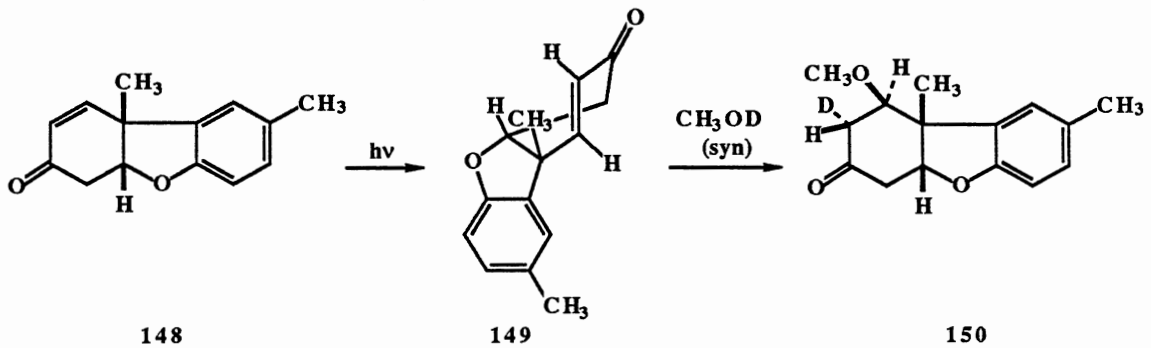
The photorearrangement of 4-*p*-anisyl-4-phenylcyclopentenone **143** has been found to generate the ester **144** by the mechanism described above.[44] The mechanism is supported by deuterium labeling studies of the C-5 methylene which indicate that the labeled methylene appears as the terminal methylene in the product. Generation of the ketene **142** via a housone intermediate, can not be excluded from the data presented.[45]

Cis-Trans Isomerization

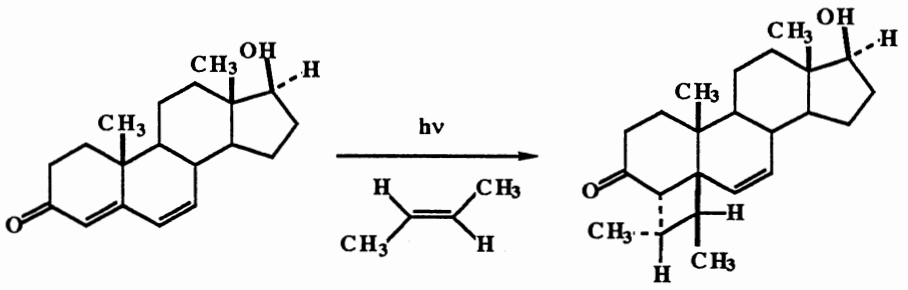
Cis-trans photoisomerization has been observed as a competitive photoreaction of cyclic α,β-unsaturated ketones. Photochemical isomerization of *cis*-2-cyclohepten-1-one (**145**), *cis*-2-cycloocten-1-one (**146**), and cis-2-cyclononen-1-one (**147**), to their trans isomers has been reported.[46-51] For these systems, isomerization occurred with exclusion of all other photochemical reactions. Further work has shown that dimerization and addition products were, in fact, ground state reactions of the highly reactive trans enones.[50,51] It was initially thought that cis-trans photoisomerizations occurred via the triplet excited state but triplet quenching of enones **145** and **146** was unsuccessful.[46] It was later realized that the reactive excited state triplet of these enones underwent cis-trans isomerization faster than intermolecular energy transfer to dienes, thus showing negative results upon quenching.[13] Other flexible ring enones have been reported to exhibit cis-trans photoisomerization. The cis isomers of benzocycloheptenones, 2,6-cycloheptadien-ones, 2,4-cyclooctadienone and benzazepinediones were all reported to undergo photoisomerization to their trans counterparts, followed by dimerization and cycloaddition processes.[52-53]



Cis-trans isomerization reactions of 2-cyclohexenones are rare. Recently, the photocycloaddition of deuterated methanol to Pummerer's ketone **148** indicated the intermediacy of a trans cyclohexenone species.[54] The author suggested that the syn addition occurs to either an excited state species or to an intermediate in which the C=C is twisted more than 90°C, as shown in **149**. Other authors have demonstrated the trans addition of electron-rich alkenes to Δ^6-testosterone (**151**).[55] Irradiation of **151**, leads exclusively to the trans [2+2] cycloaddition product.[55] The formation of the sterically strained trans-fused cycloadduct has been rationalized in terms of addition of the alkene to



148 149 150



151 152

an excited twisted enone moiety.

Recent flash photolysis studies on *cis*-2-cyclohepten-1-one (**145**) and 1-acetylcyclohexene (**153**) have indicated the presence of two transients, one long-lived and one short-lived species.[13,56,57] The long-lived transient was identified as the ground state trans enone, based on the spectral relationships to trans cycloheptene. The short-lived transient was tentively assigned to the relaxed twisted triplet excited of the state enone.

Photodimerization

Dimerizations of 2-cyclohexen-1-one (**154**) and 2-cyclopenten-1-one (**155**) to produce a mixture of syn and anti head-to-head and head-to-tail dimers have been known for some time.[46,58-60] 2-Cyclobutan-1-one (**156**) does not undergo photodimerization but instead undergoes electrocyclic ring opening reactions to afford ketenes.[61] Dimerization is the principal photoreaction for a number of 2- and 3-substituted cyclopentenones and cyclohexenones as well as substituted octalones.[23,62,63] Studies of the cyclohexenone dimerization have implicated the involvement of a π-π^* triplet species with charge-transfer character.[60] Other ring sytems have not been studied as thoroughly.

The regiochemistry and stereoselectivity of the dimerization reaction have been controlled in a variety of enone systems by choosing appropriate substituents and reaction

conditions.[64] For example, irradiation of isophorone and cyclopentenone in the presence of copper (I) salts has been found to increase the production of the head-to-head relative to the head-to-tail dimers.[65] This increase is thought to be due to the fact that copper (I) can complex with the electron pair of the enone oxygen to generate a 2:1 enone-copper complex. The complex then acts as a template for reaction, holding the two enones in position for dimerization.

Photoreduction

Photoreduction of α,β cyclic enones has been reported to occur concurrently with enone photorearrangements.[13] These photoreductions can occur by hydrogen abstraction from solvent, from a second molecule of substrate, or from intramolecular hydrogen abstraction.[13] Hydrogen abstraction from solvent is thought to be a radical process.[66] The effectiveness of solvent in causing photoreduction is directly related to its hydrogen-donor ability and thus its C-H bond dissociation energy.[66] The yields of photoreduction products are found to be highest in 2-propanol, chloroform and cyclohexane, somewhat lower in pyridine and benzene and lowest in *tert*-butanol.[13] Considering the stability of benzene, this solvent ordering is surprising. This observed reactivity was thought to be due to an initially formed enone-benzene complex, but this is still disputed.[67] Systems that are prone to rearrange, i.e. cyclic 4,4-disubstituted cyclic α,β-unsaturated ketones, usually do not undergo photoreduction in *tert*-butanol.[13] An exception to this is the photorearrangement of 4,4-dimethyl-2-cyclopenten-1-one (**157**).[68] Irradiation of **157** in *tert*-butanol affords 2-*tert*-butoxy-4,4-dimethylcyclopentanone (**158**).

There are two general photoreduction reactions for enones: a) Reduction to give pinacols or secondary alcohols; b) Reduction of the enone double bond to yield the saturated ketone with introduction of a double bond at a remote center.[13] The reaction course seems to depend on structural factors and reaction conditions.[69] Pinacols and secondary alcohols are thought to arise from initial hydrogen abstraction by the carbonyl

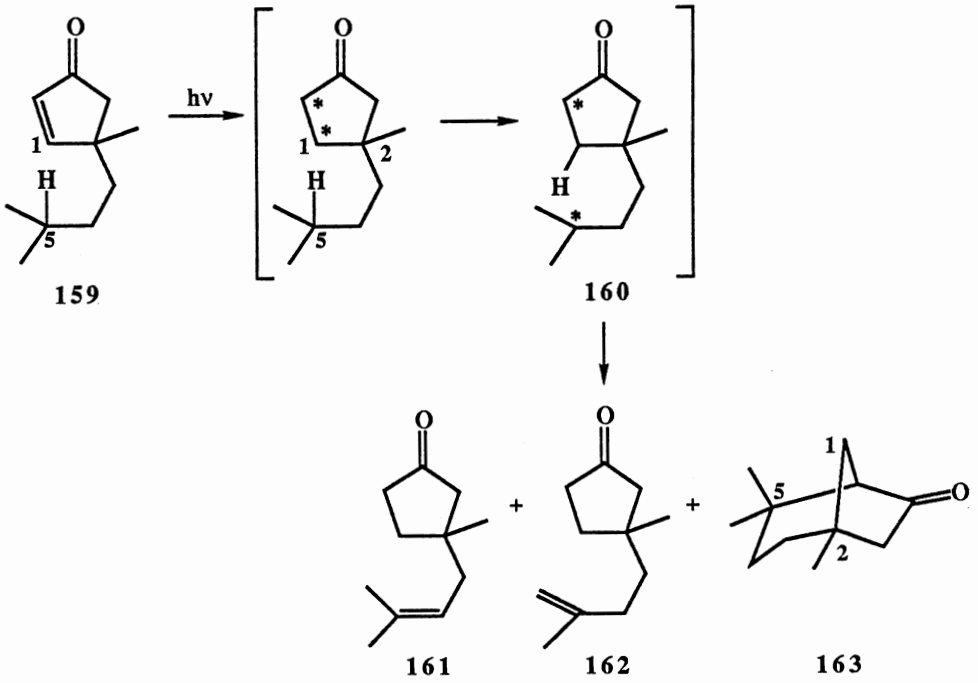
oxygen, followed by coupling of the resulting ketyl radical with another ketyl radical or solvent derived radical. The production of saturated ketones is thought to proceed by either of three mechanisms that have not been distinguished experimentally:

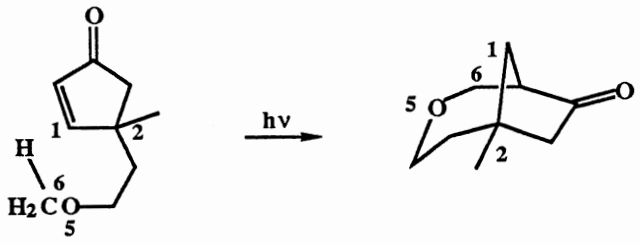
A) Initial abstraction of a solvent hydrogen by C_β, followed by transfer of a second hydrogen atom to C_α.

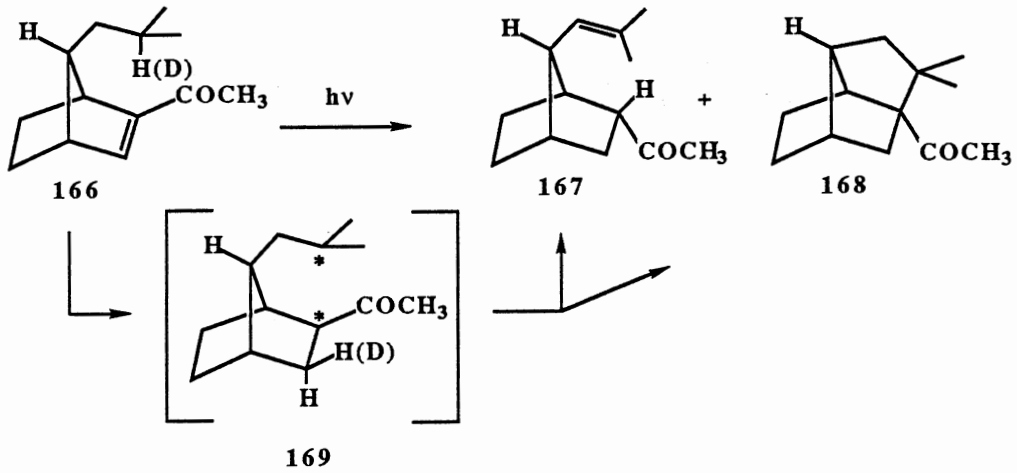
B) Initial hydrogen abstraction by C_α followed by a second hydrogen transfer to C_β.

C) Hydrogen abstraction by the carbonyl oxygen, followed by second hydrogen atom transfer to C_β and tautomerization.

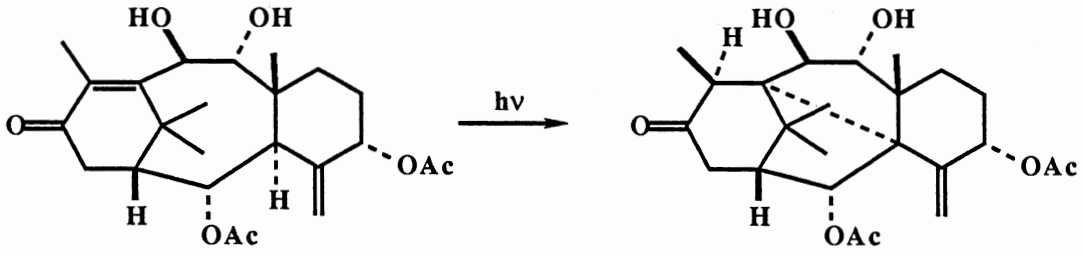
Several authors have suggested that photoreductions of enones involving initial hydrogen transfer to C_β occur via the triplet π-π^* state whereas initial transfer to the carbonyl oxygen involves the triplet n-π^* state.[70] It is thought that saturated ketones are most likely produced via mechanism A by analogy with the accepted mechanism for intramolecular hydrogen transfer of systems that have side chains in a position for hydrogen abstraction.[13] The mechanism for intramolecular hydrogen transfer is illustrated in the photolysis of enone **159**. The excited enone undergoes initial 1,5 hydrogen transfer to the C_β via a six-membered cyclic transition state to generate the diradical **160**, followed by second hydrogen transfer to C_α to afford **161-162**, or cyclization to afford **163**.[68,71] In systems that can only undergo 1,5 hydrogen transfer to C_α, as in the enone **164**, it is reported that exclusive 1,6 hydrogen transfer to the C_β occurs instead, via a seven-membered cyclic transition state.[68] The 1,6 hydrogen transfer being less efficient than the 1,5 transfer. Agosta and coworkers have demonstrated that steric or entropic factors have little effect on determining whether 1,5 or 1,6 transfer occurs.[72] The authors studied the photochemistry of enone **166** where hydrogen transfer can occur equally to either C_α or C_β. Deuterium labeling studies indicated exclusive initial hydrogen transfer to C_β upon irradiation, suggesting that electronic factors in the excited state control the specificity.


O
hν
1
H
5
2
159
160
161
162
163

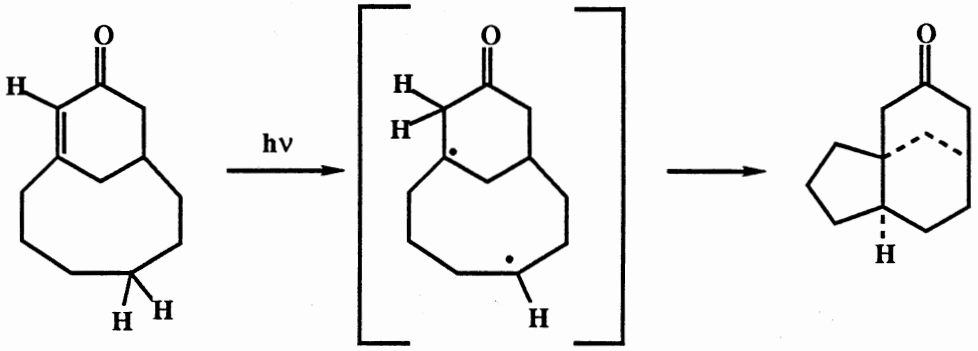

O
1
2
H
6
H2CO
5
hν
6
5
O
2
164
165


H
H(D)
COCH3
hν
166
167
168
169

There have been reports of a few exceptions to the initial C_β hydrogen transfer mechanism.[73,74] Irradiation of enones **170** and **172** afforded **171** and **174**, respectively, both deriving from initial intramolecular hydrogen transfer to C_α. In both systems, it appears that the α position may be closer to the abstracted proton then the β position due to the geometry of the molecule. Therefore initial abstraction occurs at C_α to give the observed products.



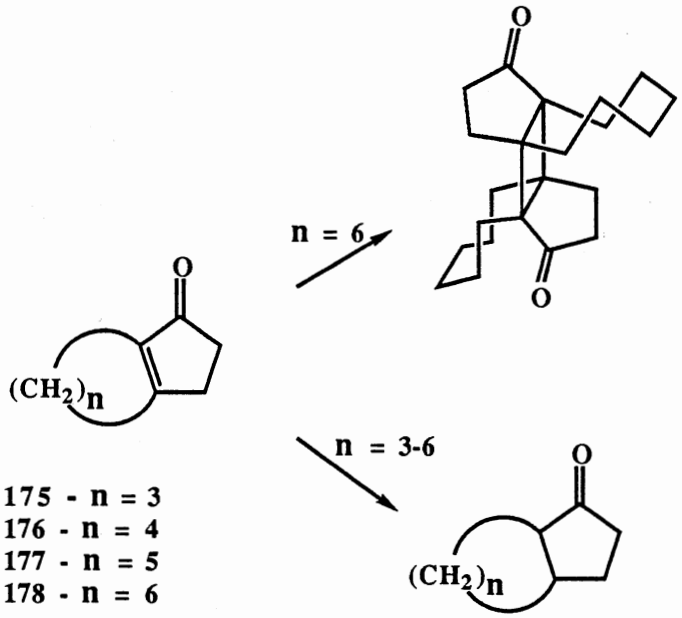
170 **171**



172 **173** **174**

A sufficient pattern of reactivity has not been established for the photoreduction of cyclic enones and, therefore, a prediction of whether reduction or dimerization will occur in a particular system is difficult to make. Factors such as degree of substitution, availability of hydrogen and reaction conditions should be considered. For example, the

flexibility of the ring attached to the cyclopentenone moiety **175-178** is considered to be the feature in determining whether intramolecular hydrogen transfer or dimerization occurs. [75]

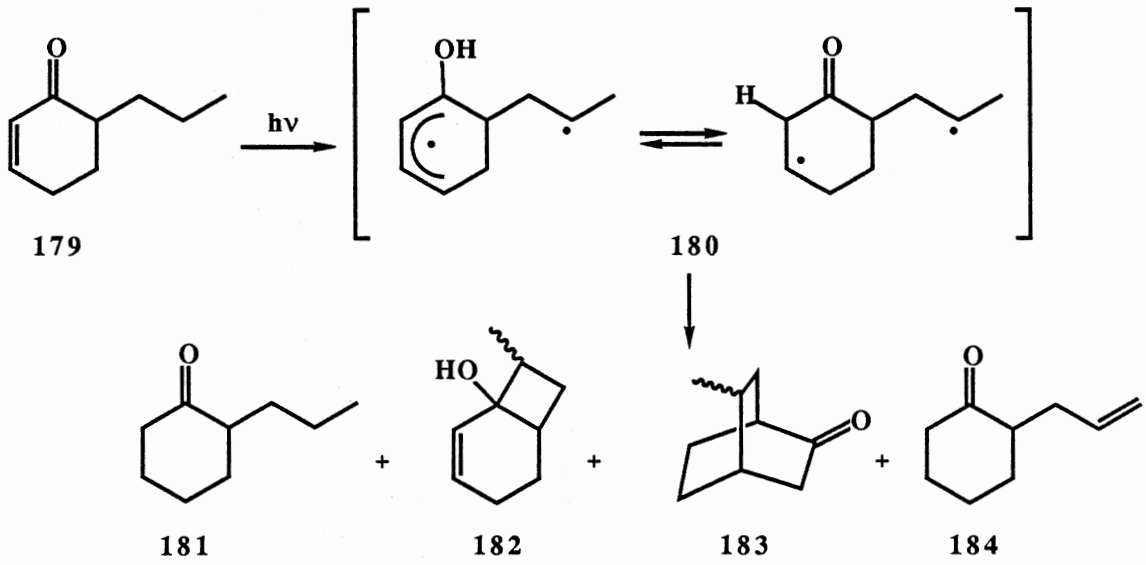


175 - n = 3
176 - n = 4
177 - n = 5
178 - n = 6

Norrish Type II

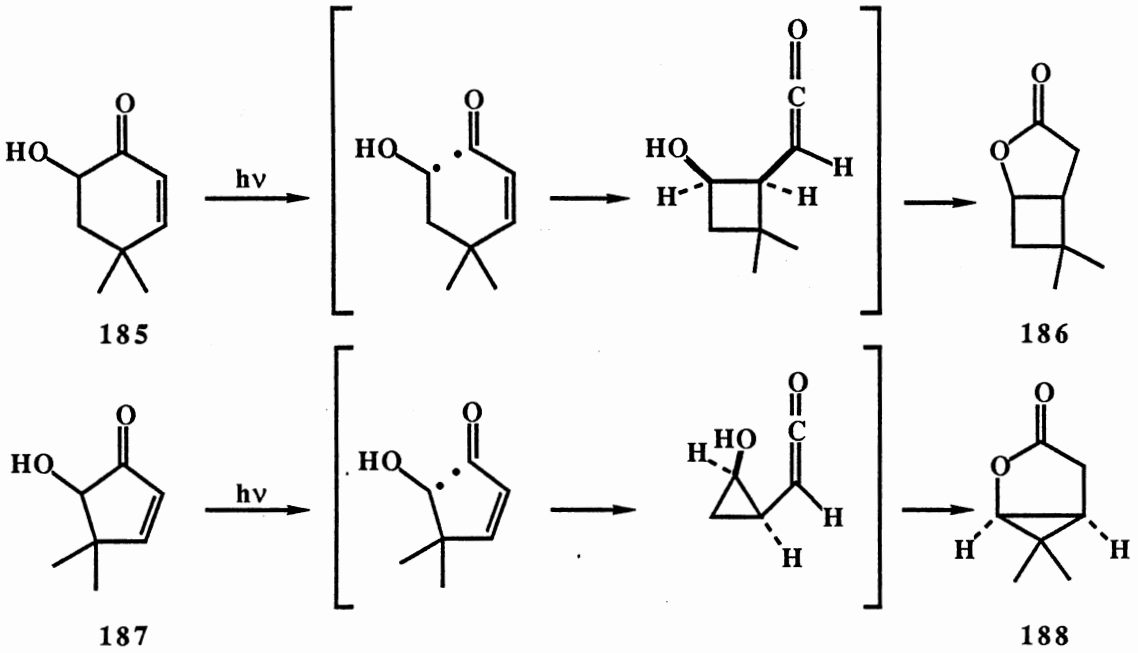
The Norrish Type II reaction, which involves intramolecular abstraction of a γ-hydrogen from a side chain of an enone by the carbonyl oxygen, has been reported for cyclic α,β-unsaturated ketones.[62,76,77] An example of this reaction is seen in the photochemistry of 6-propyl-2-cyclohexen-1-one (**179**). Irradiation of **179** in *tert*-butanol yielded four photoproducts **181-184**.[77] Two of these products, **182** and **183** are thought to arise by a Norrish Type II mechanism. Internal hydrogen transfer of the γ-proton to the carbonyl oxygen generates the diradical **180**, which then cyclizes to either the carbonyl carbon to give **182** or to Cβ to give **183**. Although it has been suggested

that this reaction occurs via a triplet state by analogy with other enone photoreactions, cyclic ketones often undergo Norrish Type II reaction via the singlet manifold.[13,77]



Norrish Type I

Cyclic and acylic ketones undergo cleavage of the bond between the α-carbon and the carbonyl carbon to generate a pair of radicals that can either react to form unsaturated aldehydes or ketenes.[13,78] This α-cleavage, called a Norrish Type I reaction, has been described for a few α-substituted cyclic α,β-unsaturated enones.[79,80] The photochemical reactions of the hydroxyenones **185** and **187**, resulted in the formation of small amounts of lactones **186** and **188**.[79,80] These lactones were thought to derive from a Norrish type I reaction. The C-1-C-6 bond in **185** and the C-1-C-5 bond in **187** were cleaved to generate the hydroxy-stabilized diradical, followed by cyclization to the ketene and lactonization. It was concluded from sensitization and quenching studies that these reactions were occurring from singlet excited states.[79,80] This conclusion along with the fact that the lactones were formed in very low yields indicated that the α-cleavage

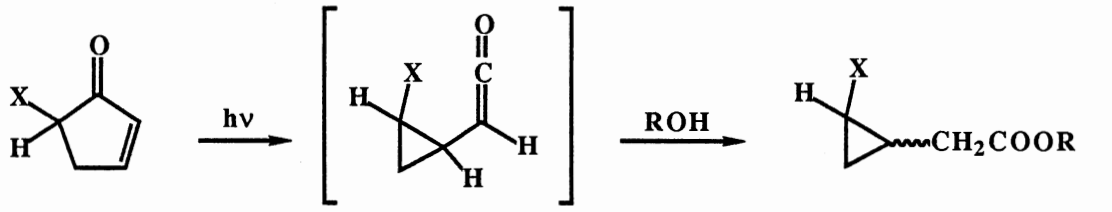


reactions of enones were occurring at the expense of intersystem crossing rather than from competition with the typical enone reaction.[13]

It was initially believed that the poor efficiency of Type A rearrangements was due to the energy wasting α-cleavage process.[81] In an attempt to determine if this was in fact the case, the photochemistry of the 4,4,6,6-tetramethyl-2-cyclohexen-1-one (**189**) was studied by Schuster.[81] The doubly substituted α carbon of the enone **189** was thought to enhance α-cleavage due to the added stabilization of the diradical intermediate produced upon C-1-C-6 cleavage. Irradiation of **189** resulted in only Type A reaction, with no products attibutable to a Norrish Type I reaction. The author believed the reason the Norrish Type I reaction was observed in the 6 and 5-hydroxy systems **185** and **187** and not in **189** derived from hydrogen bonding between the α-hydroxy and the carbonyl which provided stabilization as well as rigidity to the excited state species.[79]

The photochemistry of many other 5-substituted cyclopentenones has been reported to proceed by the Norrish Type I reaction.[82,83] Irradiation of cyclopentenones **190-192** led to the production of esters **193-195**. Initial cleavage of the C-1-C-5 bond

followed by cyclization generated the cyclopropyl-substituted ketene **196**. The intermediacy of the ketene **196** was confirmed by its IR absorption which disappeared upon treatment with methanol. The authors were reluctant to conclude on the results of sensitization and quenching experiments, which suggested that the reaction occurred via the triplet state. This was because phosphoresence and fluorescence studies indicated that the energy gap between the singlet and triplet states for these systems was only 1-2 kcal/mol.



190 - X = C_2H_5
191 - X = n-C_3H_7
192 - X = OCH_2CH_3

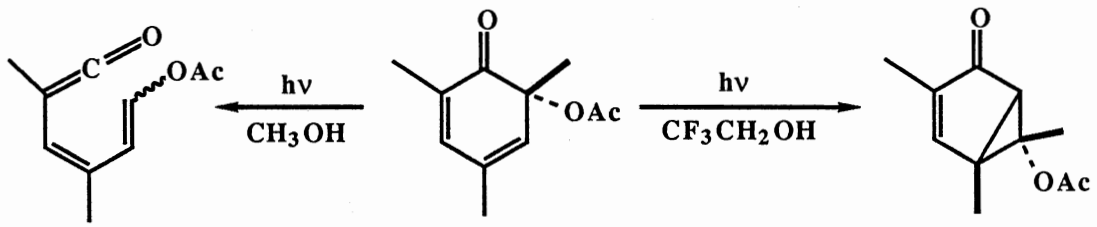
196

193 - X = C_2H_5
194 - X = n-C_3H_7
195 - X = OCH_2CH_3

The fact that 5-alkyl substituted cyclopentenones do undergo α-cleavage while 6-alkyl substituted cyclohexenones do not, has been the subject of extensive discussion.[13] It has been suggested that the n-π^* singlet and triplet energies for typical α,β-cyclohexenones are not high enough to provide the energy required for C-1-C-6 cleavage while for cyclopentenones, the excited state energies are high enough for C-1-C-5 α-cleavage.[84]

6,6-Disubstituted-2,4-cyclohexadienones preferrably undergo α-cleavage to form diene ketenes.[85,86] These reactions appear to originate from a singlet state upon direct irradiation. The production of bicyclohexanones through a Type A rearrangement from these systems occurs with more highly substituted dienones.[85,86] The reaction conditions, in particular the nature of solvent, also tend to determine which path (Type A

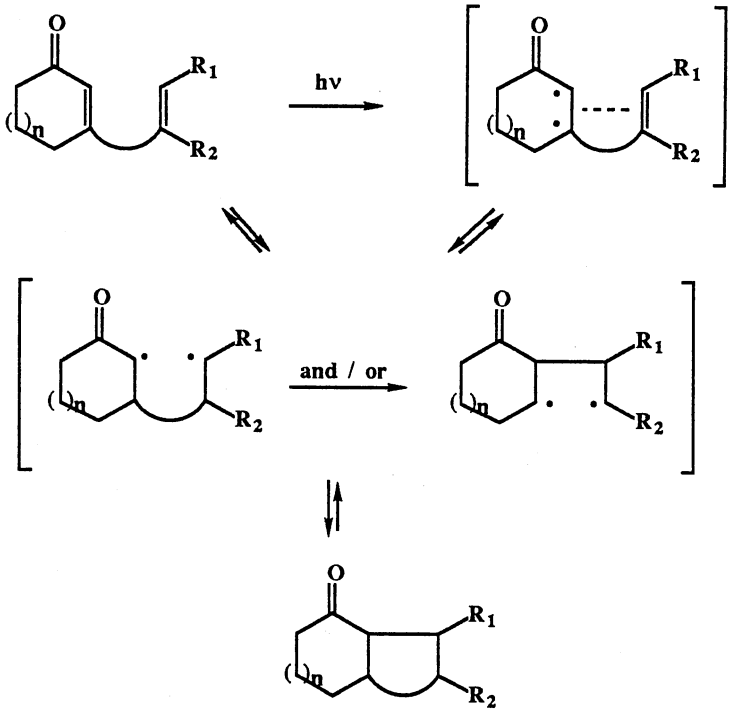
or Norrish Type I) the 6,6-disubstitued 2,4-dienone will follow.[85,86] For example, irradiation of **197** in methanol leads to production of the Norrish Type I product, ketene **198**.[85,86] In trifluorethanol, irradiation of **197** leads instead to the highly stereoselective Type A rearrangement to afford the bicyclohexanone **199**. No ketene intermediates were detected. This dependance on substitution and reaction conditions is also seen for several other tetra- and penta-methylated 2,4-cyclohexadienones.[87,88]



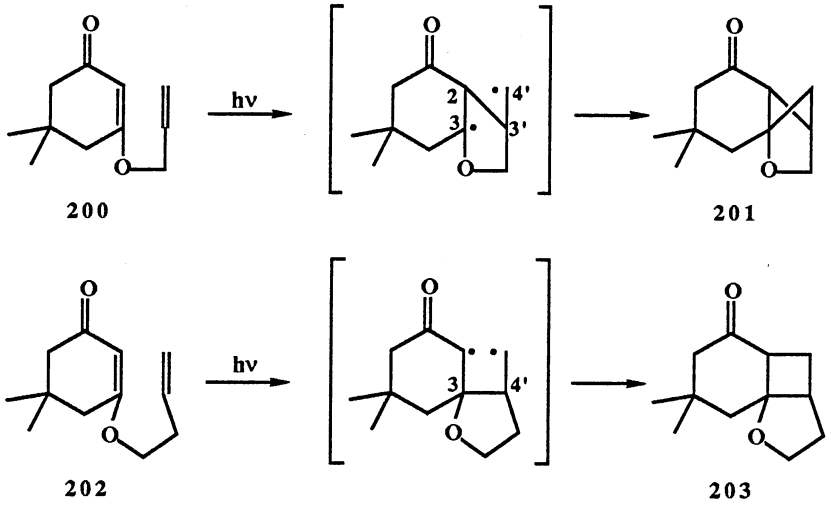
198 **197** **199**

Intramolecular [2+2] Cycloaddition

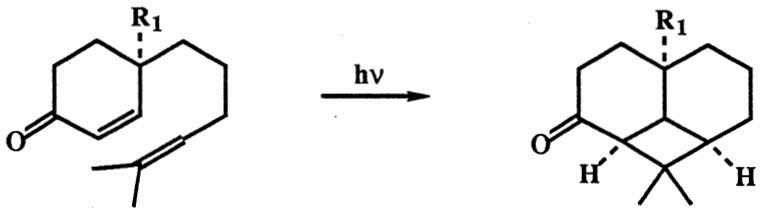
The [2+2] cycloaddition reactions of α,β-unsaturated ketones has been thoroughly reviewed.[64] Intramolecular [2+2] photoreactions of cyclic α,β-enones possessing olefin- or allene-containing side chains have also been reported.[89-92] The proposed mechanism for the intramolecular reaction involves initial n-π^* excitation of the enone followed by intersystem crossing to either the n-π^* or π-π^* triplet state. A short-lived complex between the ground state olefin and the excited state enone (an exciplex) is then formed, followed by collapse to 1,4-diradicals that can cyclize.[64,89] Direct biradical formation without exciplex formation may also be the case in some systems. In the absence of special constraints, initial 1,5-addition of the triplet enone and olefin to form a diradical possessing a five-membered ring is favored ("rule of five").[64,89] If it is not possible to form the preferred five-membered ring, a six-ring will form. An example of



the "rule of five", is illustrated in the photolysis of enones **200** and **202** to their [2+2] cycloadducts.[89] In the irradiation of **200**, initial bond formation occurs between C-2-C-3' or C-3-C-4', whereas in **201**, C-3-C-4' bonding occurs initially. This observed regioselectivity agrees well with the preference for five-membered ring formation.

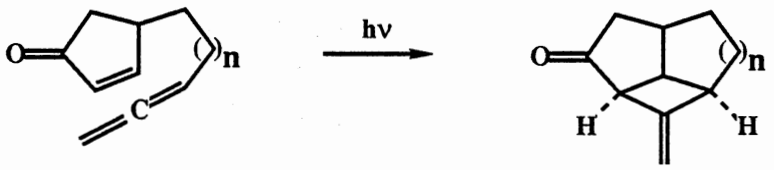


Intramolecular [2+2] cycloadditions have been reported for a large number of substituted cycloalkenones.[90-92] Substrates substituted at C-4 with olefin- or allene-containing sidechains have been found to undergo intramolecular [2+2] reactions in preference to normal enone rearrangement (Type A or aryl migration). Irradiation of enones **204** and **206** to tricyclic ketones are examples of this preference.[90,91]



204 **205**

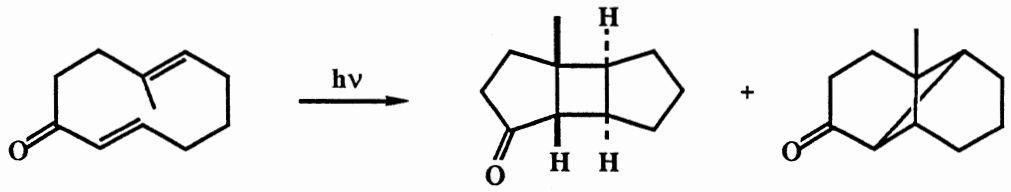
R_1 = CH_3 or Ph



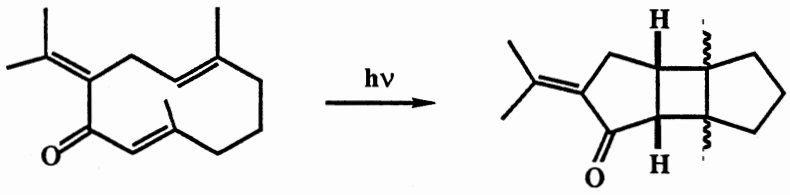
206 **207**

n = 1, 2

In cyclic enone systems of seven carbons or larger, [2+2] photocycloadditions are usually unsuccessful. This is because these systems usually undergo cis-trans isomerization in preference to the [2+2] photoreaction.[64,93] Scheffer[94] and Heathcock[95] have reported the [2+2] photocycloaddition of the ten-membered ring enones **208** and **211**. These systems are heavily biased because of the conformation of the cyclodecane ring and should be noted as an exception.

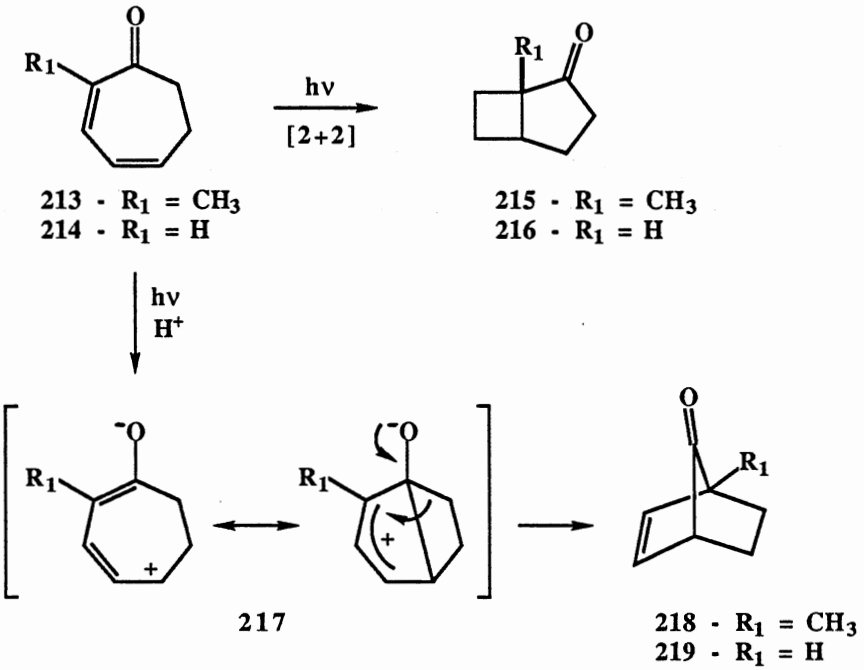


208 209 210



211 212

2,4-Cycloheptadienones have been reported to undergo the intramolecular [2+2] reaction.[96,97] Irradiation of dienones **213-214** in cyclohexane, results in the formation of the [2+2] cycloadducts **215-216.** However, when the cycloheptadienone **213-214** irradiations were carried out in acidic solvents, the norbornenone systems **218-219** were



213 - R_1 = CH_3
214 - R_1 = H

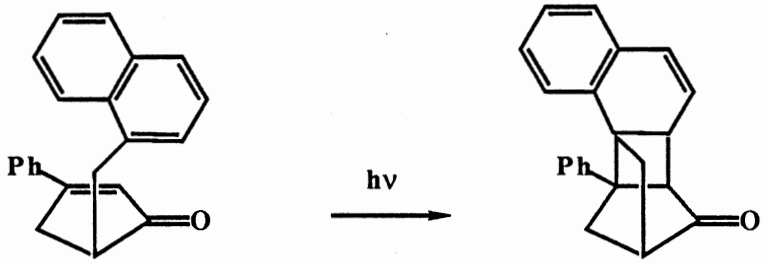
215 - R_1 = CH_3
216 - R_1 = H

217

218 - R_1 = CH_3
219 - R_1 = H

formed at the expense of the fused bicyclic products **215-216**. The norbornenone products are thought to derive from rearrangement of the dipolar species **217**. As the substitution on the 2,4-cycloheptadienone system increases additional isomers resulting from C-6-C-7 cleavage followed by ring contraction are observed.

Another interesting case of the intramolecular [2+2] cyclization reaction is seen in the photochemical studies of 5-arylmethyl-3-phenylcyclopentenones.[98] These systems are found to involve an aromatic double bond in the cyclization process. An example of this is seen in the irradiation of 5-(α-naphthylmethyl)-3-phenyl-2-cyclopenten-1-one **220**. Irradiation of **220** afforded the benzo-fused product **221**, which derived from the [2+2] cycloaddition of a naphthyl double bond and the enone π system.



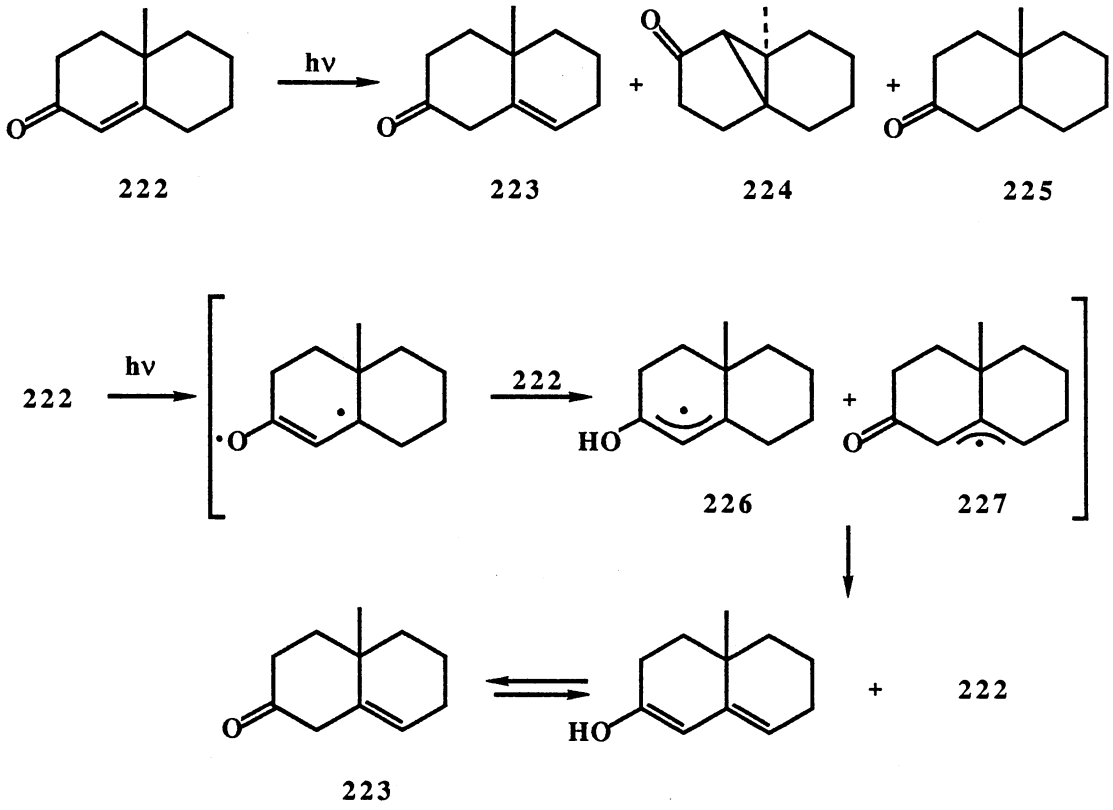
220 **221**

Deconjugation

Rearrangements of cyclic α,β-unsaturated ketones to β,γ-unsaturated ketones has been reported to occur in competition with rearrangement and dimerization in systems containing one or more γ-hydrogens.[23] It is difficult to predict when deconjugation will occur, since no pattern of reactivity has been found.[13]

The deconjugation mechanism has been examined most thoroughly in the photochemical study of $\Delta^{1,9}$-10-methyl-2-octalone (**222**).[26,99] From this study, it was proposed that an intermolecular hydrogen transfer reaction occurs between an excited

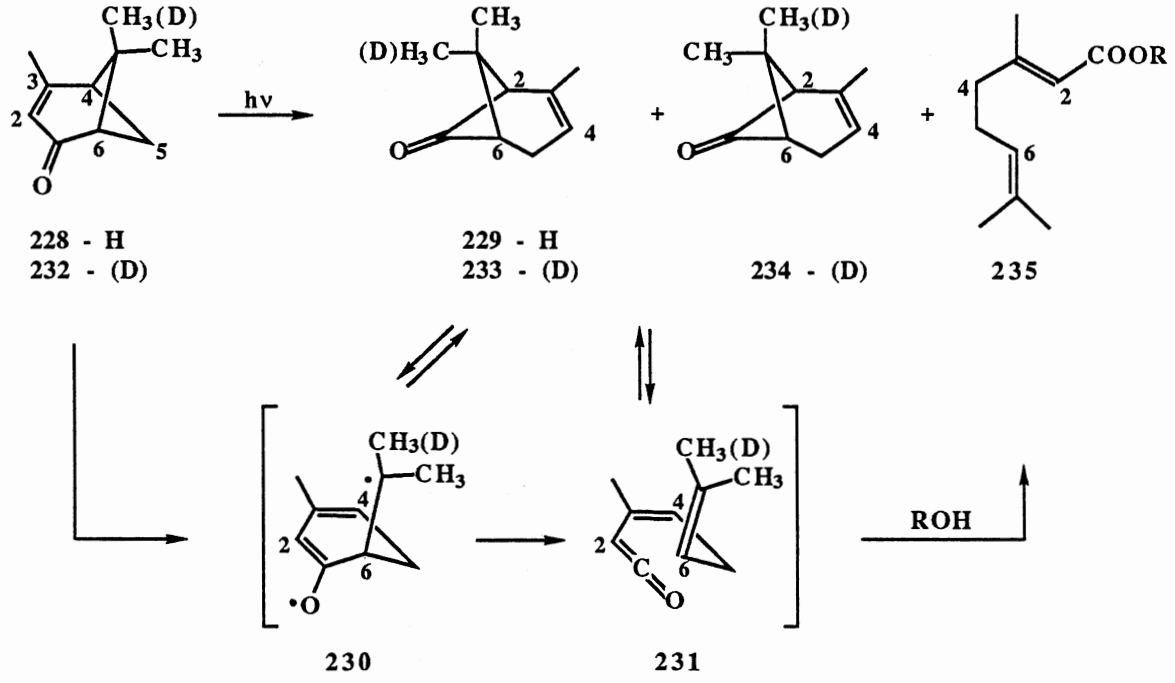
octalone triplet and an octalone ground state molecule to generate the pair of radicals **226** and **227**. A second hydrogen transfer then occurs to regenerate the enone **222** and the β,γ-unsaturated compound **223**. From sensitization and quenching studies, the reaction appears to proceed from a triplet state, the nature of which (n-π* or π-π*) is still unclear.[13]



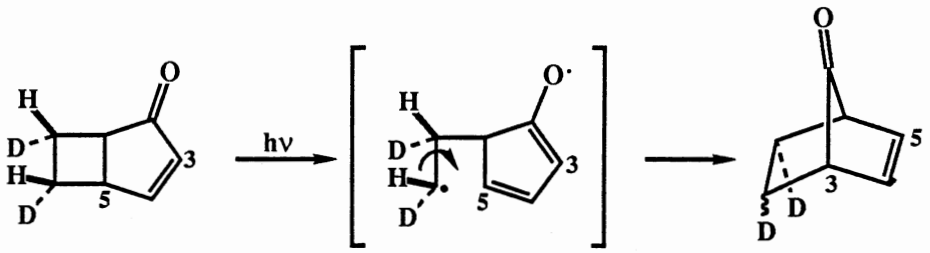
[1,3]-Sigmatropic Rearrangements

The most well-known example of the [1,3]-sigmatropic rearrangement is seen in the photoisomerization of verbenone **228** to chrysanthanone **229**.[100] The mechanism proposed for the rearrangement is illustrated below. It was initially suggested that the reaction proceeded by a stepwise process. This was later confirmed by the photochemical

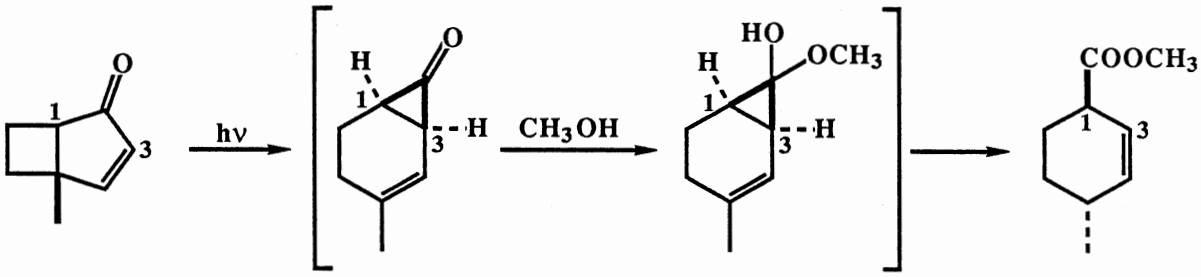
study of the deuterated system **232** which afforded the 1:1 mixture of **233**:**234**. The stepwise process was thought to proceed though the diradical **230** or the ketene **231**. Since α,β-enones do not usually undergo α-cleavage, the ketene is probably formed from the diradical.



Other examples of [1,3]-sigmatropic photorearrangements have been seen in the photorearrangement of bicyclic enones.[13,102-104] It has been reported that the sigmatropic reaction of **236** proceeds through a nonconcerted diradical mechanism to afford **237** and **238** in a 1:1 ratio.[102] Irradiation of the similar bicyclic system **239**, leads to the tetrahydrobenzoic ester **242**.[103] An initial photoisomerization by a concerted [1,3]-sigmatropic mechanism to generate the cyclopropanone **240** is supported by the observed stereoselectivity of the reaction. The cyclopropanone then reacts with methanol or methoxide followed by a thermal ring opening reaction to give **242**.

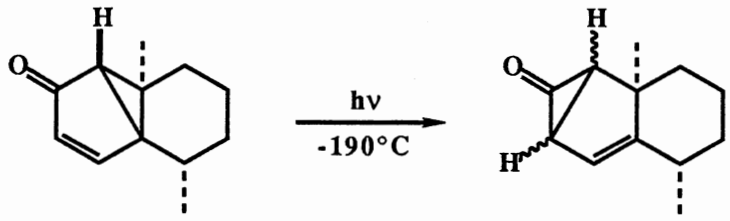


236 237- trans 238 - cis



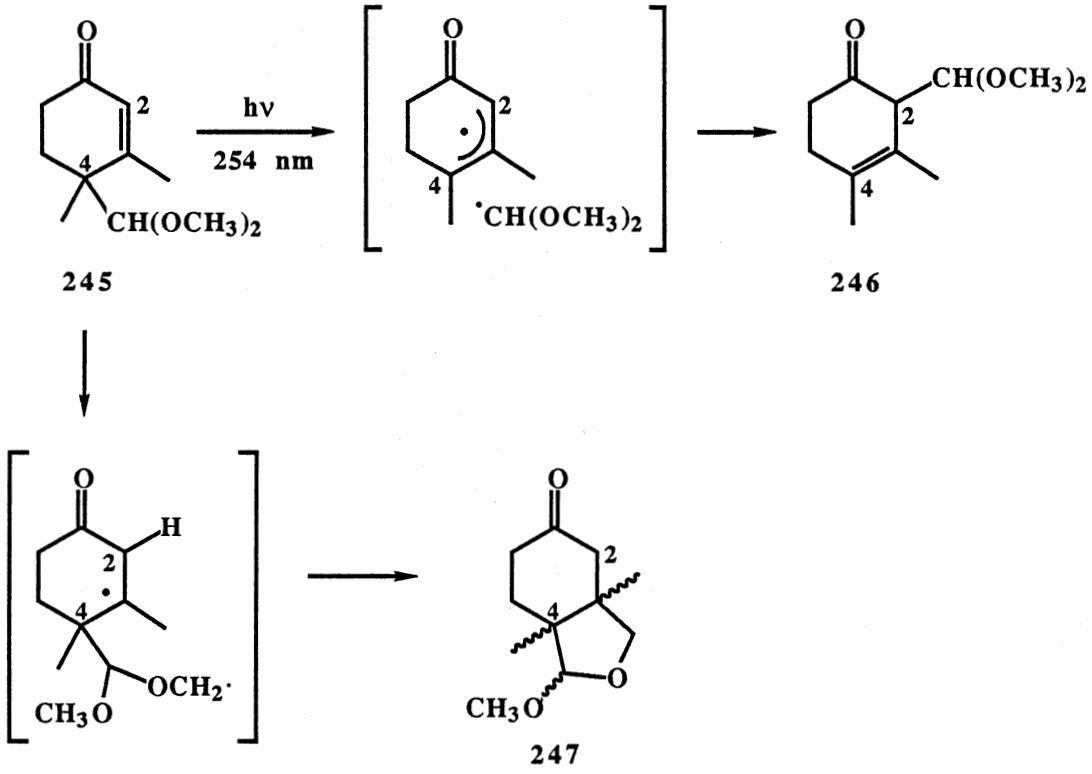
239 240 241 242

Several other photorearrangements of bicyclic ketones to cyclopropanes via a [1,3]-sigmatropic shift have been reported from low temperature matrix isolation experiments.[105,106] For example, irradiation of **243** in a glass at -190°C affords the cyclopropanone **244**.[105] Whether these cyclopropanes observed at low temperature are intermediates in room temperature reactions has been discussed.[106]



243 244

Cycloalkenones containing γ-dialkoxymethyl groups as in **245**, are also known to undergo 1,3-sigmatropic shifts upon π-π* (λ = 254 nm) irradiation.[13,107] Photolysis of **245** results in the formation of two products, **246** and **247**. The α-dialkoxymethyl-cyclohexanone system **246**, is produced by sigmatropic rearrangement of a dialkoxy-methyl substituent from C_γ to C_α. Compound **237** results from abstraction of an alkoxymethyl proton by C_α followed by cyclization of the ether radical to C_β. Normal n-π* (λ > 290 nm) excitation of γ-dialkoxymethyl substituted cycloalkenones usually affords the Type A enone rearrangement or deconjugation products.[107]

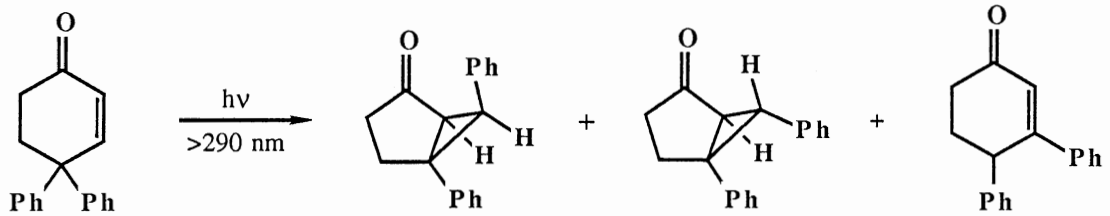


CHAPTER II

THE PHOTOCHEMISTRY OF ONE- AND TWO-CARBON ORTHO-ORTHO PHENYL-BRIDGED 4,4-DIPHENYL-2-CYCLOHEXEN-1-ONES

Introduction

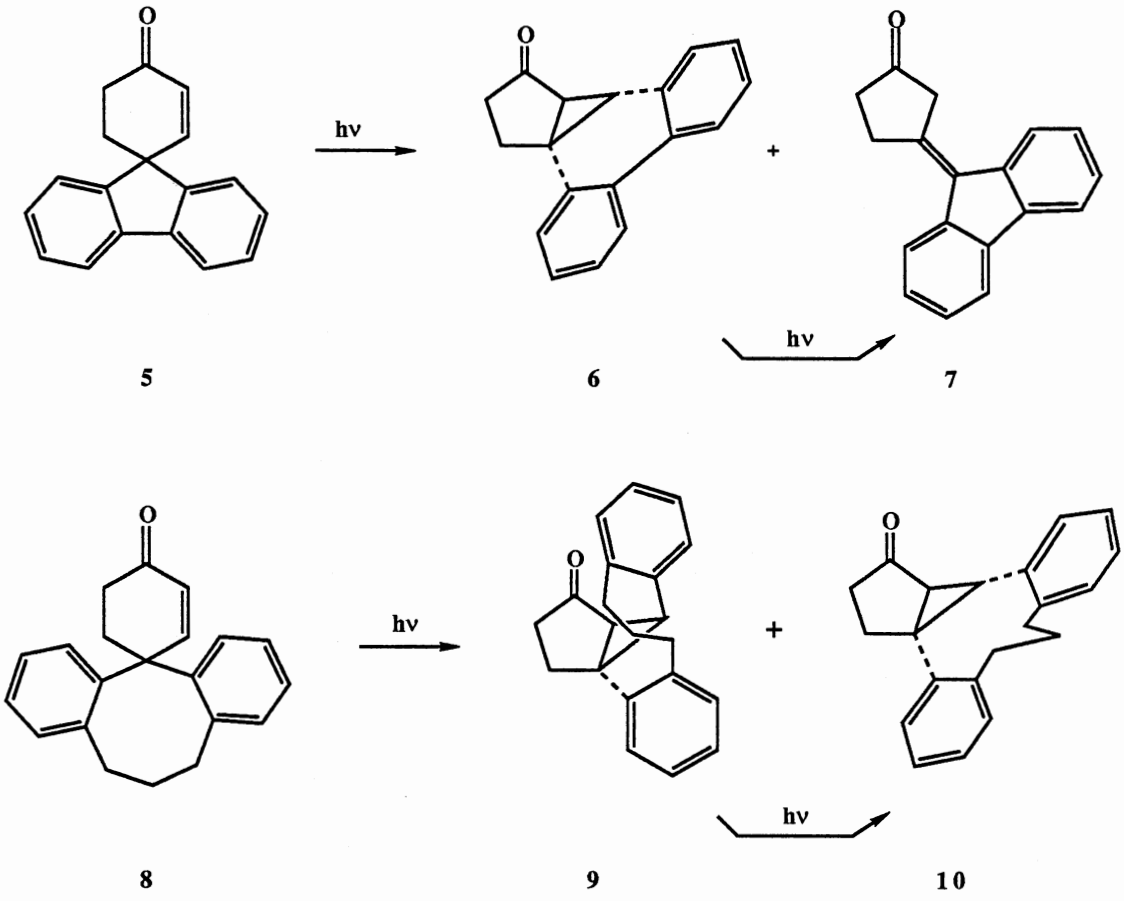
The photorearrangement of 4,4-diphenyl-2-cyclohexen-1-one has been the subject of much attention. Numerous studies have focused on the mechanism, multiplicity, migratory apptitudes and reaction rates for the rearrangement.[1-4,9-11,39,41] It was initially reported that irradiation of 4,4-diphenyl-2-cyclohexen-1-one (**1**) led to the formation of three products, the *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**2**) and (**3**), and a minor product, 3,4-diphenyl-2-cyclohexen-1-one (**4**).[1] The reaction involved γ to β aryl migration followed by either three-ring formation to give the trans and cis products, or hydride migration to give the enone. The ring closure was very stereo-selective, affording the trans and cis products in a ratio of 140:1 at low conversion.



1 **2** **3** **4**

Φ = .043 Φ = .0003 Φ = .0002

Since this initial study, a series of aryl migration reactions of 4,4-diaryl-2-cyclohexenone systems have been reported and with few exceptions, the trans isomer has been observed in kinetic preference over the cis and enone products.[5-8,14,15] It has been of particular interest in our research group to explore the possibility of altering the stereochemical outcome of the 4,4-diphenylcyclohexenone rearrangement.[16] In an attempt to exert stereocontrol over this photoreaction, the ortho positions of the two C-4 phenyl groups that normally migrate apart during the reaction course, were linked by means of an alkyl chain. It was initially proposed that the stereoselectivity of the photoreaction would be a function of the length of this chain. By decreasing the length of the bridging chain, the C-4 phenyl substituents would be inhibited from migrating apart and the normally favored trans diphenyl product would not be preferred. In an effort to establish the limits of this stereochemical control, the photochemistry of the spirofluor-enone and spirodibenzooctenone systems, (**5** and **8**, respectively), corresponding to the ortho-ortho linkages of zero- and three-carbons, were investigated.[16] It was reported that irradiation of **5**, resulted in the formation of the cis diphenyl system **6** and the β,γ-enone **7**. Extended irradiation led to photoisomerization of **6** to the photostable **7**. Irradiation of the three-carbon bridged analog **8**, afforded the trans and cis diphenyl systems **9** and **10**, in a ratio of 115:1 at low conversion. Interconversion (trans → cis) occurred upon extended irradiation to yield a predominance of the cis isomer. The mechanism proposed for production of the trans and cis isomers paralleled that of the parent 4,4-diphenylcyclo-hexenone system.[1,2,9,10] The excited enone $^3(n\text{-}\pi^*)$ undergoes phenyl migration, electron demotion and three-ring closure to generate the bicyclohexanones by either a concerted or stepwise process. Preferential formation of the less stable trans isomer, observed in the three-carbon bridged photoreaction, was attributed to a concerted reaction pathway governed by orbital overlap. An alternative rationale for the trans isomer preference, previously reported in non-bridged 4,4-diaryl systems, involves complete migration to the open C-2-C-4 diradical followed by preferential trans closure.[5-8]



Preference for the trans closure was due to the fact that formation of the cis product requires that the two phenyl rings twist past one another at a stage where the C-4 phenyl is rotationally fixed by delocalization. In the bridged system, however, the three-carbon connector serves to hold the phenyl rings away from each other, thereby relieving any steric bias disfavoring one mode of diradical closure.

The β,γ-enone, seen upon irradiation of **5**, was thought to derive from both primary and secondary photoreactions, by an incomplete Type A mechanism.[16] Initial electronic excitation and intersystem crossing of the enone **5**, followed by ring contraction and C-3-C-2 hydrogen migration yielded **7**. Photoisomerization of **6** to **7**,

resulted from external cyclopropyl bond cleavage followed by phenyl migration to the resulting radical center and C-9'-C-2 hydrogen migration.

It was concluded from these studies that by decreasing the number of carbons in the ortho-ortho phenyl linkage from three to zero, a change in the stereochemical outcome of the aryl migration reaction was observed. The absence of the trans isomer in the photoreaction of **5** was attributed to the strain imposed by the zero-carbon linkage when having to span the distance between the trans oriented phenyl rings. Production of the cis oriented phenyl product **6** was therefore enhanced, as well as the less efficient Type A process. Strain exerted by the zero-carbon bridge suppressed phenyl migration and permitted the Type A process to give the β,γ-enone. In the three-carbon bridged system, the longer carbon-carbon connector permitted formation of the trans isomer and, thus, normal aryl migration resulted.

As a continuation of the photochemical studies of ortho-ortho phenyl-bridged systems, the photochemical behavior of 10,10-dimethylspiro[anthracene-9(10*H*),1'-[2]cyclohexen]-4'-one (**14**) and 10',11'-dihydrospiro[2-cyclohexene-1,5'-[5*H*]-dibenzo[*a*,*d*]cyclohepten]-4-one (**18**), corresponding to the one and two-carbon bridged systems, was explored. It was initially anticipated that the one-carbon bridged system would exhibit either aryl migration giving an overall preference for the cis and enone diphenyl products, or diversion from the normal aryl migration course. Molecular models suggested that formation of the trans diphenyl product from **14** was possible but should be inhibited due to the strain imposed by the one carbon bridge. The cis and enone products, should, therefore, be preferred. We expected that the two carbon bridged system would also exhibit some diversion from the normal reaction course. The two carbon bridge should impose strain on the migrating phenyl, therefore inhibiting trans isomer production and enhancing cis and enone formation. Furthermore, a combination of both the added strain from the one- and two-carbon ortho-ortho linkage, along with the strain already present in bicyclic[3.1.0] systems, could increase production of the more

stable α,β-enone system. Finally, the constraint imposed by the one- and two-carbon linkages might also lead to products not derived from the aryl migration reaction.

If results from the photoreaction of the one and two-carbon bridged systems indicate a kinetic preference for the less stable trans diphenyl systems, this would suggest that the product determining stage of the reaction comes early in the reaction pathway.[7] Preference for the highly strained trans isomer, would also provide additional evidence for a concerted reaction pathway governed by orbital overlap.[16] On the other hand, the more stable cis product should arise from a stepwise mechanism.

Results

Synthesis of the Photochemical Substrates. The synthesis of the photoreactants is outlined in Figure 1. 10,10-Dimethylspiro[anthracene-9(10*H*),1'-[2]cyclohexen]-4'-one (**14**) was prepared from the commercially available anthrone (**11**). Treatment of the lithium salt of **11** with methyl iodide, according to the method of Curtin and coworkers,[108] yielded the dimethyl ketone **12**. Epoxidation using dimethyl sulfonium methylide, followed by acid-catalyzed rearrangement, afforded the homologous aldehyde **13**.[109] Michael addition-aldol annulation of this aldehyde with methyl vinyl ketone, gave the desired enone **14**, in a 5.1% overall yield.[110] The two-carbon bridged substrate **18** was prepared from commercially available dibenzosuberone (**15**). The known epoxide (**16**) and aldehyde (**17**) were prepared as above according to the procedure of Ackermann and coworkers.[109] Spiroannulation of the aldehyde with methyl vinyl ketone yielded 10',11'-dihydrospiro[2-cyclohexene-1,5'-[5*H*]dibenzo[*a*,*d*]-cyclohepten]-4-one (**18**), in a 10.3% overall yield. The poor overall yields for **14** and **18** were due largely to the 8.0 and 14.0% yields obtained in the spiroannulation step. This may have resulted from hindered approach of methyl vinyl ketone to the aldehyde anions derived from **13** and **17**. Additionally, decarbonylation appeared to be a

competitive process in the spiroannulation step for **18** since dibenzosuberane was isolated from the reaction mixture.[111]

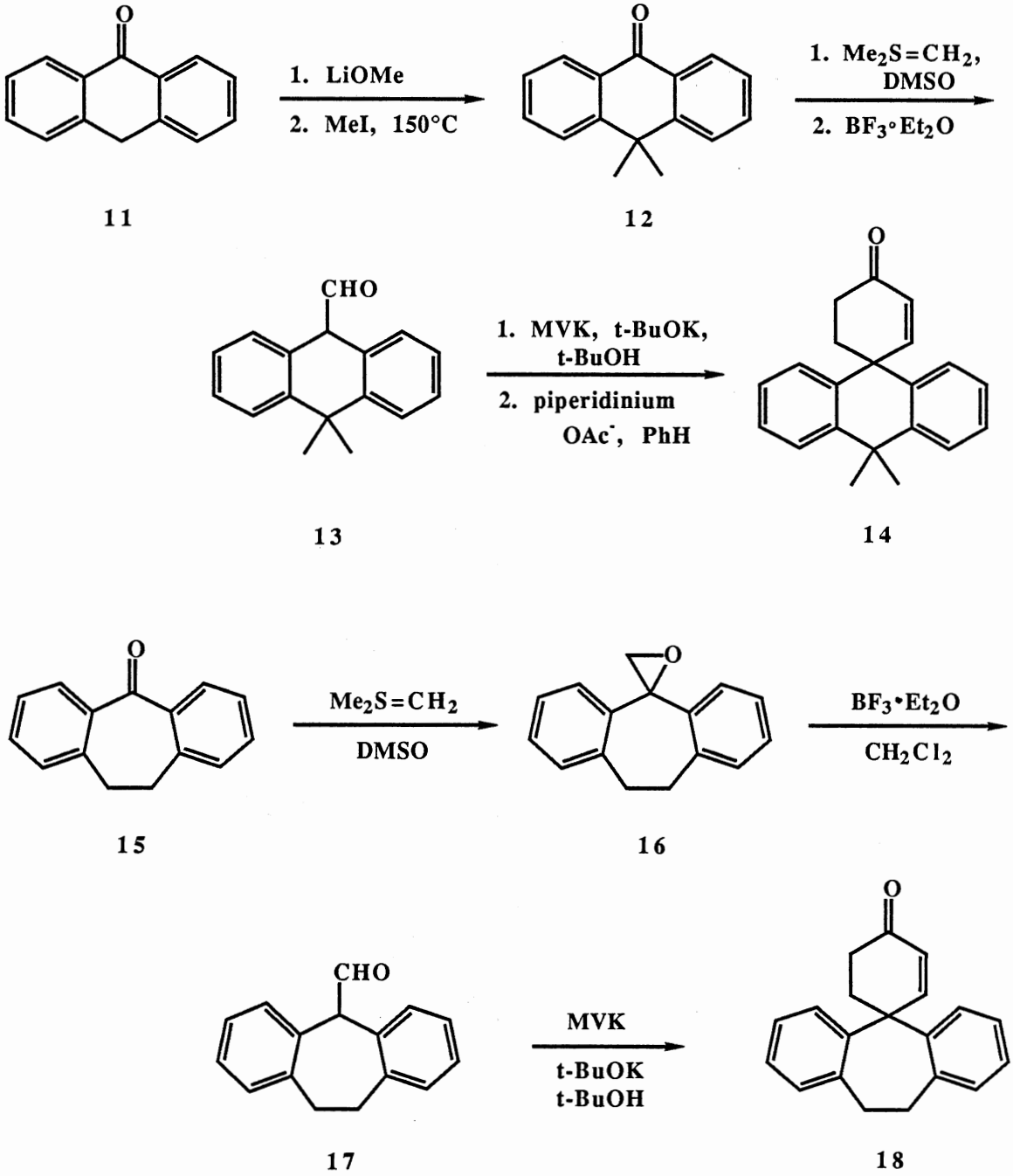


Figure 1. Synthesis of the Photochemical Reactants

Exploratory Photochemistry and Structure Elucidation of the Photoproducts. The photochemical reactions were carried out using conditions comparable to those reported for 4,4-diphenyl-2-cyclohexen-1-one.[1] Direct irradiation of a 10^{-3} M solution of **14** in degassed *tert*-butanol through Pyrex using a 450-W medium pressure Hanovia immersion apparatus led to the formation of six photoproducts at 15% conversion and fourteen photoproducts at 90% conversion. Isolation and characterization of the photoproducts was not attempted, since no apparent preference for any one product was observed. The poor selectivity observed was thought to be a result of competitive reactions such as alkyl migration of the C-10 methyl substituents or radical fragmentation reactions involving the C-10 doubly benzylic center.

Irradiation of a 10^{-3} M solution of **18** in degassed *tert*-butanol through Pyrex using a 450-W medium pressure Hanovia immersion apparatus to 95% conversion resulted in the formation of four photoproducts. Three of the photoproducts, **19** (48%), **20** (9%), and **21** (16%), were isolated and purified from the reaction mixture by preparative thin layer chromatography on silica gel. The low yield (7% by GC) and apparent instability of **22** to these prolonged slightly acidic conditions (25 elutions, 18 h) did not allow for isolation under these conditions. Since the yield of **22** was improved to 22% when the irradiation was carried out in benzene, this procedure was used to generate sufficient quantities of **22** for isolation and characterization. Compound **22** was separated and purified from the other photoproducts by direct phase HPLC on a silica Dynamax-60A Prep column (Dynamax No. #83-121-C) using 85:15 hexane:ethyl acetate. This yielded **19** (53%), **20** (2%), **21** (3%), and **22** (10%).

The elemental analysis and mass spectral data for all four photoproducts **19-22** indicated that they were isomeric with starting material. The ^{1}H and ^{13}C NMR spectra for the major product **19** showed broadened peaks indicating the presence of a conformationally mobile system. Dibenzocyclooctene ring systems have been reported to exist in flexible conformations and broadening of NMR signals for this ring system have

been observed.[112-114] Low temperature ^{1}H and ^{13}C NMR experiments were required to resolve these signals.[114] Low temperature ^{13}C NMR data (-40°C) showed only five aliphatic carbons and a carbonyl carbon signal at δ 199.2, suggesting an α,β-unsaturated cyclohexenyl ketone. The low temperature ^{1}H NMR (-40°C) showed a single vinyl absorption (δ 6.05, s, 1H) and the IR indicated a typical six-ring α,β-enone C=O absorption (1675 cm^{-1}). The spectral data were consistent with a proposed 3,4-diphenyl cyclohexenone system **19**, and confirmed by X-ray analysis to be (±)-4,4a,9,10-tetrahydrotribenzo[*a*,*c*,*e*]cycloocten-2(3*H*)-one. The ORTEP drawing of **19** is given in Figure 2.

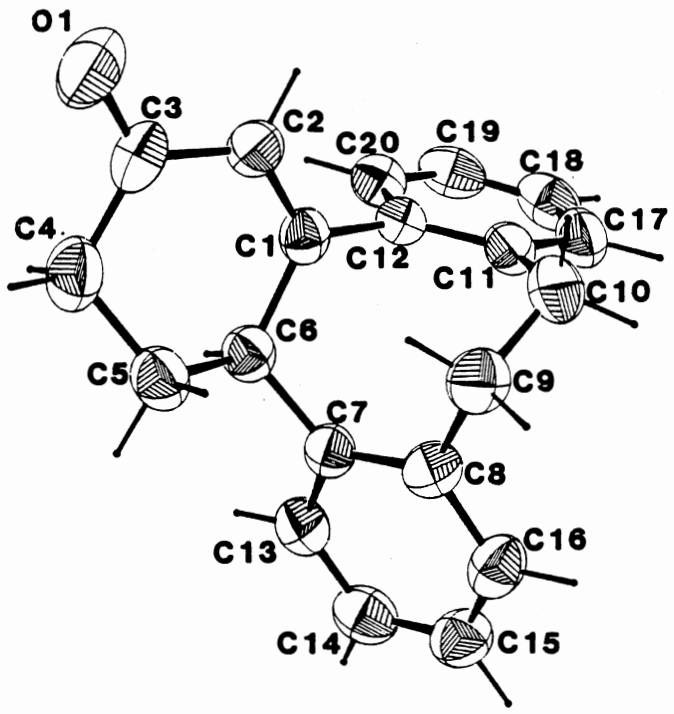
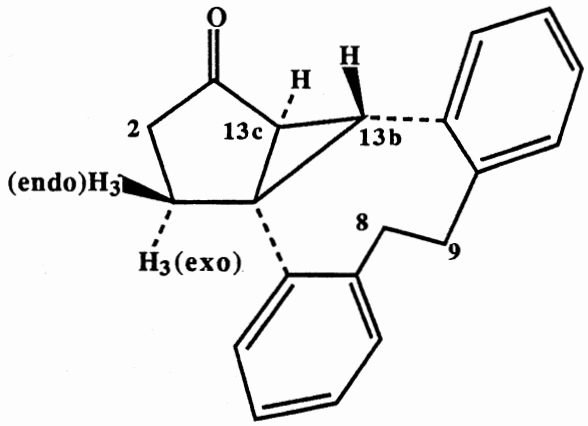


Figure 2. ORTEP Diagram for Photoproduct **19**

The high field proton NMR for photoproduct **20** was found to be very complex and defied unambiguous interpretation. Compound **20** was, therefore, subjected to a

variety of 2-D NMR experiments. The data resulting from the DEPT, HETCOR and COSY allowed initial assignment of **20** to the cis-diphenyl system. ^{13}C NMR data indicated seven aliphatic carbons, and a DEPT experiment confirmed one quaternary, two methine and four methylene carbons. The HETCOR experiment provided carbon-proton NMR correlations and is illustrated in Figure 3. The trans-oriented cyclopropyl protons (H-13c and H-13b) were assigned from the HETCOR to the doublets at δ 2.89 and 2.55 and the coupling (J = 3.0 Hz) was suggestive of a cis-diphenyl stereochemistry about the



20

cyclopropyl ring. A 3.0-4.5 Hz coupling constant is characteristic for trans-oriented cyclopropyl protons and has been encountered previously in cis-diphenyl [3.1.0]bicyclic systems.[7,16,115] A COSY experiment allowed for proton-proton correlations (Figure 4). The protons on the bridge carbons (C-8 and C-9) were assumed to correspond to the farthest downfield aliphatic signals. This assumption was based on comparisons of the NMR spectra obtained from other systems that contain a two-carbon ortho-ortho phenyl bridge as well as comparison of the NMR obtained from the non-bridged cis-diphenyl [3.1.0] system **3**. From the COSY experiment, these downfield signals (δ 3.60 and 3.02) were found to show strong short-range coupling, indicating a vicinal arrangement.

Short-range coupling of the multiplets at δ 2.71 (1H, H-3_{exo}), 2.42 (2H, H-2) and 2.22 (1H, H-3_{endo}) indicated that these corresponded to the adjacent α and β methylene protons (H-2 and H-3, respectively). The HETCOR experiment indicated that the protons represented by the δ 2.71 and 2.22 multiplets, (H-3_{exo} and H-3_{endo}) respectively, were on the same methylene carbon. This methylene carbon (C-3) was further upfield than the carbon signal corresponding to the δ 2.42 (H-2) absorption. This indicated that the α and β proton assignments (H-2 and H-3) were correct. Deshielding of one of these protons (H-3_{exo}) suggested that it may possess an edge-on orientation relative to the C-4 phenyl ring. The IR C=O absorption (1722 cm^{-1}) along with the ^{13}C carbonyl signal at δ 213.3 provided additional evidence for a five-ring cyclopropyl-conjugated carbonyl. The structure of **20** was confirmed by X-ray structure analysis to be (±)-(3a*S**,13bα,13cβ)-2,3,8,9,13b,13c-hexahydro-1*H*-dibenzo[*a*,*e*]cyclopenta[1,3]-cyclopropa[1,2-*c*]cycloocten-1-one. The ORTEP drawing is shown in Figure 5.

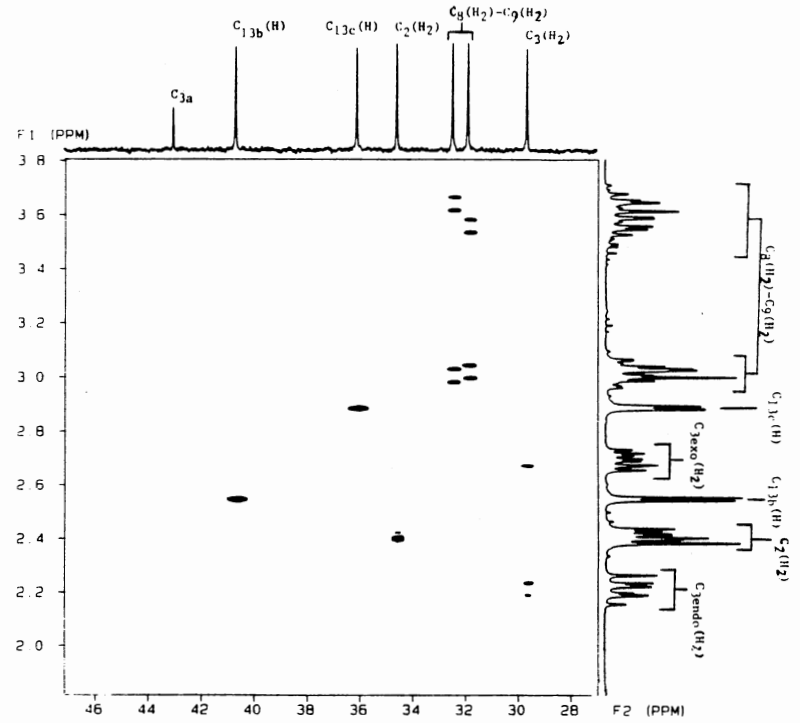


Figure 3. HETCOR of the 46-28 ppm Region for **20**

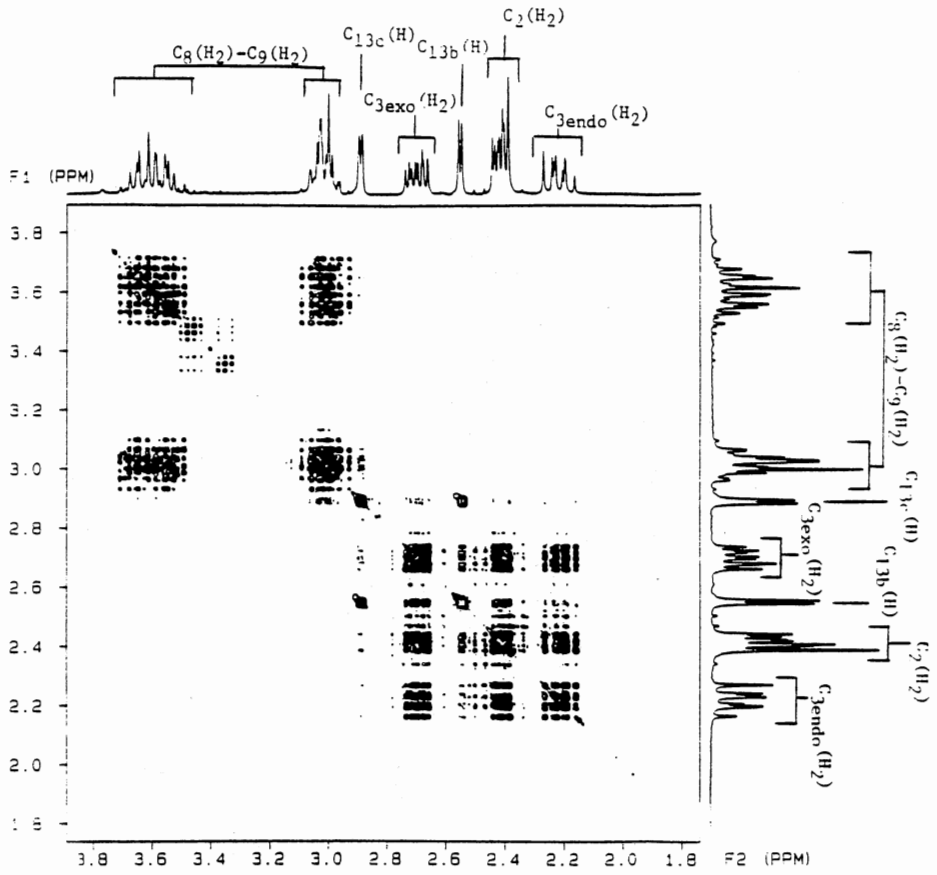


Figure 4. COSY of the δ 3.8-1.8 Region of **20**

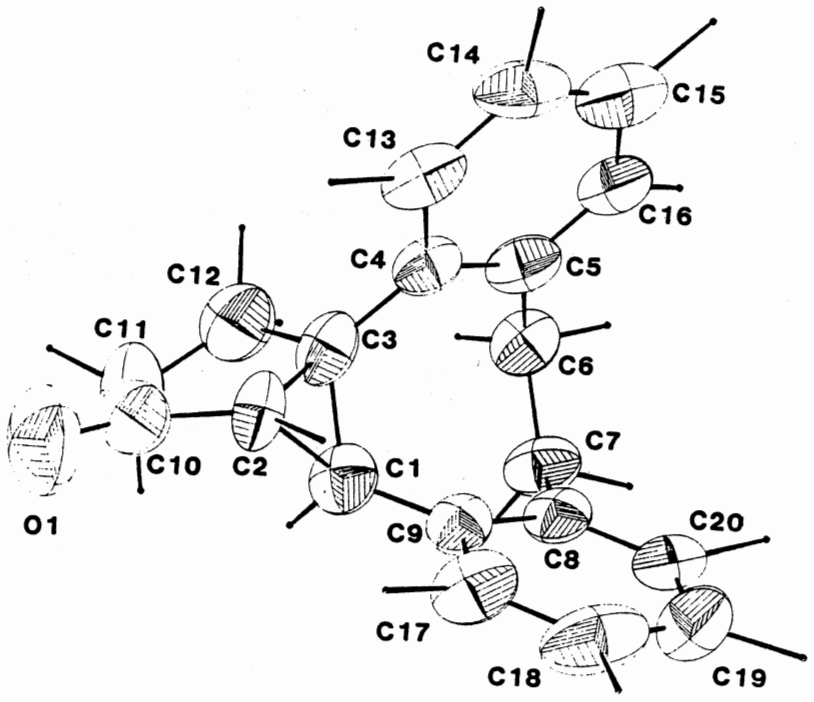
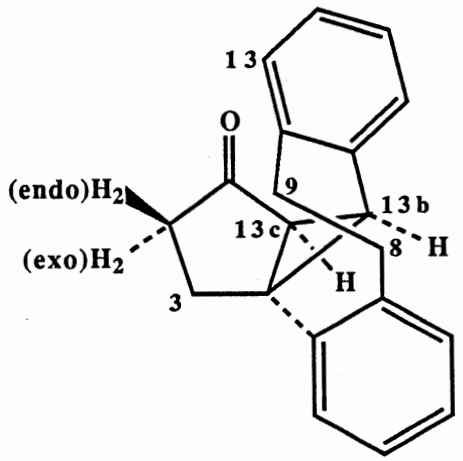


Figure 5. ORTEP Diagram for **20**

The spectral data for compound **21** was very similar to that observed for **20**. The ^{13}C NMR data showed seven aliphatic and twelve aromatic carbon signals, along with a carbonyl signal (δ 214.7) consistent with a cyclopropyl-conjugated five-ring carbonyl. As in **20**, the high field NMR for **21** was very complex and interpretation was inconclusive. It was, therefore, necessary to obtain 2-D NMR information. DEPT, HETCOR, and COSY experiments provided evidence for the trans-diphenyl system **21**. These are illustrated in Figures 6 and 7. The DEPT experiment allowed assignment of the carbon multiplicities. The seven aliphatic carbon signals corresponded to one quaternary, two methines and four methylenes. From the HETCOR data, carbon-proton correlations were determined. The methine carbons (C-13c and C-13b) were assigned to the proton doublets at δ 2.81 and 2.64. The 9.5 Hz methine-methine coupling was consistent with cis-oriented cyclopropyl protons (i.e. trans-oriented phenyls) in accord with literature values of 9.5-10 Hz.[7,16,115] The COSY experiment provided proton-proton correlations. From the COSY, the proton signal at δ 2.30, was found to be coupled to the methine proton signal (H-13c) at δ 2.81. This signal (δ 2.30) was assigned to the H-2_{exo}. The



21

observed coupling between the H-13c and the H-2_{exo} signals was thought to be due to the fact that the bridged system was very rigid and allowed for a strong W-coupling.[116] Strong coupling of the H-2_{exo} signal and the complex signal centered at δ 2.01 (3H) was observed from the COSY. This suggested that this complex corresponded to the other α-proton (H-2_{endo}) as well as the β-protons (H-3). Shielding of endo α-protons (as in H-2_{endo}) relative to exo α-protons (as in H-2_{exo}) has been previously observed in trans-diphenyl [3.1.0] systems.[7] These observations have been attributed to the fact that the endo-proton pokes into the π cloud of the C-13b-substituted phenyl and is thus, shielded. Assignment of the protons on the two-carbon bridge (C-8 and C-9) was made to the remaining downfield coupled aliphatic signals. This assignment was again based on NMR comparisons of similar systems. From the 1-D proton NMR spectrum, it was noted that one of the aromatic signals appeared slightly upfield from the other aromatic signals. This may be the result of the ortho proton (H-13) of the endo phenyl ring sitting near the shielding cone of the carbonyl. The spectral data obtained were consistent with the proposed trans-diphenyl system **21**.

Assignment of **21** to the trans-diphenyl system was confirmed by lithium-liquid ammonia degradation. The degradation scheme is depicted in Figure 8. Structure elucidation of cyclopropyl ketones by lithium-liquid ammonia reductive cleavage of carbonyl conjugated three-ring bonds has been previously reported.[14] In contrast to lithium-liquid ammonia reductions of non-phenyl bridged [3.1.0] bicyclic systems, where both external cyclopropyl bonds (bonds a and c) and the internal cyclopropyl bond (bond b) were cleaved, lithium-liquid ammonia reduction of tricyclic compounds **6**, **9** and **10** cleaved only the external cyclopropyl bond (bond a).[16] This selective cleavage was thought to be due to strain exerted by the phenyl-phenyl connector on the external bond.[16] This ortho-ortho connector also makes the cyclopropyl system more rigid, allowing the orbitals of the external three-ring bond to lock into better alignment with the carbonyl π system that will contain the odd-electron of the radical anion.

The only difference in structure between the cis and trans systems (**20** and **21**) is the stereochemistry about C-13b. Reduction of these compounds with lithium-liquid ammonia would destroy this asymmetric center and produce the common degradation product **23**. Since the stereochemistry of C-13b in **20** was already established by X-ray analysis, production of the common product from reduction of **20** and **21**, would confirm the stereochemistry and, thus, structure for **21**. Reduction under these conditions did, indeed, yield the spiroadduct **23** confirming the two related structures. Structural assignment of **23** was made based on its spectral data (IR, Low Temp ^{1}H NMR and ^{13}C NMR) along with spectral comparison of the lithium-liquid ammonia products obtained from reduction of **6**, **9** and **10** previously reported.[16] These observations, taken together, established **21** to be (±)-(3a*R**,13bα, 13cα)-2,3,8,9,13b,13c-hexahydro-1*H*-dibenzo[*a*,*e*]cyclopenta[1,3]cyclopropa[1,2-*c*]cycloocten-1-one.

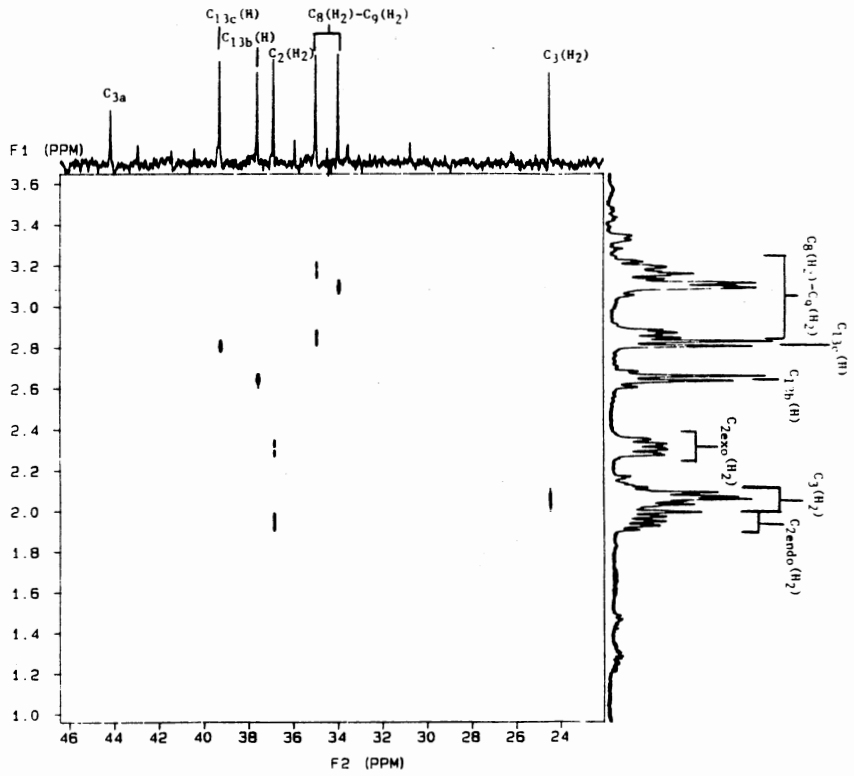


Figure 6. HETCOR of the 46-22 ppm Region for **21**

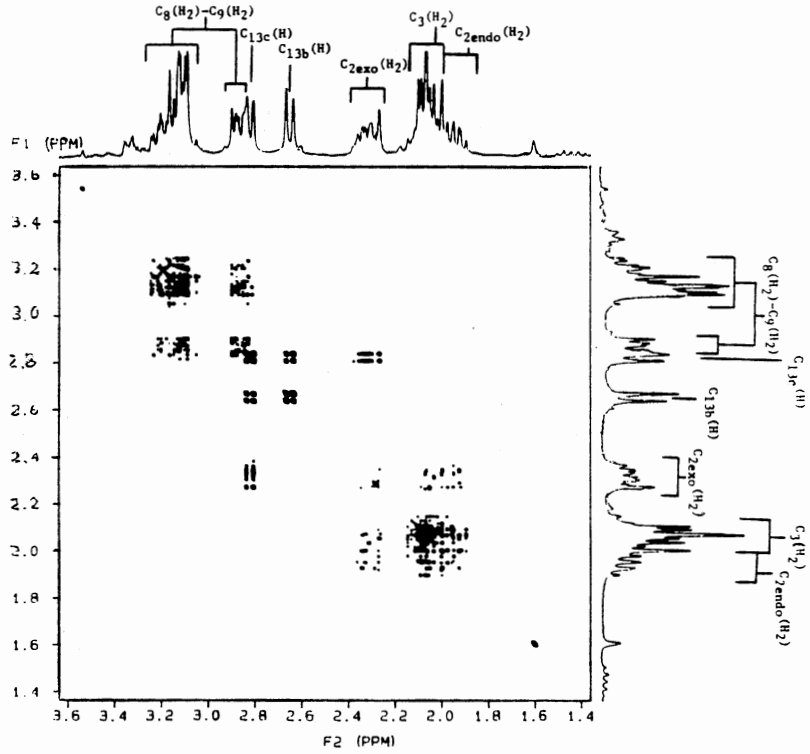


Figure 7. COSY of the δ 3.6-1.4 Region for **21**

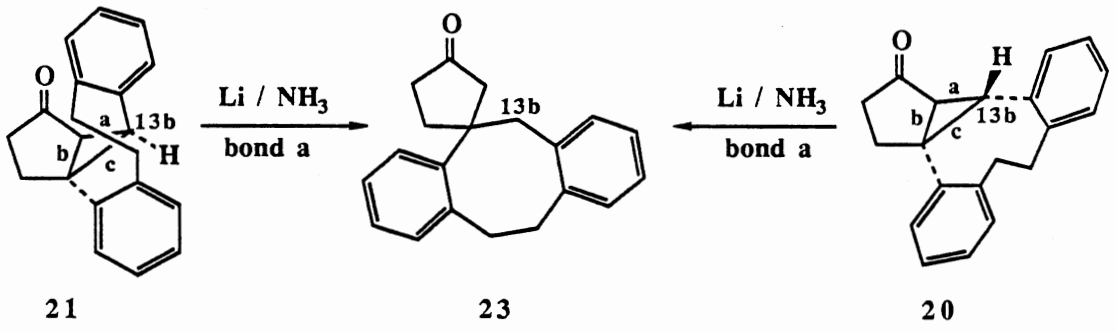
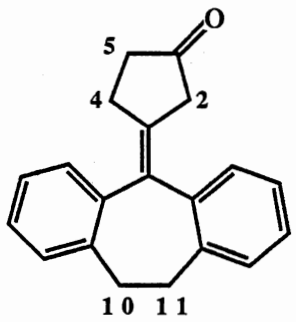


Figure 8. Li/NH_3 Reductions of **20** and **21**

The identity of the fourth photoproduct **22** was determined from its spectral data to be 3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene)cyclopentanone. ^{13}C NMR data revealed only five aliphatic signals, all corresponding to methylene carbons. The proton NMR showed no vinyl absorptions, and two complex multiplets corresponding to four and six protons. These overlapping proton signals made it necessary to run a proton shift reagent experiment.[117] The shifted spectrum (10 mg $Eu(fod)_3$) showed an AB doublet (2H), two multiplets (2H each), an AB multiplet (2H), and a multiplet (2H) (Figure 9). The chemical shifts *vs* $Eu(fod)_3$ concentration were plotted and the least squares lines were extrapolated to zero concentration to obtain the initial resonance positions of these protons (Figure 10).[117] The slopes of the least squares lines (Δm) were determined and are tabulated along with the initial shifts (IS) in Table 2.[117,118] These slopes (Δm) have been reported to be directly proportional to the reciprocal of the lanthanide-proton distances, i.e. as the distance decreases, Δm increases.[118,119] Therefore, the slopes determined from the shift reagent experiments indicated that the AB doublet (centered at δ 4.54, 10 mg $Eu(fod)_3$, 2H) and the multiplet (δ 3.49, 10 mg $Eu(fod)_3$, 2H) corresponded to protons very near the lanthanide ion and, thus, the carbonyl group. [Note: It is presumed that the lanthanide shift reagent coordinates with the ketone carbonyl.] Selective proton decoupling experiments on the shifted spectrum in



22

conjunction with the shift reagent data (Δm, IS) allowed for assignment of these signals.[117,119] The AB doublet was found to be coupled only to itself, indicating the isolated methylene at C-2. The two protons attached to C-2 are nonequivalent because the two-carbon ortho-ortho phenyl bridge does not allow for a completely planar aromatic system. Therefore the two protons see different magnetic environments and appear as an AB doublet. Additionally, the large coupling constant for the AB doublet, J = 21 Hz, obtained from the unshifted spectrum has been noted for other geminal methylene protons.[121] Decoupling of the multiplet at δ 3.49 (Δm = 0.93) revealed coupling to the AB multiplet centered at δ 3.33. These two signals were, therefore, assigned from this observation and the large Δm for the δ 3.49 signal, to the α and β methylene protons on C-5 and C-4 of the cyclopentenone ring. Irradiation of the multiplet at δ 3.47 simplified the signal at δ 2.99. This observed coupling, along with the small slopes (Δm = 0.165, 0.086) indicated that these signals corresponded to the two-carbon ortho-ortho phenyl bridge protons on C-10 and C-11. Finally, the IR C=O absorption (1715 cm^{-1}), the ^{13}C carbonyl signal at δ 209.8 and the UV data provided additional support for a nonconjugated carbonyl. Thus, the final photoproduct was assigned the β,γ-enone structure **22**.

Compound **22** was stable to 0°C but was observed to decompose after 24 h at room temperature. This room temperature instability made it difficult for unequivocal assignment by chemical means or X-ray structure analysis. Attempts at independent synthesis of **22**, by a variety of synthetic methods, proved unsuccessful. Despite these setbacks, a synthetic route developed in this work, served to establish a novel and new approach to an important series of antidepressant drug analogs. This route is illustrated in Figure 11. The impetus for this unconventional approach to the alcohol **27**, was the poor yield (< 5%) obtained in the Grignard reaction of 4-bromomagnesio-1-cyclopentene and dibenzosuberone (**15**), coupled with the difficulty in preparing 4-bromocyclopentene (**24**). Therefore, the method involving ring closure of the di-Grignard[122] **25** on ethyl 3-

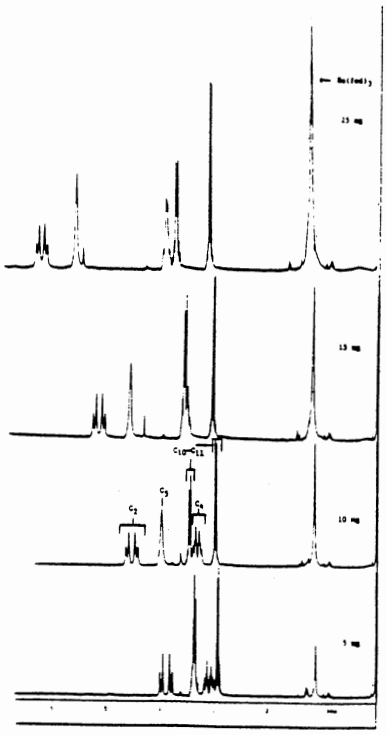


Figure 9. Effect of $Eu(fod)_3$ on **22**. Clarification of the Aliphatic Proton Region for **22**

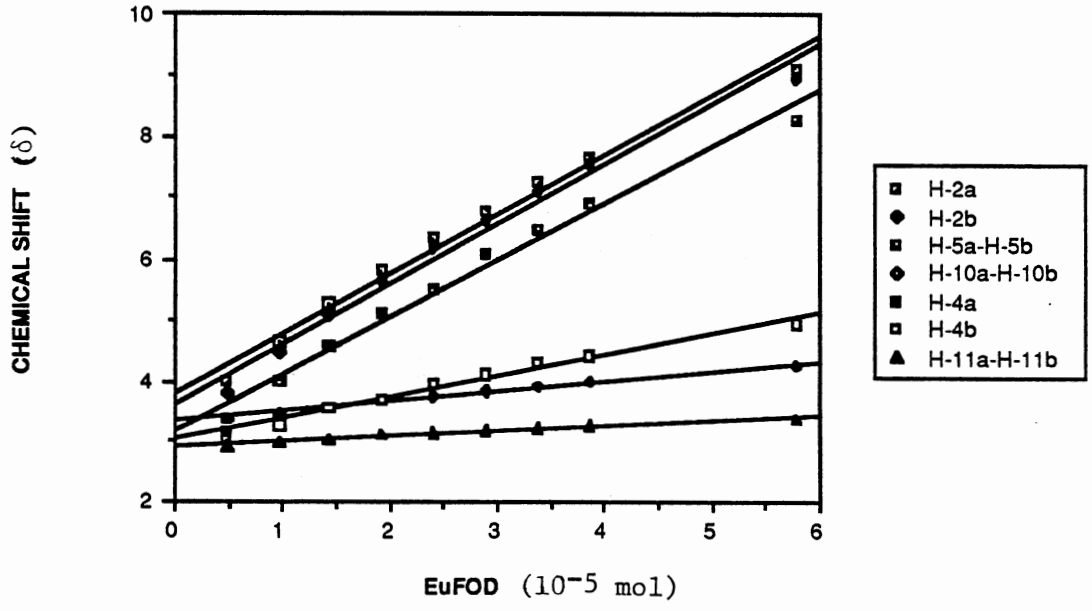


Figure 10. Chemical Shift *vs* Moles Shift Reagent for the Aliphatic Protons of **22**

TABLE 2

SLOPES AND INITIAL PROTON SHIFTS FOR **22**

Proton	Slope (Δm)	Initial Proton Shift, (IS, δ)
H-2a	0.973	3.84
H-2b	0.981	3.64
H-5a-H-5b	0.931	3.19
H-10a-H-10b	0.165	3.34
H-4a	0.345	3.06
H-4b	0.363	2.99
H-11a-H-11b	0.086	2.92

cyclopentenecarboxylate[123] (**26**) was proposed and attempted. This reaction, without optimization, proceeded in 40% yield to generate the alcohol **27**. Future work will focus on using this method to synthesize heteroatom systems incorporating the dibenzocycloheptene ring system. Related systems have been shown to exhibit significant antidepressant activity, i.e. amitriptyline-HCl, protriptyline-HCl.[124,125]

All four photoproducts appear to be the result of primary and secondary photoreactions. Control irradiations of **20** and **21** in benzene and *tert*-butanol indicated that trans to cis and cis to trans interconversion was occurring in addition to rearrangement to the photostable enone **19**. Compound **22** was also formed upon independent irradiation of **20** and **21**, but it was not clear whether this was the result of photoisomerization of **20**, **21** or both. The percent conversion of **22** was as great as 16% when the irradiations of **20** and **21** were carried out in benzene. However, when

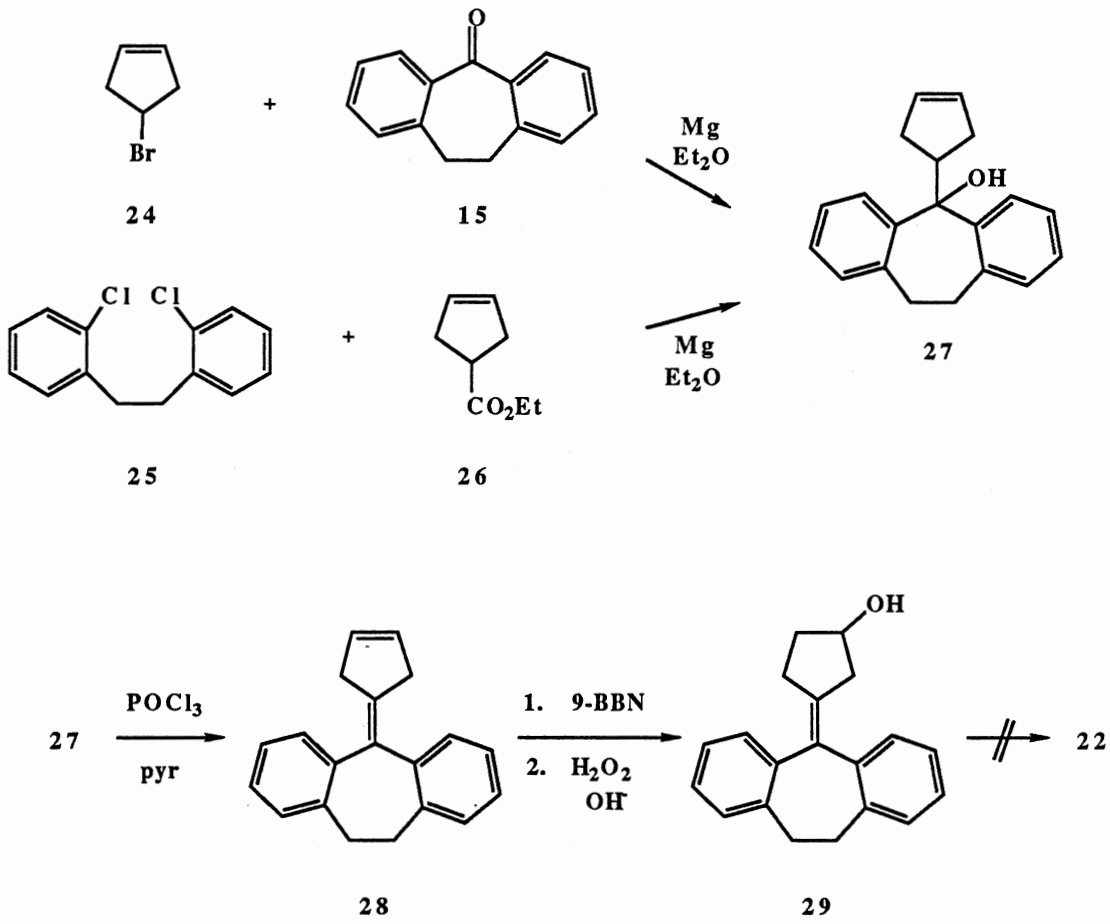


Figure 11. Proposed Synthetic Route to **22**

the irradiations of **20** and **21** were run in *tert*-butanol, less than 10% of **22** was produced. Some return to spiro compound **18** (< 2%) was observed for both **20** and **21** when the reactions were carried out in *tert*-butanol. Independent irradiation of **22** indicated no photoisomerization. This compound appeared to be photoinert for 3 h, at which time photodecomposition began to occur. The photochemistry of **18** is summarized in Figure 12.

Reaction Profiles and The Behavior of The Photoproducts. The reaction profile for irradiation of **18** in *tert*-butanol is depicted in Figure 13. From this, it can be seen that the enone system **19**, was clearly the major product of the reaction.

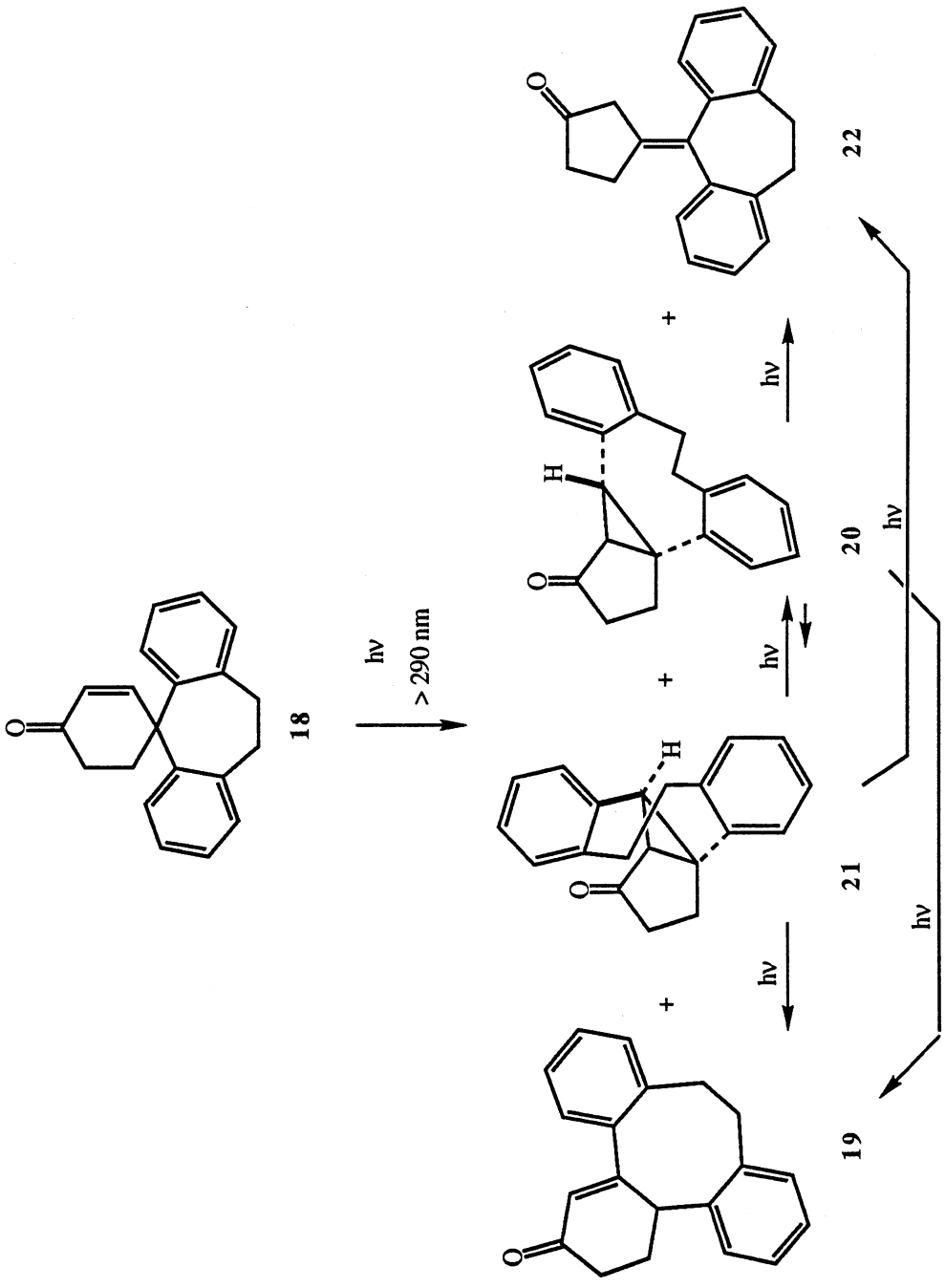


Figure 12. Photochemistry of Compound **18**

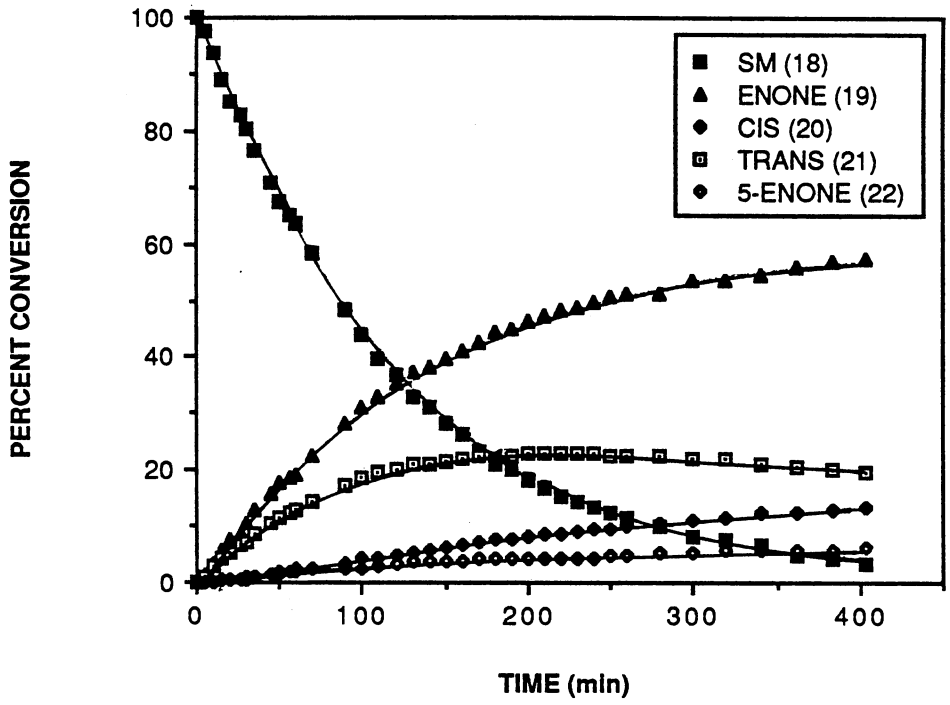


Figure 13. Reaction Profile for Irradiation of **18** in *tert*-Butanol

Production of the trans and enone products, **19** and **21**, was rapid and nearly linear at low conversion. The cis and β,γ-enone products, **20** and **22**, were formed to a lesser extent and at a much slower rate. The β,γ-enone appeared to be a very minor photoproduct, formed in only 5% at 90% conversion of starting material. Compounds **20** and **22** were detected at 6% conversion, where 0.3% each of **20** and **22** could be reproducibly detected. The large stereoselectivity for trans isomer formation reported previously for the non-bridged 4,4-diphenyl enone system appeared to be lost in the two-carbon bridged system.[1,2,9,10] In this bridged system, the earliest detected ratio of trans:cis isomers was *ca.* 10:1. In the later stages of the reaction, the cis isomer appeared to be formed as a result of secondary photoreaction of the trans. This isomerization was

verified in the independent irradiation of the trans isomer **21** (Figure 14). This trans to cis conversion appeared to be more energetically favored than the cis to trans isomerization. This can be seen from the reaction profile for the control irradiation of **20** (Figure 15). Rearrangement to the enone **19**, was observed in irradiations of both **20** and **21**, leading to the conclusion that **19** was both a primary and secondary photoproduct. Independent irradiations of **20** and **21** were also observed to give **22**. The formation of the β,γ-enone **22** was too slow to account for all of this product produced at low conversions of **18**. This would suggest that **22** was the result of both primary and secondary photoreactions. Whether the α,β- or β,γ-enones, **19** and **22**, were formed from reaction of both **20** and **21** was unclear since the latter two compounds interconvert photochemically. Control irradiations of **19** and **22** indicated that both photoproducts were photoinert to these irradiation conditions.

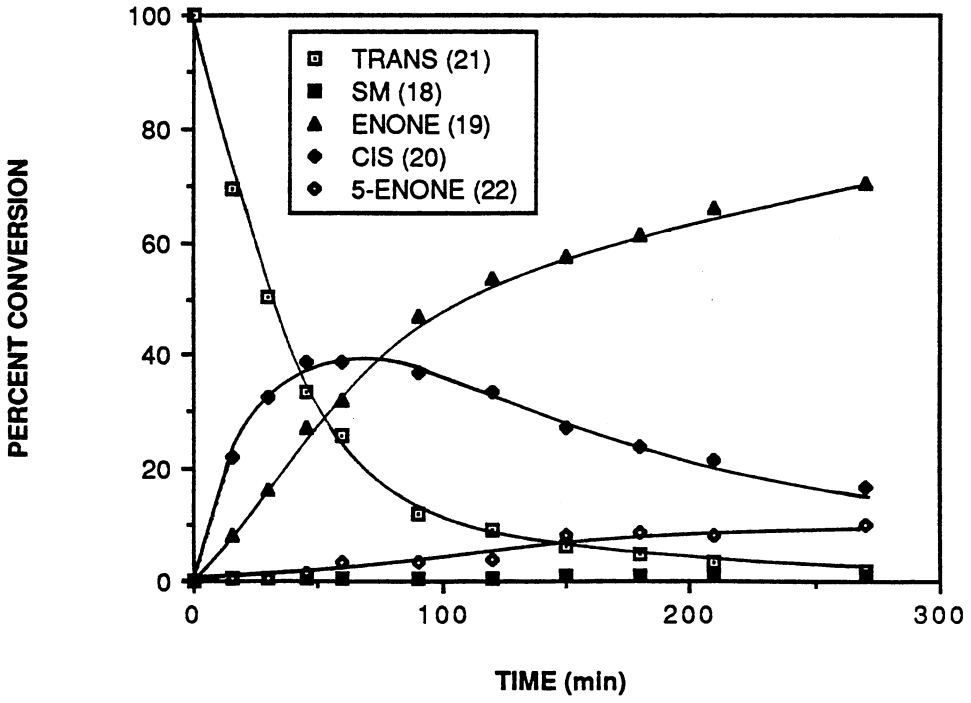


Figure 14. Reaction Profile for Irradiation of **21** in *tert*-Butanol.

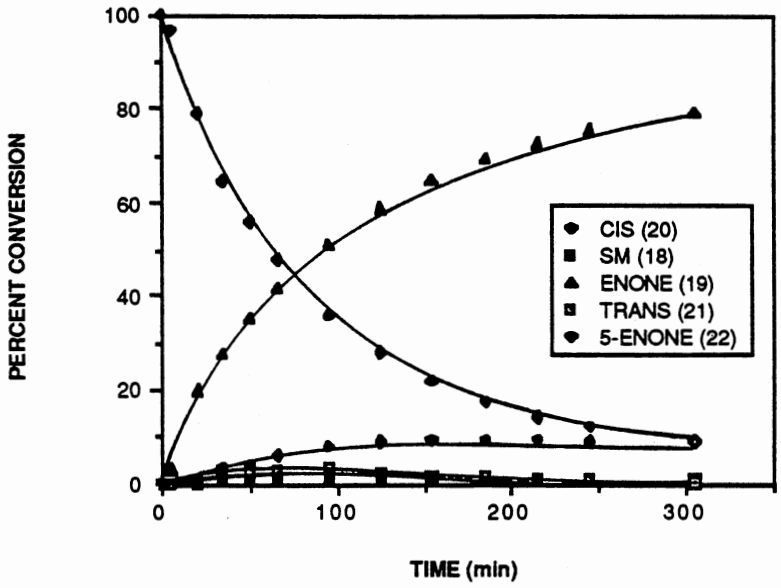


Figure 15. Reaction Profile for Irradiation of **20** in *tert*-Butanol.

The reaction profile for irradiation of **18** in benzene is presented in Figure 16. Irradiation of **18** in this solvent, kinetically produced the trans isomer over the enones **19** and **22** and the cis product **20**. The α,β-enone **19** was again the photodynamic product. The β,γ-enone **22** was formed in 17% at 90% conversion of starting material, and in as high as 22% during the course of reaction. Under these conditions, **22** was no longer a minor product with respect to the trans and cis systems. As the reaction proceeded, it appeared that the β,γ-enone was formed at the expense of the cis and trans isomer. This was confirmed by control irradiations of both **21** and **20** (Figure 17 and 18). Again, it was not clear whether **22** was formed from **20**, **21** or both. In benzene, trans to cis interconvert with a strong preference for the cis. Superimposed on this isomerization process was the conversion of both trans and cis to the enone **19**. The spiro compound **18**, was not observed in the photoreaction of **20** or **21** in benzene as it was in the *tert*-butanol irradiations.

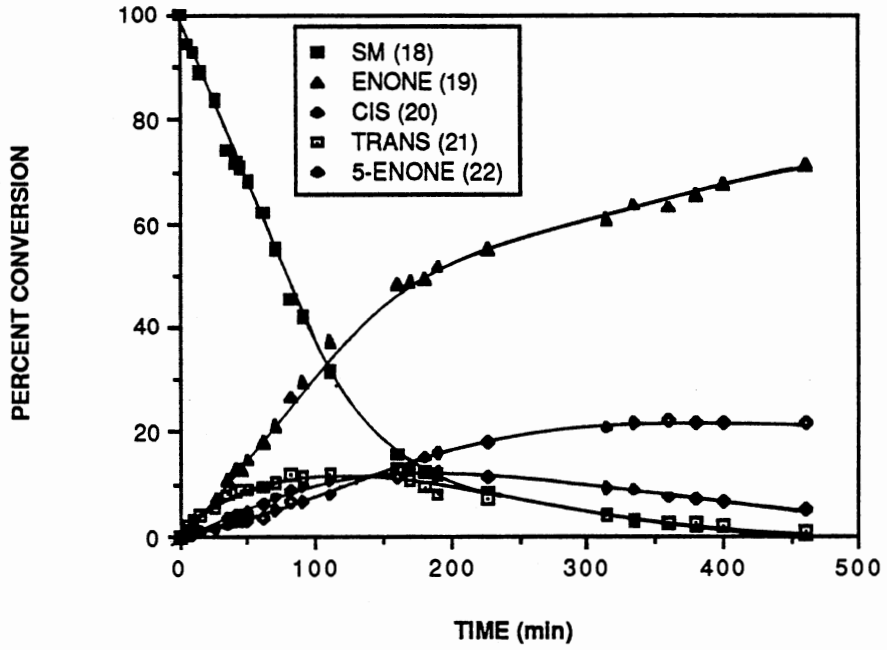


Figure 16. Reaction Profile for Irradiation of **18** in Benzene

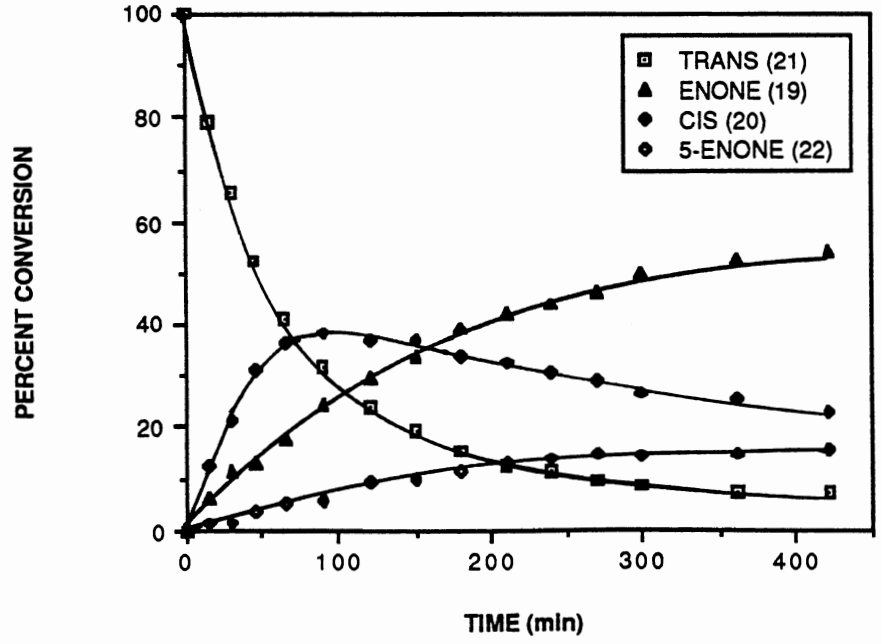


Figure 17. Reaction Profile for Irradiation of **21** in Benzene.

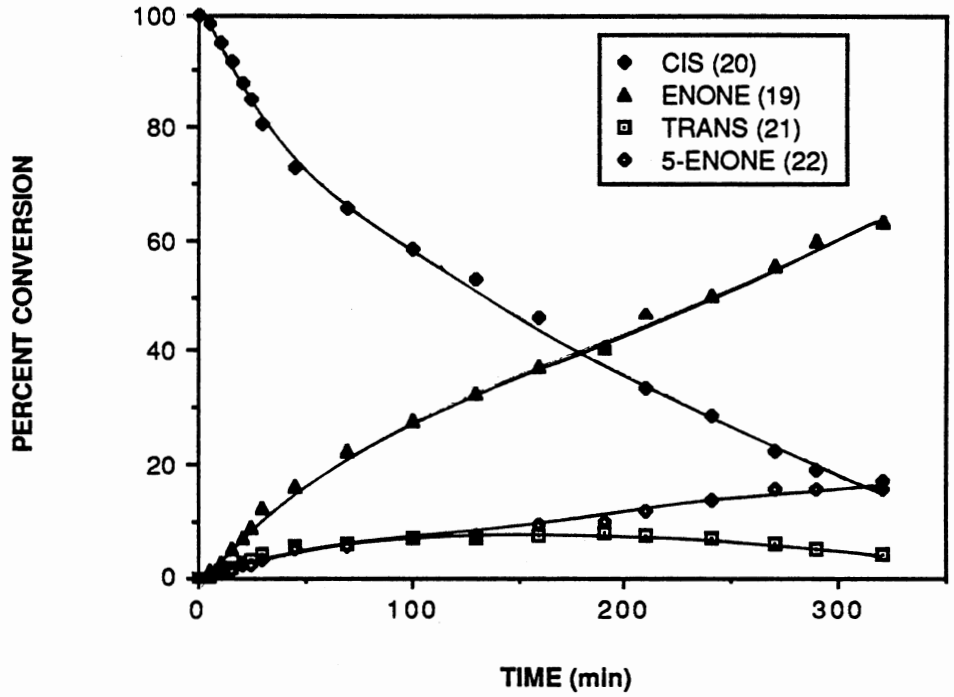


Figure 18. Reaction Profile for Irradiation of **20** in Benzene.

Preference for trans isomer formation can be clearly seen in the reaction profile for the irradiation of **18** in cyclohexane (Figure 19). The trans isomer was the major product to 90% conversion of starting material and both the trans and cis isomers were produced in preference to the α,β-enone **19**. Secondary photoreaction of the trans isomer was apparent by the disappearance of **21** and the increase in **19**, **20** and **22** at a stage when the spiro compound was essentially 100% reacted. Formation of the β,γ-enone **22** was also enhanced in this solvent, comprising 15% of the reaction mixture at 90% conversion of starting material.

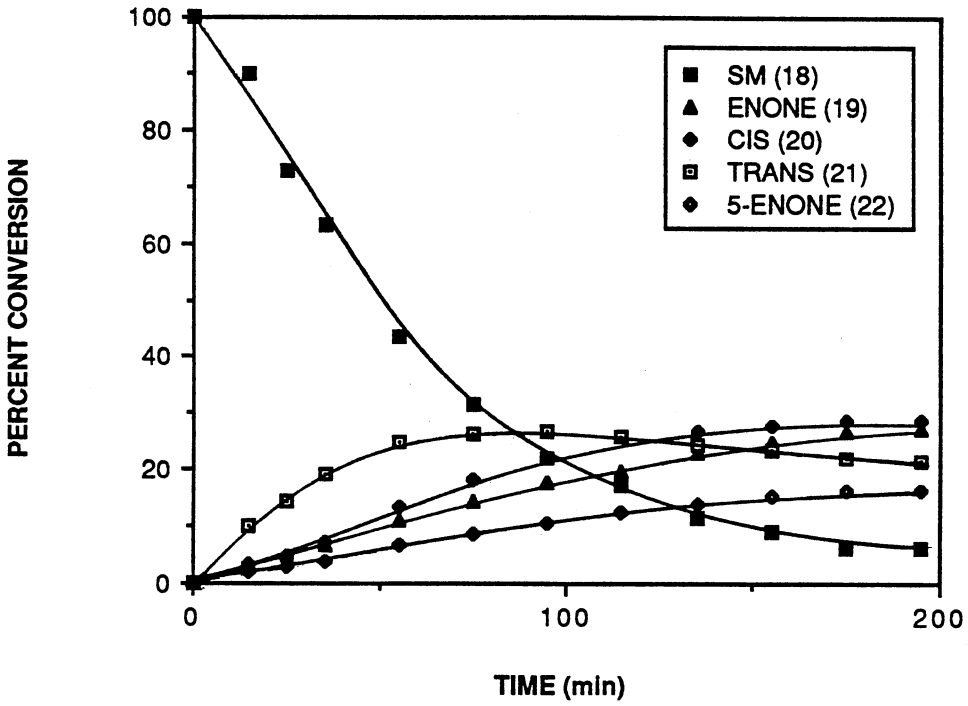


Figure 19. Reaction Profile for Irradiation of **18** in Cyclohexane.

Mechanistic and Interpretive Discussion. The rearrangement of the two-carbon bridged system **18**, presumably proceeds in a manner similar to that observed for the zero- and three-carbon bridged systems previously reported.[16] The enone, undergoes initial n-π^* electronic excitation followed by intersystem crossing to the triplet (Figure 20). Rearrangement of the triplet by phenyl migration then proceeds through either a concerted or a stepwise mechanism. Concerted migration and C-2-C-4 three-ring closure would generate the trans system **21**. Complete migration to the diradical **31** in the stepwise mechanism, followed by C-2-C-4 bonding would generate either the cis or trans isomer. From this diradical, overlap of the p-orbitals at C-2 and C-4 from above the plane of the paper (top-top) generates the cis system. Overlap of the C-2 and C-4 orbitals

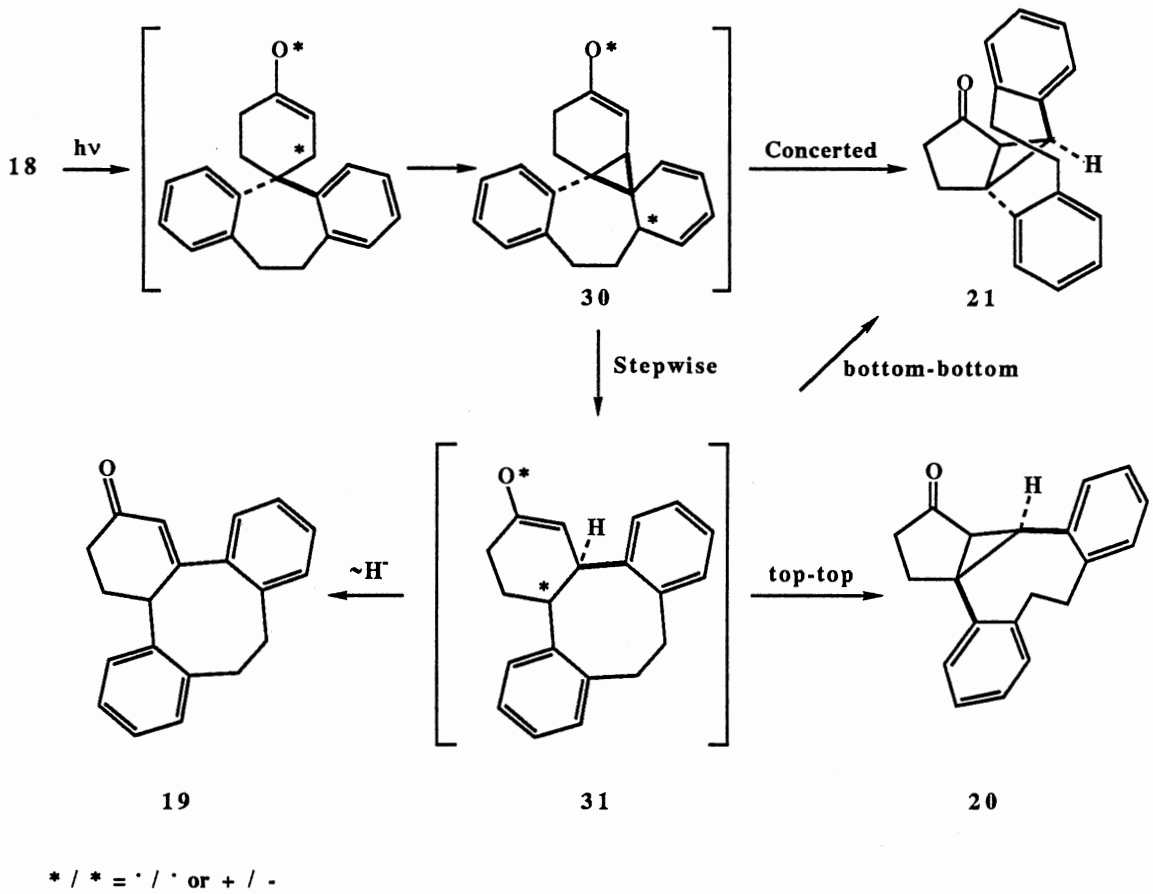
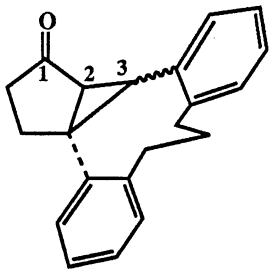


Figure 20. Aryl Migration Pathways for Photochemical Conversion of **18**.

from behind the plane of the paper (bottom-bottom) would give the trans system. It has been noted that closure to give the trans system (bottom-bottom) is preferred for the non-bridged 4,4-diphenylcyclohexenone systems.[5-8] This was ascribed to the requirement that for closure to give the cis isomer, the C-3 and C-4 phenyls, which are initially in a transoid orientation, must twist past each other at a stage when the C-4 delocalized phenyl is restricted from rotation. This twisting is considered energetically unfavorable. Closure of the bottom-bottom lobes of the p-orbitals on C-2 and C-4 to give the trans isomer is energetically preferred since the phenyl rings are already in a transoid conformation and do not pass one another upon closure. In the two-bridged system, preferential trans

isomer formation from the diradical **31**, should not be observed. This is due to the fact that the two-carbon connector serves to fix the two phenyl rings in an almost orthogonal arrangement. This allows for the production of both cis and trans products since the phenyls are already twisted away from each other prior to closure. Without any steric bias, closure of the diradical should occur to form the most thermodynamically stable system. The cis system would appear to be the more stable of the two [3.1.0] isomers by analogy with the trans and cis three-carbon bridged systems, **9** and **10**.[16] In the three-carbon analog, the difference in product stability was indicated by the change in the C-1-



9 or 10

C-2-C-3 angle in the cis system as compared to the trans. It was previously reported that the C-1-C-2-C-3 angle of 114° observed for **9**, is opened to 121° in **10**.[16] This would suggest that the C-2-C-3 bond of the trans system is more strained than the corresponding bond in the cis molecule. The strain in the two-carbon analog **21**, should be even more significant than that observed in **9**, since the carbon-carbon connector must span the same distance between ortho phenyl positions as does the three-carbon system, but must do so with one less carbon. Additional strain in the trans system relative to the cis isomer is also evidenced by the efficient trans to cis conversion; the reverse reaction occurs to only a small extent. Therefore, the cis isomer should be more stable and, thus, formed preferentially from C-2-C-4 closure of the diradical **31** in the stepwise process.

It is proposed that the enone **19**, derives from a hydride migration process (Figure 20).[2] This process involves complete phenyl migration to the diradical **31**, followed by electron demotion to the zwitterion intermediate **31**. 1,2-Hydride migration from C-3 to C-4 then occurs to generate the enone **19**. Production of **19**, through a concerted pathway would require coplanarity of the σ bond of the migrating hydride and the incipent carbocation at C-4.[126] This preferred orbital alignment is not indicated from molecular models and, thus, reaction through a stepwise process is suggested.

While there is ample precedent for 1,2-hydride shifts, 1,2-hydrogen atom migrations have not been reported.[127] It is therefore reasonable to assume that the 1,2-migration occurs from the dipolar intermediate **31** and not from the diradical species. Additionally, independent generation of the proposed zwitterion intermediates (for similar diaryl dienone and bicyclohexanone systems) under nonphotochemical conditions yielded the same photorearrangement products.[17,18]

The minor product is thought to be the result of an incomplete Type A process (Figure 21).[16] Type A photorearrangements have been been reported for a number of 4,4-dialkylated cyclohexenones.[13] This process involves migration of the C-4-C-5 bond followed by C-2-C-4 bond formation to generate a 6,6-disubstituted lumiketone (i.e. **33**).[13] In the incomplete Type A process, the C-4-C-5 bond migrates as before but, instead of C-2-C-4 bond formation, hydrogen migration occurs from C-3 to C-2 to generate the β,γ isomer **22**. The Type A rearrangement has been reported to be a concerted process.[13,27,28] The incomplete reaction, on the other hand, would be expected to occur through a stepwise mechanism since poor alignment of the C-3 hydrogen and the C-4-C-5 orbitals would discourage a concerted process. This mechanism is summarized in Figure 21.

Type A reactivity has been observed in 4-phenyl substituted systems while the incomplete Type A process has not.[38,39] It is not intuitively obvious why the incomplete Type A reaction was observed in preference to the Type A process in the two-carbon

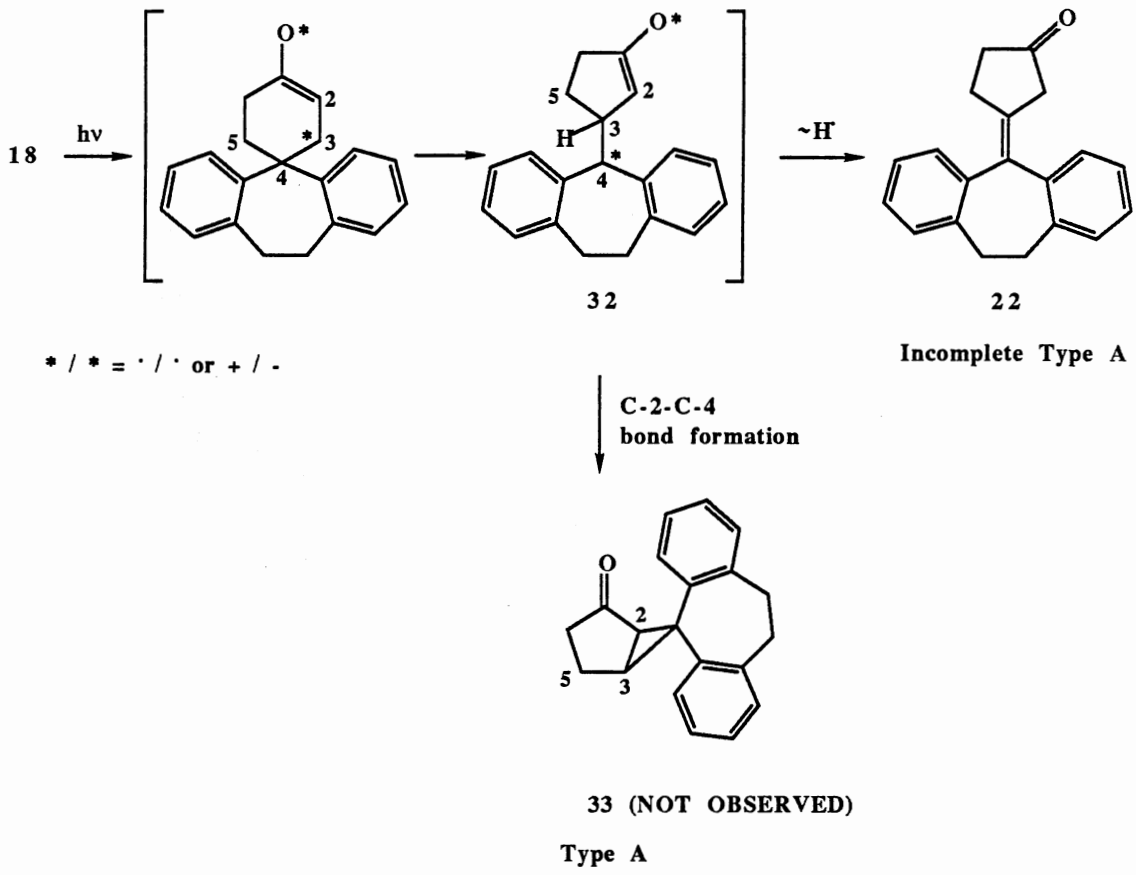
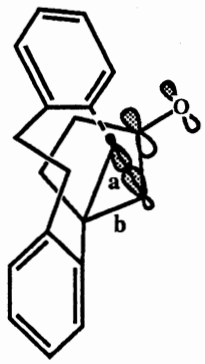


Figure 21. Incomplete Type A Reaction from **18.**

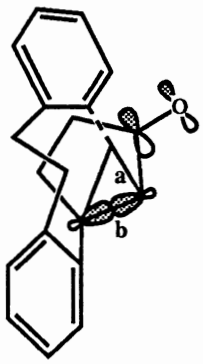
bridged system as well as in the zero-carbon bridged analog. It was initially suggested that the very stabilized doubly benzylic Type A intermediates generated in these bridged systems, may have longer triplet lifetimes. These longer-lived triplets would then allow for a slower 1,2-migration and more of the incomplete process. However, if this were the case, incomplete Type A reactivity would be observed in systems such as 4-methyl-4-phenylcyclohexenone and 4,5-diphenylcyclohexenone that have been reported to undergo Type A reaction.[38,39] Both of these 4-aryl substituted systems are capable of generating stabilized intermediates upon ring contraction in the Type A process.[38,39] This would

suggest that the incomplete process observed in the bridged cyclohexenones may be the result of steric hindrance which would prohibit approach of the C-2 carbon to the doubly benzylic radical center. Further studies of sterically congested 4,4-dialkylated cyclohexanone systems may provide information regarding this question. It is also possible that the increased lability of the external three-ring bond in the Type A product may cause it to react as fast as it is formed, preventing observation or isolation. A greater understanding of the factors that enhance the incomplete Type A process would allow for development of a novel route to β,γ-enones.

The mechanism for trans and cis isomerizations (Figure 22) involves initial electronic excitation and intersystem crossing, followed by three-ring bond cleavage.[9,10,16] Cleavage of the external bond (bond a) of **21**, followed by rotation about bond c and reclosure would generate the cis isomer **20**. Alternatively, opening of the internal bond (bond b) of **21**, followed by top-top C-2-C-4 orbital overlap would generate the cis system. Preference for external three-ring bond cleavage has been reported previously and attributed to the greater overlap between the carbonyl π^* orbital and the orbitals comprising the external cyclopropyl ring bond (bond a).[2,9,23,128] The two-carbon bridge should help to align these orbitals even better by locking the external cyclopropyl bond and the π^* orbital into a nearly parallel arrangement (see structures **21a** and **21b**).[16] In the isomerization of **20** and **21** to the enone **19** and the spiro compound



21a



21b

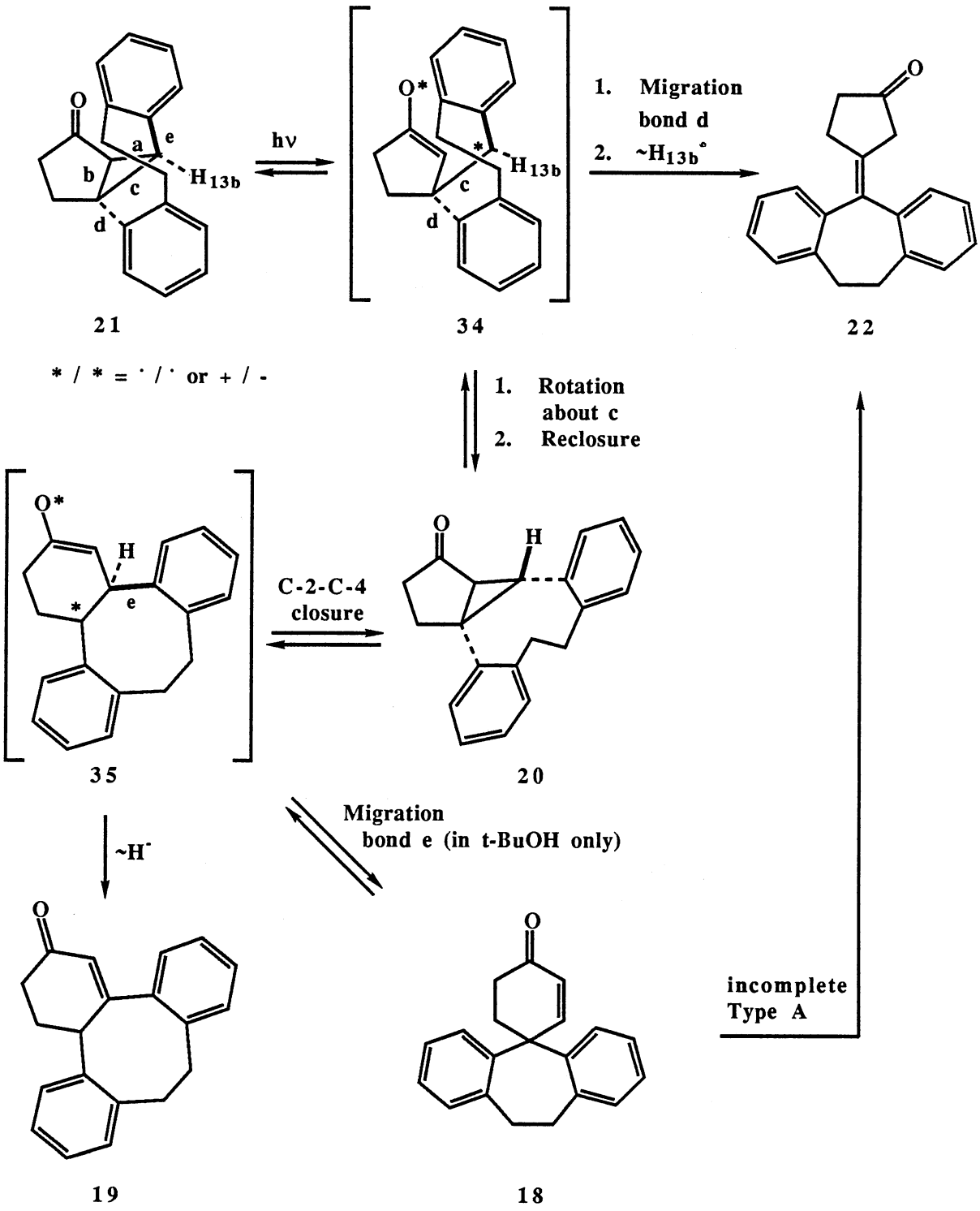


Figure 22. Mechanistic Summary of Photoisomerization Reactions

18, fission of the internal cyclopropyl bond (bond b) must occur (Figure 22). Once bond b is cleaved, electron demotion and hydride migration from C-3 to C-4 produces the α,β-enone **19.** Fission of the internal cyclopropyl bond (bond b), followed by bond e migration would give the spiro compound **18.**

Rearrangement of the cis and or trans isomer to the β,γ-enone **22**, is thought to arise from intermediate **34**, generated from external ring bond (bond a) cleavage (see Figure 23). Migration of the bond d in **34** to the radical center, followed by hydrogen migration from C-13b-C-2, would afford the β,γ system **22**. Internal three-ring bond cleavage to give **35**, followed by migration of bond e and then incomplete Type A reaction may also intervene (see Figure 22). The absence of any spiro compound **18** in the control irradiations of **20** or **21** in benzene and cyclohexane, where the β,γ-enone is

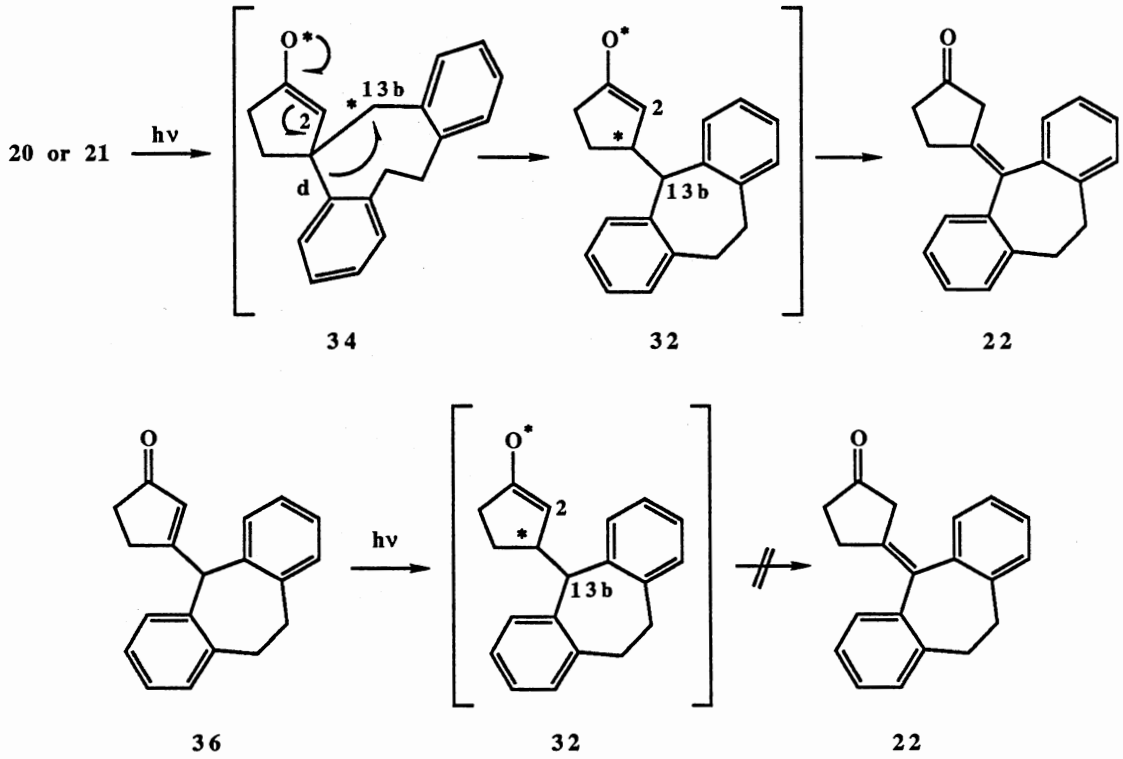


Figure 23. Attempt to Establish Reaction Pathway for Formation of **22.**

formed to a larger extent, would seem to indicate that this bond e migration-incomplete Type A process is not the major pathway for β,γ-enone formation.

The conjugated isomer 3-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptenyl)-2-cyclopenten-1-one **36**, was synthesized and photolyzed in an attempt to independently synthesize the β,γ-enone **22** and also to provide additional information regarding the reaction pathway for formation of **22** (Figure 23). One would initially expect that the photochemical reactions of **36**, **20** and **21** would proceed through a common intermediate. Therefore, one might expect **22** to be observed upon irradiation of **36**. This, however, was not the case. Despite this observation, information regarding the indentity of the excited state intermediate could not be concluded because of the differences in energy barriers, rates of intersystem crossing, multiplicities and energy states for conversion that would result from starting with different reactants (**36**, **20**, **21**).

The enhanced formation of the α,β-enone product in *tert*-butanol is of much interest. Few cases of predominant enone formation have been reported for 4,4-diarylcyclohexenone systems.[6,15] Of the cases reported, the 4,4-diaryl substituents have been bulky groups (i.e. di-α-napthyl), and the enhanced enone formation has been rationalized by the severe aryl-aryl steric interaction observed upon three-ring closure of the open diradical.[15] Although this seems reasonable for the cases reported, steric interactions do not appear to be a factor in the preferential α,β-enone formation observed in the two-carbon bridged system. Reference to molecular models suggests that this preference is the result of the difficulties encountered in cyclopropyl bond formation. In the two carbon bridged system, the C-2-C-4 orbitals may be forced out of alignment in what would appear to be the lowest energy conformation. The two carbon connector enforces rigidity in the system, making it very difficult to acquire the proper alignment for C-2-C-4 overlap. Therefore, cyclopropyl bond formation is much slower, allowing the hydride migration (α,β-enone formation) and incomplete Type A processes (β,γ-enone formation) to become competitive.

Enone products are not observed in the three-carbon bridged system because the additional carbon in the phenyl-phenyl connector enables flexibility and allows C-2-C-4 alignment to be attained. Therefore, the normal aryl migration process is observed. Although, this flexibility and orbital alignment is observed in the nonbridged 4,4-diphenylcyclohexenone system **1**, the α,β-enone **4** is observed as a minor product. This likely results from interaction of the cis diphenyl groups in the open diradical generated from **1**, allowing the hydride migration to become a competitive process. This interaction is relieved in the three-carbon bridged system since the bridging alkyl chain serves to hold the phenyl rings away from each other upon three-ring closure.

As in the two-carbon bridged system, the zero-carbon analog is extremely rigid, making it difficult to acquire the proper alignment for top-top C-2-C-4 overlap required for closure to the cis diphenyl product. Bottom-bottom overlap of these carbons, needed to close the trans diphenyl product, is geometrically forbidden. Therefore, the hydride migration and incomplete Type A processes become competitive with cyclopropyl bond formation. A combination of factors may then make the Type A process more competitive than the hydride migration. These factors are as follows:

1) Upon incomplete Type A reaction of **5**, the intermediate **37** is generated (Figure 24). This intermediate is much more stabilized than the Type A intermediate **32** (see Figure 23) formed in the two-carbon system due to the planar system in **37** allowing for complete delocalization.
2) The aryl migration pathways require bridging of the C-4 phenyl to the C-3 odd electron center. In substrate **5**, this results in the formation of an extremely strained 6-3-5 ring system **38**, which would tend to inhibit this process (Figure 24).

The combination of having a very stabilized Type A intermediate coupled with the inhibited phenyl migration, may make the incomplete Type A process preferred over

hydride migration, resulting in predominant formation of the β,γ-enone **7**. In the two-carbon bridged system, the Type A process, although competitive with the hydride

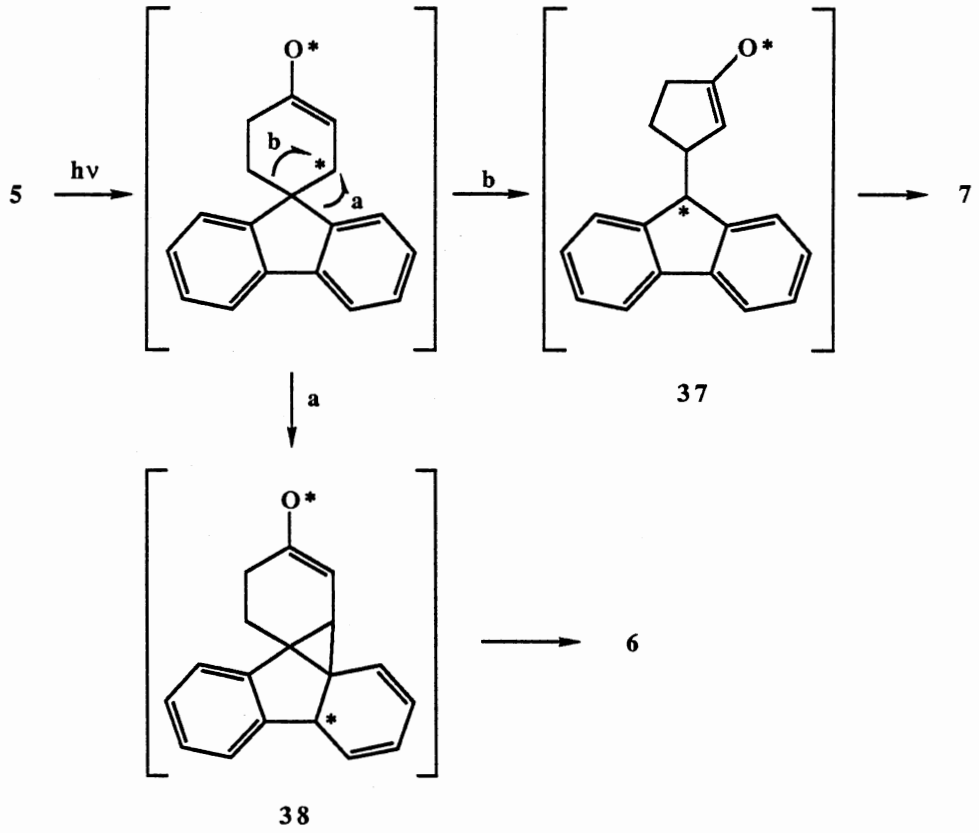


Figure 24. Factors Influencing Photoreactivity of **5**.

migration (as seen by production of the β,γ-enone **22**), is not preferred over hydride migration. This altered selectivity may be due to the reduced strain in the half-migrated intermediate **30** (a 6-3-7 ring system, see Figure 20) relative to **37**.

Solvent effects have been noted in the photochemistry of 4,4-disubstituted cyclohexenones.[2,13,38] These effects include changes in the quantum efficiency and product distribution. In 4,4-diphenylcyclohexenone, a change in the solvent polarity

from benzene to *tert*-butanol was reported to enhance the production of the 3,4-disubstituted enone **4**.[2] The ratio of trans to cis isomer, **2** and **3**, was essentially unchanged but the proportion of the enone **4** was increased by 16-fold.[2] In 4,4-disubstituted systems that undergo both Type A and aryl migration reactions, it has been reported that the Type A $^3(\pi\text{-}\pi^*)$ reaction is enhanced in polar, protic solvents while the aryl migration $^3(n\text{-}\pi^*)$ is enhanced in nonpolar solvents.[13,38] These observations have been attributed to an inversion of the two close lying $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ triplets.[2,13,38] The more polar $\pi\text{-}\pi^*$ state is stabilized by the polar (alcohol) solvents as evidenced by the red shift of λ_{max} in these solvents.[129] In the two-carbon bridged system **18**, a change from *tert*-butanol to benzene and cyclohexane led to an increase in the incomplete Type A product **22** and a decrease in the trans:cis ratio. This would imply that the β,γ-enone **22** derives from reaction of a $^3n\text{-}\pi^*$ state rather than $^3\pi\text{-}\pi^*$ state as previously reported for Type A reactions.[24] This increase in β,γ-enone formation may be due to the change in the electronic environment about the carbonyl oxygen. Hydrogen bonding at the carbonyl oxygen is increased in *tert*-butanol and may somehow make the incomplete Type A reaction less efficient. This would be a plausible explanation for why the α,β-enone product **19** is both kinetically and thermodynamically preferred in *tert*-butanol and only thermodynamically preferred in benzene and cyclohexane. Hydrogen bonding at the excited state carbonyl oxygen should make hydride migration more efficient relative to cyclopropyl ring formation.[2]

In summary, the present work has shown that carbon bridging of the phenyl substituents that normally migrate apart in the aryl migration reaction does alter the stereoselectivity as well as the reaction mechanism. The length of the connecting bridge determines which reaction pathway is followed. Future work in this area will explore the use of ortho-ortho connectors that could be easily removed following the photochemical rearrangement, such as heteroatom containing bridges.

Experimental

Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded with a PE-681 instrument and are referenced to polystyrene. ^{1}H-NMR and ^{13}C-NMR were measured as solutions in $CDCl_3$ at 300 MHz and 75 MHz, respectively, on a Varian XL-300 superconducting FT instrument, unless indicated otherwise; chemical shifts are reported in δ units relative to internal Me_4Si. UV spectra were recorded in absolute ethanol using a Varian DMS-200 spectrophotometer. Mass spectra were recorded at 70 eV on a VG ZAB-2SE or a VG TS-250 instrument. Elemental analyses (± 0.4%) were performed by Galbraith Laboratories, Knoxville, TN.

All reactions were run under an atmosphere of dry nitrogen. Solvents used in photochemical runs were purified in the following manner: *tert*-butanol was distilled from CaH_2; benzene was sequentially washed with concentrated H_2SO_4 (2x), 5% $KMnO_4$ in 10% aqueous H_2SO_4 (2x), and 10% aqueous KOH, then dried over anhydrous $MgSO_4$ and distilled from CaH_2. All photochemical reactions were degassed with dry, oxygen-free nitrogen for 1 h prior to and during irradiation. Column chromatography was performed on silica gel (Grace, grade 62, 60-200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored with a hand-held UV lamp. Preparative thick layer chromatography (PTLC) was performed on Analtech (No. 02015) preparative silica gel uniplates with fluorescent indicator. Reactions were monitored and kinetic measurements were made on a capillary GC (Varian 3400) with FI detection on a 6 m X 0.1 mm SE-30 column programmed between 100-300°C.

10,10-Dimethyl-9(10*H*)-anthracenone (12). The procedure of Curtin and coworkers[108] was used. The lithium salt of anthrone was prepared by reacting 36.5 g (0.19 mol) of anthrone (**11**) in 400 mL of toluene with a suspension of lithium methoxide prepared from 2.8 g (0.40 g-atom) of lithium metal in 42 mL of methanol.

After 15 min, the solution was gently heated with a steady stream of nitrogen to remove the toluene and methanol. When the salt became dry it was transferred into a bomb reactor containing 150 mL (342 g, 2.41 mol) of methyl iodide and 1 mL of *tert*-butanol. The bomb was sealed, flushed with nitrogen and heated at 150°C for 60 h. Once cooled, the excess methyl iodide was recovered by distillation, the residue was digested in ether and washed with Claisen's alkali (350 g KOH and 250 g distilled water, diluted to 1 L volume with absolute methanol). The ether layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a yellow solid. Filtration through a 25 cm x 5 cm alumina column using hot Skelly-B yielded 29.5 g (0.13 mol, 70%) of 10,10-dimethyl-9(10*H*)-anthracenone (**12**) as a white solid, mp. 97-98°C, lit.[108] mp. 96.5-98°C. The spectral data were: IR ($CHCl_3$) 1662, 1603, 1390, 1370 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, 2 H, J = 1.5, 7.9 Hz), 7.67 (m, 4 H), 7.44 (m, 2 H), 1.74 (s, 6 H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 183.8, 150.5, 133.4, 130.0, 127.4, 126.7, 126.6, 37.8, 32.9.

9,10-Dihydro-10,10-dimethylspiro[anthracene-9',2-oxirane] (39). The general procedure described by Ackermann and coworkers[109] was employed. To a suspension of 2.88 g (0.06 mol, 50% dispersion) of oil-free sodium hydride in 150 mL of dry DMSO was added 8.56 g (38.5 mmol) of 10,10-dimethyl-9(10*H*)-anthracenone (**12**). The mixture was stirred to effect solution of the ketone and then 12.0 g (59.0 mmol) of trimethylsulfonium iodide was added slowly. The mixture was stirred at 23°C for 3.5 h, then poured into 800 mL of ice water containing NaCl, extracted with benzene, washed with water (8x), saturated aqueous NaCl (1x), water (3x) and dried over anhydrous Na_2SO_4. Concentration *in vacuo* yielded a light yellow solid. Recrystallization from ether afforded 8.43 g (35.7 mmol, 93%) of 9,10-dihydro-10,10-dimethylspiro[anthracene-9',2-oxirane] (**39**) as a pale yellow solid, mp. 49-51°C. This compound decomposes after a few days at RT. The spectral data were: IR ($CHCl_3$) 2990, 1390, 1365, 1045 cm^{-1}; ^{1}H-NMR (400 MHz, $CHCl_3$) δ 7.56 (dd, 2 H, J = 1.0,

7.9 Hz), 7.42 (dd, 2 H, J = 1.6, 7.3 Hz), 7.35-7.25 (cplx, 4 H), 3.18 (s, 2 H), 1.91 (s, 3 H), 1.42 (s, 3 H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 145.6, 134.6, 127.8, 126.5, 123.9, 122.2, 63.2, 55.4, 38.9, 35.2, 25.7; MS, *m/e* (%) 236 (22), 221 (51), 207 (95), 192 (100), 178 (37); HRMS, exact mass calcd for $C_{17}H_{16}O$ *m/e* 236.1201, found *m/e* 236.1213.

9,10-Dihydro-10,10-dimethylanthracene-9-carboxaldehyde (13). The general procedure of Ackermann and coworkers[109] was followed. To a stirred solution of 8.0 g (33.9 mol) of 9,10-dihydro-10,10-dimethylspiro[anthracene-9',2-oxirane] (**39**) in 188 mL methylene chloride was added dropwise 2.00 mL (2.32 g, 16.3 mmol) of boron trifluoride etherate. The solution was stirred at 23°C and monitored by GC; the reaction was complete in 2.5 h. The reaction mixture was washed successively with saturated aqueous Na_2CO_3 (3x), water (8x), saturated aqueous NaCl (1x), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting pale yellow solid was recrystallized from ether to give 7.76 g (32.9 mmol, 97%) of 9,10-dihydro-10,10-dimethylanthracene-9-carboxaldehyde (**13**) as a pale yellow solid, mp. 50-52°C. The spectral data were: IR ($CHCl_3$) 2985, 2800, 2700, 1723,1390, 1365 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.40 (d, 1 H, J = 3.2 Hz), 7.64 (d, 2 H, J = 8.0 Hz), 7.28 (m, 6 H), 4.86 (d, 1 H, J = 3.1 Hz), 1.79 (s, 3 H), 1.54 (s, 3 H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.7, 144.3, 129.1, 128.3, 127.7, 127.4, 126.6, 58.8, 38.4, 36.7, 30.7; MS, *m/e* (%) 236 (0.5), 207 (100), 193 (20), 192 (89), 191 (25), 189 (12), 178 (20); HRMS, exact mass calcd for $C_{17}H_{16}O$ *m/e* 236.1201, found *m/e* 236.1201.

10,10-Dimethylspiro[anthracene-9(10*H*),1'-[2]cyclohexen]-4'-one (14). The method described by Plieninger and coworkers[110] for the preparation of spiro[2-cyclohexene-1,9'-fluoren]-4-one was used. To a solution of potassium *tert*-butoxide prepared from 0.13 g (0.003 g-atom) of potassium in 2.0 mL of *tert*-butanol was added a 25-mL benzene solution of 5.8 g (24.6 mmol) of 9,10-dihydro-10,10-dimethylanthracene-9-carboxaldehyde (**13**) dropwise via syringe. After stirring 10 min,

2.05 mL (1.73 g, 24.7 mmol) of methyl vinyl ketone was added dropwise and the reaction was stirred at 23°C for 10 h. The reaction mixture was then cooled to 0°C and poured into 1 *M* NaOH at 0°C and ether extracted. The combined organic layers were washed with 1 *M* NaOH (until no enol reaction with $FeCl_3$ was seen), water, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The resulting orange-brown oil was dissolved in 50 mL of benzene containing piperidinium acetate generated from 0.96 mL of piperidine and 0.56 mL of acetic acid. An additional 0.24 mL of acetic acid was added and the resulting solution was refluxed with a Dean-Stark trap for 8 h. The solution was concentrated *in vacuo*, then dissolved in ether and washed with 1 *M* HCl, saturated aqueous Na_2CO_3, and water. The ether layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The resulting yellow-brown oil was column chromatographed on a 60 cm x 2.5 cm slurry packed silica gel column eluted with increasing concentrations of ether in hexane. The compounds eluted as follows: 1% ether in hexane, 0.82 g (3.69 mmol, 15%) of 10,10-dimethylanthrone (**12**); 1.5% ether in hexane, 0.58 g (2.46 mmol, 10%) of starting material **13**; 4.0% ether in hexane, an 80/20 mixture of the desired product **14** and an unknown impurity. The mixture was recrystallized from ether in hexane (3x) to give a pale yellow solid. Compound **14** was still slightly impure so a final purification was carried out using three 20 cm x 20 cm silica gel PTLC plates eluted with 2.5% ether in hexane (7x). One band was scraped from the plates to give 0.57 (1.97 mmol, 8%) of 10,10-dimethyl-spiro[anthracene-9(10*H*),1'-[2]cyclohexen]-4'-one (**14**) as a white solid, mp. 95-96°C. The spectral data for **14** were: IR ($CHCl_3$) 3000, 1680, 1498, 1460 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.65 (m, 2 H), 7.38 (m, 4 H), 7.24 (m, 2 H), 6.92 (d, 1 H, J = 10.1 Hz), 6.49 (d, 2H, J = 10.1 Hz), 2.46 (t, 2 H, J = 6.7 Hz), 2.22 (t, 2 H, J = 6.7 Hz), 1.82 (s, 3 H), 1.64 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 199.8, 154.6, 143.2, 136.6, 130.4, 127.8, 127.6, 127.5, 127.3, 127.3, 127.2, 127.1, 126.3, 44.7, 42.4, 38.1, 36.4, 33.98, 31.7; UV (abs. EtOH) λ_{max} (ε) 320 (72), 239 (11642), 211 (22234); MS, *m/e* (%) 288 (13), 274 (22), 273 (100), 246 (17), 245 (84), 216 (13),

202 (21); HRMS, exact mass calcd for $C_{21}H_{20}O$ *m/e* 288.1514, found *m/e* 288.1508. Anal. Calcd for $C_{21}H_{20}O$; C, 87.45; H, 6.99. Found: C, 87.33; H, 6.85.

Exploratory Direct Photolysis of 10,10-Dimethylspiro[anthracene-9(10*H*),1'-[2]cyclohexen]-4'-one (14). The general procedure described by Zimmerman[1] for the photolysis of 4,4-diphenyl-2-cyclohexenone was followed. A solution of 100 mg (0.35 mmol) of 10,10-dimethylspiro[anthracene-9(10*H*),1'-[2]cyclohexen]-4'-one (**14**) in 320 mL of degassed *tert*-butanol in a Kreil flask (Ace no. 6963) was irradiated through Pyrex using a 450-W medium pressure Hanovia immersion apparatus. The reaction was stopped at 90% conversion of starting material as determined by GC. At 15% conversion of starting material, 6 photoproducts were observed. At 90% conversion of starting material, 14 photoproducts were observed. Isolation of the photoproducts was not attempted.

10,11-Dihydrospiro[5*H*-dibenzo[*a*,*d*]cycloheptene-5',2-oxirane] (16). The epoxide was prepared according to the procedure described by Ackermann and coworkers.[109] To a suspension of 9.56 g (0.24 mol, 60% dispersion) of oil-free sodium hydride in 600 mL of dry DMSO was added 32.2 g (0.15 mol) of dibenzosuberone (**15**). The mixture was stirred to effect solution of the ketone and then 48 g (0.23 mol) of trimethylsulfonium iodide was added slowly and stirred at 23°C for 4 h. The reaction mixture was poured into 1 L of ice water containing NaCl and extracted with benzene. The extract was washed with water (6x), saturated aqueous NaCl (1x), dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to yield a yellow solid Recrystallization of the crude product from absolute ethanol afforded 29.5 g (0.13 mol, 86%) of 10,11-dihydrospiro[5*H*-dibenzo-[*a*,*d*]cycloheptene-5',2-oxirane] (**16**) as a pale yellow solid, mp. 76-78°C, lit.[109] mp. 76-78°C. The spectral data were: IR ($CHCl_3$) 2925, 1305, 1020 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.52 (m, 2 H), 7.20-7.09 (cplx, 6 H), 3.44 (m, 2 H), 3.16-2.96 (cplx, 4 H); ^{13}C-NMR ($CDCl_3$) δ 138.7, 138.5, 128.9, 127.7, 126.2, 124.1, 59.3, 58.4, 32.6; MS *m/e* (%) 222 (11), 221 (19), 193 (100), 178

(29), 165 (14), 115 (27); HRMS, exact mass calcd for $C_{16}H_{14}O$ *m/e* 222.1045, found *m/e* 222.1044.

10,11-Dihydro-5*H*-dibenzo[*a,d*]cycloheptene-5-carboxaldehyde (17). The aldehyde was prepared by the method of Ackermann and coworkers.[109] To a stirred solution of 28.0 g (0.13 mol) of 10,11-dihydrospiro[5*H*-dibenzo[*a,d*]cycloheptene-5',2-oxirane] (**16**) in 700 mL of methylene chloride was added dropwise 7.52 mL (8.7 g, 0.06 mol) of boron trifluoride etherate. The solution was then stirred at 23°C and monitored by TLC; the reaction was complete in 2.5 h. The solution was washed successively with saturated aqueous Na_2CO_3 (3x), water (8x), saturated aqueous NaCl (1x), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting yellow solid was recrystallized from ether to give 24.1 g (0.11 mol, 86%) of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene-5-carboxaldehyde (**17**) as a pale yellow solid, mp. 77-78°C, lit.[109] mp. 77-78°C. The spectral data were: IR ($CHCl_3$) 2920, 2815, 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 9.84 (s, 1 H), 7.24-7.13 (cplx, 8 H), 4.58 (s, 1 H), 3.21 (A of ABm, 2 H), 2.88 (B of ABm, 2 H); ^{13}C-NMR ($CDCl_3$) δ 199.5, 140.3, 133.8, 131.6, 130.4, 128.0, 126.5, 67.7, 32.6; MS, *m/e* (%) 222 (25), 194 (30), 193 (100), 178 (39), 165 (13); HRMS, exact mass calcd for $C_{16}H_{14}O$ *m/e* 222.1045, found *m/e* 222.1044.

10',11'-Dihydrospiro[2-cyclohexene-1,5'-[5*H*]dibenzo[*a,d*]cycloheptene]-4-one (18). To a 25-mL benzene solution of 5.6 g (0.025 mol) of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene-5-carboxaldehyde (**17**) and 4.2 mL (3.5 g, 0.05 mol) of methyl vinyl ketone was added dropwise during 45 min a solution of potassium *tert*-butoxide prepared from 0.24 g (.006 g-atom) of potassium in 4.0 mL of dry *tert*-butanol. The solution was stirred at 23°C for 36 h, diluted with ether, washed with saturated aqueous NH_4Cl, water and saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting dark brown viscous oil was purified by column chromatography on an 80 cm x 2.5 cm slurry packed silica gel column eluted

with increasing concentrations of ether in hexane. The compounds eluted as follows: 0% ether in hexane, dibenzosuberane **40**; 1% ether in hexane, dibenzosuberone **15**; 3% ether in hexane, starting material **17**; 6% ether in hexane, 10',11'-dihydrospiro[2-cyclohexene-1,5'-[5*H*]dibenzo[*a,d*]cyclohepten]-4-one (**18**). Decolorization of **18** with activated charcoal followed by recrystallization twice from ether yielded 0.96 g (3.5 mmol, 14%) of **18** as a white solid, mp. 109-110°C. The spectral data were: IR ($CHCl_3$) 2950, 2878, 1690, 1605 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.45 (dd, 2 H, J = 3.6, 7.2 Hz), 7.26-7.15 (cplx, 7 H), 6.43 (d, 1 H, J = 10.3 Hz), 3.38 (A of ABm, 2 H), 3.00 (B of ABm, 2 H), 2.71 (t, 2 H, J = 6.4 Hz), 2.13 (t, 2 H, J = 6.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 199.7, 158.2, 142.0, 140.5, 130.9, 130.5, 128.6, 127.2, 126.2, 52.3, 40.9, 35.8, 34.8; UV (abs. EtOH) λ_{max} (ε) 322 (69), 224 (13776); MS, *m/e* (%) 274 (100), 246 (79), 245 (38), 217 (54), 215 (40), 202 (54), HRMS, exact mass calcd for $C_{20}H_{18}O$ *m/e* 274.1358, found *m/e* 274.1358. Anal. Calcd for $C_{20}H_{18}O$; C, 87.55; H, 6.62. Found: C, 87.42; H, 6.72.

Exploratory Direct Photolysis of 10',11'-Dihydrospiro[2-cyclohexene-1,5'-[5*H*]dibenzo[*a,d*]cyclohepten]-4-one (18).

A. In *tert*-Butanol: The general procedure described by Zimmerman[1] for the photolysis of 4,4-diphenyl-2-cyclohexen-1-one was followed. A solution of 1.00 g (3.65 mmol) of 10',11'-dihydrospiro[2-cyclohexene-1,5'-[5*H*]dibenzo[*a,d*]cyclohepten]-4-one (**18**) in 1.2 L of degassed *tert*-butanol in a Kreil flask (Ace no. 6963) was irradiated through Pyrex using a 450-W medium pressure Hanovia immersion apparatus. The reaction was stopped after 95% conversion of starting material (by GC) and concentrated under vacuum. The earliest detected product ratio was seen at 11% conversion of **18**, which corresponded to a 12.0:1.1:16.5:1.0 ratio of **21**:**20**:**19**:**22**. The crude residue was purified on nine, 20 cm x 20 cm silica gel PTLC plates eluted with 2.5% ether in hexane (25x). Five bands were separated from the plates but only four of the bands were one component bands. From the fastest moving band was isolated 0.16 g

16%) of (±)-(3a*R**,13bα,13cα)-2,3,8,9,13b,13c-hexahydro-1*H*-dibenzo[*a,e*]cyclopenta[1,3]cyclopropa[1,2-*c*]cycloocten-1-one (**21**) as a white solid, mp. 108-110°C; IR ($CHCl_3$) 2940, 2855, 1725 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.29 (d, 1 H, J = 7.1 Hz), 7.25-7.15 (cplx, 6 H), 7.04 (d, 1 H, J = 7.1 Hz), 3.21-3.05 (cplx, 3 H), 2.86 (m, 1 H), 2.81 (d, 1 H, J = 9.5 Hz), 2.64 (d, 1 H, J = 9.5 Hz), 2.30 (m, 1 H), 2.11-1.92 (cplx, 3 H); ^{13}C-NMR ($CDCl_3$) δ 214.7 (C), 145.6 (C), 144.6 (C), 142.8 (C), 134.3 (C), 131.2 (CH), 130.3 (CH), 127.4 (CH), 126.9 (CH), 126.7 (CH), 126.5 (CH), 125.9 (CH), 125.6 (CH), 44.8 (C), 39.9 (CH), 38.2 (CH), 37.5 (CH_2), 35.6 (CH_2), 34.6 (CH_2), 25.2 (CH_2); UV (abs. EtOH) λ_{max} (ε) 321 (69), 211 (18639); MS, *m/e* (%) 274 (88), 246 (34), 232 (34), 217 (100), 215 (52), 202 (39), 115 (39); HRMS, exact mass calcd for $C_{20}H_{18}O$ *m/e* 274.1358, found *m/e* 274.1344. Anal. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.62. Found: C, 87.16; H, 6.88.

A second band proved to be a mixture of **19** and **22**. Rechromatography of the mixture on one 20 cm x 20 cm silica gel PTLC plates was unsuccessful. Compound **22** appeared to be unstable under these prolonged slightly acidic conditions.

The third band yielded 0.02 g (0.07 mmol, 2%) of **18**.

The fourth band yielded 0.09 g (0.33 mmol, 9%) of (±)-(3a*S**,13bα,13cβ)-2,3,8,9,13b,13c-hexahydro-1*H*-dibenzo[*a,e*]cyclopenta[1,3]cyclopropa[1,2-*c*]cycloocten-1-one (**20**) as a white solid. Recrystallization from absolute ethanol in chloroform afforded an analytical sample: mp. 123-125°C; IR ($CHCl_3$) 2938, 1722 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.08-6.94 (cplx, 8 H), 3.68-3.53 (cplx, 2 H), 3.02 (m, 2 H), 2.89 (d, 1 H, J = 3.0 Hz), 2.71 (m, 1 H), 2.55 (d, 1 H, J = 3.0 Hz), 2.42 (m, 2 H), 2.22 (m, 1 H); ^{13}C-NMR ($CDCl_3$) δ 213.3 (C), 140.3 (C), 139.4 (C), 138.1 (C), 135.4 (C), 130.5 (CH), 129.7 (CH), 129.4 (CH), 129.0 (CH), 127.6 (CH), 127.3 (CH), 126.7 (CH), 126.3 (CH), 43.1 (C), 40.7 (CH), 36.2 (CH), 34.6 (CH_2), 32.5 (CH_2), 31.9 (CH_2), 29.7 (CH_2); UV (abs. EtOH) λ_{max} (ε) 261 (195), 215 (13442); MS, *m/e* 274 (77), 246 (41), 232 (34), 217 (100), 215 (53), 218 (37), 202 (39), 115 (34); HRMS,

exact mass calcd for $C_{20}H_{18}O$ *m/e* 274.1358, found *m/e* 274.1344. Anal. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.62. Found: C, 87.15; H, 6.77.

The fifth band afforded 0.48 g (1.75 mmol, 48%) of (±)-4,4a,9,10-tetrahydrotribenzo[*a,c,e*]cycloocten-2(3*H*)-one (**19**) as a white solid. Recrystallization from ether afforded an analytical sample: mp. 125-127°C; IR ($CHCl_3$) 2960, 1675 cm^{-1}; ^{1}H-NMR ($CDCl_3$, -40°C, major conformer) δ 7.17-6.91 (cplx, 8 H), 6.05 (d, 1 H, J = 2.8 Hz), 3.95 (m, 1 H), 3.52 (m, 1 H), 3.08 (m, 1 H), 2.98-2.70 (cplx, 4 H), 2.39 (m, 2 H); ^{13}C-NMR ($CDCl_3$, -40°C, major conformer) δ 199.2, 169.3, 140.1, 138.5, 138.3, 136.2, 130.1, 129.7, 129.5, 127.8, 127.3, 127.3, 126.7, 126.5, 125.5, 49.7, 38.0, 35.9, 32.4, 28.7; UV (abs. EtOH) λ_{max} (ε) 265 (sh, 7333), 229 (14419); MS, *m/e* (%) 274 (100), 232 (20), 217 (53), 215 (30), 202 (28); HRMS, exact mass calcd for $C_{20}H_{18}O$ *m/e* 274.1358, found *m/e* 274.1344. Anal. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.62. Found: C, 87.60; H, 6.81.

B. In Benzene: A solution of 1.0 g (3.65 mmol) of **18** in 1.2 L degassed purified benzene was photolyzed using conditions identical to those described above. The rearrangement was stopped after 98% conversion of starting material (by GC) and concentrated under vacuum. The earliest detected product ratio was seen after 5% conversion of **18**, which corresponded to a 6.6:1.0:5.5:1.2 ratio of **21**:**20**:**19**:**22**. The residue was passed through a 5.0 cm silica gel plug with 8% ether in hexane to remove any polymeric material and then concentrated *in vacuo*. The resulting yellow oil was purified by HPLC on a Waters 590 programmable HPLC, using a silica gel Dynamax-60A (No. 83-121-C) prep column eluted with 85:15 hexane:ethyl acetate. At a flow rate of 10 mL/min, 250 μL injections containing 60 mg of the product mixture could be separated; a total of 12 injections were made. The first eluted band afforded 0.02 g (0.07 mmol, 2%) of the trans ketone **21**. The second and third band coeluted. The fourth band yielded 0.10 g (0.36 mmol, 10%) of 3-(10-11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-ylidene)cyclopentanone (**22**) as a colorless oil. The fifth band yielded 0.03 g (0.11

mmol, 3%) of the cis ketone **20**. The sixth band afforded 0.53 g (1.93 mmol, 53%) of the enone **19**. The spectral data for **22** were: IR ($CHCl_3$) 2930, 2840, 1715 cm^{-1}; ^1H-NMR (400 HMz, $CDCl_3$) δ 7.05-6.92 (cplx, 8 H), 3.39-3.13 (cplx, 4 H), 3.94-2.74 (cplx, 6 H); ^{13}C (100 HMz, $CDCl_3$) δ 209.8, 142.0, 141.2, 138.3, 138.1, 135.7, 132.6, 129.7, 129.5, 127.1, 127.0, 126.0, 125.9, 45.1, 39.2, 33.7, 33.6, 31.8; UV (abs. EtOH) λ_{max} (ε) 325 (187), 295 (280), 219 (10879); MS, *m/e* (%) 275 (22), 274 (100), 232 (32), 217 (53), 216 (39), 215 (27); HRMS, exact mass calcd for $C_{20}H_{18}O$ *m/e* 274.1358, found *m/e* 274.1353. Anal. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.62. Found: C, 87.13; H, 6.63.

Single Crystal X-Ray Structure Determination of (±)-4,4a,9,10-Tetrahydrotribenzo[*a,c,e*]cycloocten-2(3*H*)-one (19). A crystal of **19** was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table 3) were determined by least squares refinement of the best angular positions for 15 independent reflections (2θ > 15°) during normal alignment procedures using molybdenum radiation (λ = 0.71069Å). Data (1933 independent points after removal of space group forbidden and redundant data) were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured every 97 reflections. As the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. After removal of redundant and space forbidden data, observed reflections [1272, $I > 3.0\sigma(I)$] were used for solution of carbon and oxygen positions of the structure by direct methods.[130] Refinement[131] of scale factor, positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. A difference Fourier synthesis did not allow location of all hydrogen positions, therefore all hydrogen positions were calculated using a C-H

distance of 0.97Å and appropriate geometry. All hydrogen atoms were included in the final refinement with isotropic thermal parameters but their positional and thermal parameters were held fixed. A difference Fourier revealed no electron density of interpretable level. Scattering factors were taken from Cromer and Mann.[132]

The final cycle of refinement [function minimized $\Sigma(|F_o| - |F_c|)^2$] leading to a final agreement factor, R = 4.8% [$R = (\Sigma| |F_o| - |F_c| | / \Sigma|F_o|) \times 100$]. In the final stages of refinement, a weight of $1/\sigma(F)^2$ was used, R_w = 6.3%. Appendix A, Tables 7-9 lists bond angles and distances, positional parameters, and final anisotropic thermal parameters for **18.**

Single Crystal X-ray Structure Determination of (±)-(3a*S,13bα,13cβ)-2,3,8,9,13b,13c-hexahydro-1*H*-dibenzo[*a*,*e*]cyclopenta[1,3]cyclopropa[1,2-*c*]cycloocten-1-one (20).** A crystal of **20** was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table 3) were determined by least squares refinement of the best angular positions for 15 independent reflections (2θ > 15°) during normal alignment procedures using molybdenum radiation (λ = 0.71069Å). Data (2020 independent points after removal of space group forbidden and redundant data) were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. Observed reflections [923, $I > 3.0\sigma(I)$] were used for solution of carbon and oxygen positions of the structure by direct methods using MULTAN80.[130] Refinement[131] of scale factor, positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. The positions of the hydrogen atoms were located from a difference Fourier synthesis and were included

TABLE 3

CRYSTAL DATA FOR **19** AND **20**

	19 (enone)	**20** (cis)
formula	$C_{20}H_{18}O$	$C_{20}H_{18}O$
MWT	274.4	274.4
a, Å	13.576(6)	6.820(4)
b, Å	11.232(5)	8.492(3)
c, Å	9.786(5)	14.059(10)
α, deg	90.0	90.40(4)
β, deg	99.66(4)	88.86(5)
γ, deg	90.0	110.87(4)
V, $Å^3$	1471.0(12)	760.7(7)
F(000)	584	292
μ(MoKα), cm^{-1}	0.693	1.006
λ(MoKα), Å	0.71069	0.71069
D_{calcd}, g cm^{-3}	1.239	1.198
Z	4	2
obsd refl	1272	923
R, (%)	4.8	8.1%
space group	$P2_1/n$	$P\bar{1}$

(with hydrogen positional and thermal parameters fixed) in the final cycles of refinement [function minimized, $\Sigma(|F_o|-|F_c|)^2$] leading to a final agreement factor, R = 8.1% [R = (Σ|

$|F_o| - |F_c| \,| / \Sigma|F_o|) \times 100]$. Scattering factors were taken from Cromer and Mann.[132] In the final stages of refinement, a weight of $1/\sigma(F)^2$ was used. Appendix A, Tables 10-12 lists bond angles and distances, positional parameters, and final anisotropic thermal parameters for **20**.

General Procedure for Lithium-Liquid Ammonia Reductions. To 20 mg (2.88 mmol) of freshly cut lithium wire was added 40 mL of liquid ammonia (distilled from Li) at -78°C. To the resulting dark blue solution was added 110 mg (0.40 mmol) of photoproduct (**20** or **21**) in 4 mL of dry tetrahydrofuran all at once. The solution was still dark blue upon addition and remained blue after stirring for 1 h at -78°C. Approximately 200 mg of solid ammonium chloride was added slowly and the ammonia was evaporated on a stream of dry nitrogen. Saturated aqueous NH_4Cl was added and the solution was ether extracted. The combined ether extracts were washed with water, saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The oil was purified by PTLC. The following results were obtained.

Reduction of **21** afforded a pale yellow oil which was purified on one 20 cm x 20 cm silica gel PTLC plate eluted with 2.5% ether in hexane (6x). The fastest moving of two bands yielded 5',6',11',12'-tetrahydrospiro(cyclopentane-1,5'-dibenzo[*a*,*e*]cyclo-octen)-3-one (**23**). Compound **23** was crystallized from ether in hexane to afford 33 mg (0.12 mmol, 30%) of a white solid, mp. 94-96°C; IR ($CHCl_3$) 2922, 1740 cm^{-1}; ^{1}H-NMR ($CDCl_3$, -30°C) δ 7.12-6.89 (cplx, 6 H), 6.84 (d, 1 H, J = 6.9 Hz), 6.69 (d, 1 H, J = 7.8 Hz), 3.92 (d, 1 H, J = 13.9 Hz), 3.69 (m, 1 H), 3.46 (m, 1 H), 3.20 (d, 1 H, J = 17.6 Hz), 3.09-2.88 (cplx, 3 H), 2.91 (d, 1 H, J = 14.4 Hz), 2.52 (d, 1 H, J = 17.6 Hz), 2.41-2.32 (cplx, 2 H), 2.15 (m, 1 H); ^{13}C-NMR ($CDCl_3$, -30°C) δ 220.0, 141.8, 138.7, 138.4, 137.7, 131.1, 130.2, 128.6, 126.8, 126.4, 126.2, 126.0, 126.0, 54.6, 50.0, 47.2, 36.3, 36.2, 35.6, 33.5; UV (abs. EtOH) λ_{max} (ε) 326 (86), 211 (41520); MS, *m/e* (%) 276 (54), 207 (27), 133 (19), 129 (42), 113 (38), 105 (100);

HRMS, exact mass calcd for $C_{20}H_{20}O$ *m/e* 276.1514, found *m/e* 276,1503. Anal. Calcd for $C_{20}H_{20}O$: C, 86.91; H, 7.30. Found: C, 86.70; H, 7.34.

The second band yielded 47 mg (0.17 mmol, 43%) of starting material **21**.

Reduction of **20** afforded a pale yellow oil that was purified on one 20 cm x 20 cm silica gel PTLC plate eluted with 2.5% ether in hexane (12x). The fastest moving of two bands yielded 52 mg (0.19 mmol, 47%) of **20**. The second yielded compound **23**. Rerystallization from ether in hexane afforded 23 mg (0.08 mmol, 21%) of the spiro cyclopentanone **23**. The reduction product was identical by TLC, GC, mp, IR, ^1H NMR, ^{13}C NMR, MS, and elemental analysis with material isolated from the reduction of **23**.

General Procedure: Reaction Profiles. Solutions of 100 mg (0.36 mmol) samples of **18** in both 305 mL of degassed anhydrous *tert*-butanol and 305 mL of degassed purified benzene and 50 mg (0.18 mmol) samples of **19**, **20**, **21** and **22** in both 160 mL of degassed *tert*-butanol and 160 mL of degassed purified benzene were irradiated as above in the Hanovia apparatus. The reaction was monitored by GC analysis of 0.2 mL concentrated aliquots. Compound **18** was irradiated at 5-min intervals for the first hour, 10-min intervals for the next 3 h and at 20-min intervals thereafter for a total photolysis time of 6.5 h. Compounds **19**, **20**, **21** and **22** were irradiated at 15-min intervals for the first hour, 30-min intervals for the next 3 h, and at 60-min intervals thereafter for total photolysis times ranging from 4.5-7.0 h. The samples were found to be stable to the GC conditions. Peak areas were determined from electronic integration of the peaks relative to internal benzophenone standard.

Control Experiment. Photostability of the Photoproducts. In a typical control run, 0.18 mmol of the photoproduct was photolyzed as a 0.001 *M* solution in *tert*-butanol and in benzene using conditions identical to those described above. The reactions were monitored by GC as above; the individual compounds were found to be stable to these thermal conditions. For the irradiation of **21** in *tert*-butanol, the earliest

detected product ratio was seen at 30% conversion of **21**, which corresponded to a 73.7:26.7:1.0:1.0 ratio of **20**:**19**:**22**:**18**. In benzene, the earliest detected product ratio was seen at 20% conversion of **21**, which corresponded to a 9.7:4.7:1.0 ratio of **20**:**19**:**22**. Irradiation of **20** in *tert*-butanol yielded an earliest detected product ratio of 1.2:66.7:1.3:1 0 of **21**:**19**:**22**:**18** at 21% conversion of **20**. In benzene, the earliest detected product ratio was seen at 5% conversion of **20**, which corresponded to a 1.4:3.3:1.0 ratio of **21**:**19**:**22**. Compounds **19** and **22** were found to be photochemically inert to irradiation in both *tert*-butanol and benzene with decomposition of **22** occurring after 3 h.

^{1}H-HMR Shift Reagent Experiment. In a typical run, the ^{1}H-NMR spectra were recorded with increasing concentrations of shift reagent. To a 0.07 *M* solution of the photoproduct **22** in $CDCl_3$ was added 5 mg (0.005 mmol) quantities of the solid shift reagent Resolve-Al EuFOD™ ($Eu(fod)_3$). After each 5 mg addition the NMR was taken. This sequential 5 mg addition was continued until a total of 60 mg (0.058 mmol) of shift reagent had been added. The response curve is shown in Figure 10 of Chapter 2 along with a table of the slopes (Δm) and the initial proton resonances (IS) in Table 2.

4-Bromo-1-cyclopentene (24). The procedure of Rice and Bartlett[133,134] was followed. [Note: This procedure has been reported to be hazardous, see ref.-134.] A 175 g (2.66 mol) sample of freshly cracked cyclopentadiene was dissolved in 125 mL of petroleum ether and cooled to -30°C using a CCl_4/dry ice bath. A solution of 427 g (2.66 mol) of bromine dissolved in 225 mL of petroleum ether was added slowly during 2 h, keeping the temperature below -30°C. Once the addition was complete, the mixture was poured into a 1 L Erlenmeyer, cooled to -78°C and the solvent was decanted. The residue was dissolved in *ca.* 700 mL ether and reduced immediately with lithium aluminum hydride.

To a 0°C solution of 44 g (1.3 mol) of lithium aluminum hydride in 565 mL of ether was added the dibromide solution during 2 h. The reaction mixture was stirred at

23°C for 12 h and then refluxed for 34 h. Once cooled, the mixture was filtered through Celite® keeping the filter flask under ice. The filtrate was poured onto ice, the organic layer was separated and dried over $CaCl_2$ and the ether was removed by vacuum distillation. The crude residue was distilled at reduced pressure to yield 20 g (0.13 mol, 5.1%) of 4-bromo-1-cyclopentene (**24**); bp. 40-42°C (35 mm Hg), lit .[133] bp 43°C (35 mm Hg). The spectral data were: IR 3038, 1590, 1440 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.77 (s, 2 H), 4.59 (septet, 1 H, J = 3.3 Hz), 2.97 (dd, 2 H, J = 6.8, 17.2 Hz), 2.78 (dd, 2 H, J = 2.8, 16.8 Hz); ^{13}C-NMR ($CDCl_3$) δ 128.5, 48.4, 44.7.

5-(3-cyclopentenyl)-5-hydroxy-10,11-dihydro-(5*H*)-dibenzo[*a,d*]-cycloheptene (27). A modification of the method of Praefeke and Weichsel[135] was employed. To 0.52 g (0.021 mol) of activated magnesium in 5 mL of ether was added one-third of a solution of 3.0 g (0.02 mol) of 4-bromo-1-cyclopentene (**24**) in 25 mL of ether. A few drops of 1,2 dibromoethane was added to initiate reaction, and the remaining alkyl halide solution was added and refluxed with heat for 1 h. The reaction mixture showed a positive Gillman test[136] at this time. The mixture was cooled to 23°C and a solution of 4.16 g (0.02 mol) of dibenzosuberone (**15**) in 30 mL of ether was dripped in slowly. Once all the ketone was added, the mixture was refluxed for 45 min. The solution was poured into cold saturated aqueous NH_4Cl and extracted with ether. The organic layer was then washed with saturated aqueous $NaHSO_4$ and saturated aqueous NaCl, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by column chromatography on a 60 cm x 2.5 cm silica gel column slurry packed in hexane and eluted with increasing concentrations of ether in hexane. The compounds eluted as follows: 0% ether in hexane, dibenzosuberane **40**; 1% ether in hexane, dibenzosuberone **15**; 1.5% ether in hexane, 0.14 g (0.51 mmol, 2.5%) of 5-(3-cyclopentenyl)-5-hydroxy-10,11-dihydro-(5*H*)-dibenzo[*a,d*]cycloheptene (**27**); 4% ether in hexane, 1.19 g (5.2 mmol, 26%) of (5*H*)-dibenzo[*a,d*]cyclohepten-5-ol (**41**). Compound **27** was isolated as a colorless oil. The spectral data for **27** were: IR 3520,

2930, 1600, 1490, 1060 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.89 (dd, 2 H, J = 1.9, 7.5 Hz), 7.21-7.06 (cplx, 6 H), 5.63 (s, 2 H), 3.70 (quintet, 1 H, J = 8.3 Hz), 3.52 (A of ABm, 2 H), 2.98 (B of ABm, 2 H), 2.33 (A of ABm, 2 H), 2.21 (s, 1 H), 1.95 (B of ABm, 2 H); ^{13}C-NMR ($CDCl_3$) δ 144.5, 137.4, 130.7, 130.2, 127.1, 126.1, 125.8, 78.9, 46.7, 33.9, 33.7; MS, FAB/DP, Nitrobenzyl alcohol matrix, $[M + H]^+$ 277.2201.

Compound **41** was isolated as a white solid, 90-92°C, lit. [137] mp. 91-93°C. The spectral data for **41** were: IR ($CHCl_3$) 3420, 1490, 1450 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 2 H), 7.13 (m, 6 H), 5.86 (s, 1 H), 3.35 (m, 2 H), 3.04 (m, 2 H), 2.33 (s, 1 H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.5, 138.8, 130.1, 127.9, 127.0, 126.1, 76.4, 32.3.

5-(3-cyclopentenyl)-5-hydroxy-10,11-dihydro-(5*H*)-dibenzo[*a,d*]-cycloheptene (27). To the Grignard reagent prepared from 5 g (0.02 mol) of 1,2-bis-(2-chlorophenyl)ethane[122] (**25**) and 1.2 g (0.05 mol) of magnesium powder in 20 mL of tetrahydrofuran was added 2.8 g (0.02 mol) of ethyl-3-cyclopentenecarboxylate[123] (**26**) in 5 mL of tetrahydrofuran. The reaction mixture was stirred for 1 h at 23°C then refluxed for 3 h. The solution was poured into saturated aqueous NH_4Cl and extracted with ether. The ether extracts were washed with water (3x), saturated aqueous NaCl (1x) and dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by column chromatography on a 80 cm x 2.5 cm slurry packed silica gel column eluted with ether in hexane. The compounds eluted as follows: 0% ether in hexane, diphenylethane; 1.5% ether in hexane, 2.10 g (7.6 mmol, 38%) of 5-(4-cyclopentenyl)-5-hydroxy-10,11-dihydro-(5*H*)-dibenzo[*a,d*]cycloheptene (**27**) as a colorless oil. The spectral data matched those reported above.

5-(3-Cyclopenten-1-ylidene)-10,11-dihydro-(5*H*)-dibenzo[*a,d*]-cycloheptene (28). To a 0°C solution of 0.4 g (1.45 mmol) of 5-(3-cyclopentenyl)-5-hydroxy-10,11-dihydro-(5*H*)-dibenzo[*a,d*]cycloheptene (**27**) in 13.2 mL of pyridine was added 2.6 mL (4.27 g, 0.028 mol) of phosphorous oxychloride. The mixture was

stirred for 15 min at 0°C and then heated to an oil-bath temperature of 85°C for 8 h. The reaction mixture was cooled to 23°C, poured onto ice and extracted with ether. The combined ether extracts were washed with 1 *M* HCl, water, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl. The organic phase was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was chromatographed on two 20 cm x 20 cm silica gel PTLC plates eluted with hexane (9x). The fastest moving band yielded 0.33 g (1.28 mmol, 88%) of 5-(3-cyclopenten-1-ylidene)-10,11-dihydro-(5*H*)-dibenzo[*a,d*]-cycloheptene (**28**) as a colorless oil. The spectral data were: ^{1}H-NMR ($CDCl_3$) δ 7.29 (m, 2 H), 7.13 (m, 6 H), 5.78 (s, 2 H), 3.33 (m, 4 H), 2.80 (m, 4 H); ^{13}C-NMR ($CDCl_3$) δ 141.5, 139.1, 137.7, 134.8, 129.7, 129.1, 129.0, 128.5, 126.8, 125.6, 38.6, 32.6.

3-(10,11-Dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-ylidene)cyclopentanol (29). The general procedure of Brown and coworkers[138] was followed. To 3.64 mL of a 0.5 *M* solution of 9-BBN in tetrahydrofuran was added a solution of 0.47 g (1.82 mmol) of 5-[3-cyclopenten-1-ylidene]-10,11-dihydro-(5*H*)-dibenzo[*a,d*]cycloheptene (**28**) in 9 mL of tetrahydrofuran dropwise with stirring. The reaction mixture was allowed to stir for 3.5 h at 23°C at which time a mixture of 1.1 mL of ethanol and 0.36 mL of 6 *M* NaOH were added. To this solution was added 0.73 mL of 30% H_2O_2 very slowly. The solution was heated to 50°C for 1 h and then diluted with water. The solution was saturated with Na_2CO_3, extracted with ether and the extract washed with saturated aqueous Na_2CO_3. Drying over anhydrous Na_2SO_4 and concentration *in vacuo* yielded a yellow oil. The crude alcohol was chromatographed on two 20 cm x 20 cm silica gel PTLC plates, eluted with 2% ether in hexane (5x). The first band yielded starting material (**28**), the second band afforded an impure sample of compound **29**. The second band was therefore rechromatographed on two 20 cm x 20 cm silica gel PTLC plates eluted with 8% ether in hexane (11x). From the second band was isolated 0.25 g (0.91 mmol, 49.7%) of 3-(10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-ylidene)cyclo-

pentanol (**29**) as a colorless oil. The spectral data were: IR 3400, 1225 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.25-7.10 (cplx, 8H), 4.45 (m, 1 H), 3.69 (m, 1 H), 3.32 (m, 2 H), 2.87 (m, 2 H), 2.55 (m, 1 H), 2.47-2.10 (cplx, 2 H), 1.99 (m, 1 H), 1.82-1.64 (cplx, 2 H); ^{13}C-NMR ($CDCl_3$) δ 141.8, 139.9, 138.0, 129.2, 129.1, 128.9, 128.8, 128.6, 126.8, 126.7, 125.6, 125.5, 125.5, 125.4, 72.9, 42.1, 34.7, 32.7, 32.5, 28.8.

10,11-Dihydro-(5*H*)-dibenzo[*a,d*]cycloheptene (40). The procedure of Leonard and Gagneux[139] was followed. To a solution of 23 g (0.11 mol) of dibenzosuberone (**15**) in 450 mL of 95% ethanol was added 23 g (1.0 g-atom) of sodium metal during 30 min, maintaining the solution at reflux. Once the addition was complete, the mixture was cooled and then poured into *ca.* 500 mL of ice-water. The solution was extracted with ether, the organic phase dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Filtration through a 25 cm x 5 cm alumina packed column with hot Skelly-B yielded 14.1 (0.07 mol, 66%) of 10,11-dihydro-(5*H*)-dibenzo[*a,d*]cycloheptene (**40**) as a white solid, 74-76°C, lit.[139] mp. 72-75°C. The spectral data were: IR ($CHCl_3$) 2940, 1500, 1100 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.16-7.06 (cplx, 8 H), 4.08 (s, 2 H), 3.14 (s, 4 H); ^{13}C-NMR ($CDCl_3$) δ 139.2, 138.9, 129.5, 128.9, 126.5, 126.0, 40.9, 32.4.

3-(10,11-Dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-2-cyclopenten-1-one (36). To a 0°C solution of 1.55 g (8.0 mmol) of 10,11-dihydro-(5*H*)-dibenzo[*a,d*]cycloheptene (**40**) in 10 mL tetrahydrofuran was added 5.7 mL of a 1.4 *M* *n*-BuLi solution in hexane dropwise during 30 min. The resulting orange solution was stirred 15 min at 0°C and then 1.0 mL (1.05 g, 8.4 mmol) of 3-ethoxy-2-cyclopenten-1-one in 3 mL of tetrahydrofuran was added dropwise during 5 min. The solution turned darker orange upon addition. The reaction mixture was stirred 1 h at 23°C, poured into saturated aqueous NH_4Cl and ether extracted. The combined organic extracts were washed with water, saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude material was purified by column chromatography on a 60 cm x 2.5 cm slurry packed silica gel column eluted with

increasing concentration of ether in hexane. The compounds eluted as follows: 0% ether in hexane, 0.85 g (4.4 mmol, 54%) of **40**; 1% ether in hexane, 0.06 g (0.14 mmol, 1.8%) of the pinacol dimer of dibenzosuberone (**42**); 10% ether in hexane, 0.72 g (2.64 mmol, 33%) of 3-(10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-2-cyclopenten-1-one (**36**). Compound **42** was isolated as a white solid, mp. 282-284°C; IR ($CHCl_3$) 3440, 2870, 1450 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.00 (m, 4 H), 6.89 (m, 4 H), 6.62 (m, 4 H), 6.45 (dd, 4 H, J = 1.3, 7.6 Hz), 4.70 (s, 2 H), 3.68 (A of ABm, 4 H), 2.94 (B of ABm, 4 H); ^{13}C-NMR ($CDCl_3$) δ 139.3, 139.2, 131.9, 130.0, 126.3, 125.1, 60.7, 33.9.

Compound **36** was recrystallization from ether to give a pale yellow solid, mp. 112-114°C; IR ($CHCl_3$) 2920, 1695, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.19-7.09 (cplx, 8 H), 5.53 (d, 1 H, J = 1.8 Hz), 4.69 (s, 1 H), 3.19 (A of ABm, 2 H), 2.77 (B of ABm, 2 H), 2.34-2.26 (cplx, 4 H); ^{13}C-NMR ($CDCl_3$) δ 208.7, 185.0, 139.3, 137.3, 131.0, 130.6, 130.3, 127.5, 126.1, 58.1, 35.5, 32.0, 30.2; MS, *m/e* (%) 274 (35), 193 (49), 192 (25), 191 (100), 178 (121), 115 (17); HRMS, exact mass calcd for $C_{20}H_{18}O$ *m/e* 274.1358, found *m/e* 274.1354.

Attempted Photochemical and Chemical Deconjugation of 36. The general procedure of Ringold and Malhotra[140] was followed. To a -78°C solution of 0.012 mL (8.7 mg, 0.08 mmol) of diisopropylamine in 15 mL of tetrahydrofuran was added 0.07 mL of a 1.3 *M* solution of *n*-BuLi in hexane. The lithium diisopropylamine was allowed to stir 20 min and a solution of 24.3 mg (0.09 mmol) of 3-(10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-2-cyclopenten-1-one (**36**) in 2.5 mL tetrahydrofuran was added dropwise at -78°C. The enolate was stirred 15 min, 0.015 mL (0.016 g, 0.09 mmol) of HMPA was added and stirring was continued for 5 min. The reaction was then quenched with 2.5 mL of 10% aqueous acetic acid at -78°C. The mixture was poured into saturated aqueous $NaHCO_3$ and ether extracted. The organic layer was washed with

water, saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting pale yellow oil proved to be starting material **36**.

Photochemical attempts at deconjugation were carried out using the conditions described by Shiloff and Hunter[141] for the deconjugation of isophorone, as well as the method of Taylor[142] for the deconjugation of 3-diphenylmethyl-2-cyclohexen-1-one. Solutions of 100 mg (0.36 mmol) samples of **36** in 305 mL of degassed ethyl acetate and 305 mL of *tert*-butanol were irradiated through Pyrex using a 450-W medium pressure Hanovia immersion apparatus. Both irradiations led to a 85:15 photostationary mixture of **36** and an unknown product **43**. Attempts at isolation of **43** were unsuccessful.

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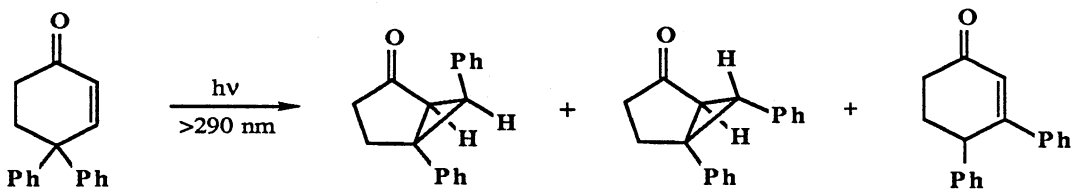
CHAPTER III

PHOTOCHEMISTRY OF (±)-4,4a,5,6-TETRAHYDRO-4a-METHYL-6,6-DIPHENYL-2(3*H*)-NAPHTHALENONE, A RIGID LINEAR DIENONE

Introduction

One branch of our work has focused on extending studies of the photochemical 4,4-diaryl-2-cyclohexen-1-one rearrangement. The parent reaction, depicted in Figure 25, was first described[143] in 1964 and has been thoroughly studied.[1,2,9-11] Low conversion photolysis of **1** at 300-340 nm (n→π*), leads to the formation of the *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**2t** and **2c**, respectively) in a ratio of *ca.* 140:1 as well as a small amount of 3,4-diphenyl-2-cyclohexen-1-one (**3**). Throughout our efforts in this area, this pioneering study has served as a benchmark for comparison of product structures, reaction stereoselectivity and mechanistic interpretation. We report, here, the synthesis and photochemistry of 4,4a,5,6-tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**4**), an analog of compound **1** having an extended π system.



1 2t 2c 3

Figure 25. Photochemistry of 4,4-Diphenyl-2-cyclohexen-1-one (**1**).

Our initial objective was to determine whether the rearrangement would proceed in the extended dienone system. If reaction occurred, the degree of stereoselectivity in the phenyl migration and the effect of the angular methyl on the product stereochemistry were important questions. The methyl group was incorporated into our substrate to preclude aromatization, help control the regiochemistry of double bond introduction and prevent migration of the double bond to the β,γ position during irradiation. Finally, with the extended conjugation, it was hoped that further information would be gleaned regarding the energy requirements of the reaction.

Earlier investigations of linear dienone photochemistry[144,145] have shown several characteristic reaction modes depending upon the structure of the substrate. Acyclic 2,4-pentadienone derivatives are generally observed to undergo cis-trans isomerization reactions. Linear homoannular cyclohexadienones rearrange to bicyclohexenones or to diene ketenes which further react with alcohol solvents. Finally, heteroannular dienones normally do not show any notable unimolecular photoreactivity but, instead, dimerize or enter into reactions with added olefins. The lone exception to this is found in steroidal dienones where intramolecular reactions have been observed when radical-stabilizing functionality (e.g. ethers and alkenes) is present on the angular carbon bound to C-10. These reactions involve hydrogen abstraction by the α-carbon of the excited enone followed by cyclization at the β-enone carbon. In the current substrate, phenyls are positioned such that phenyl migration can occur. Thus, we expected *a priori* that some normal enone rearrangement would be observed.

Results

Synthesis of the Photoreactant. The synthesis of the photosubstrate used in this study is outlined in Figure 26. The methylated enone **5** was prepared according to the general procedure of Zimmerman and coworkers[143] for the synthesis of the unsubstituted enone. Hydrogenation of this compound[146] followed by Robinson annulation

yielded the fused enone **7**. Finally, oxidation of **7** with chloranil in *tert*-butanol[147] gave the desired 4,4a,5,6-tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**4**). The overall yield for the sequence was 8.2%.

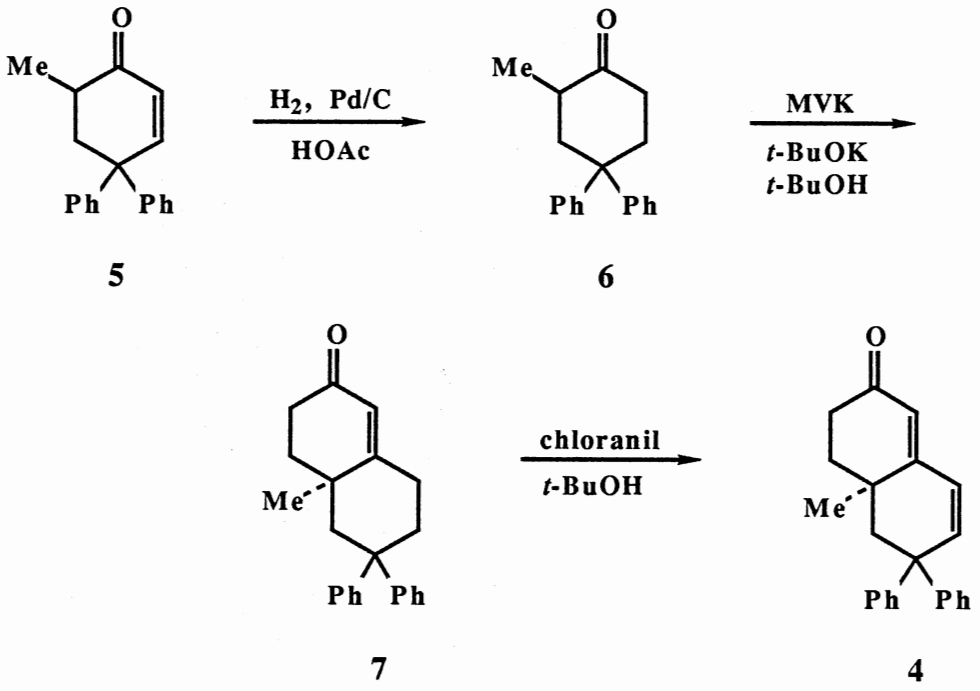


Figure 26. Synthesis of Photochemical Substrate **4**

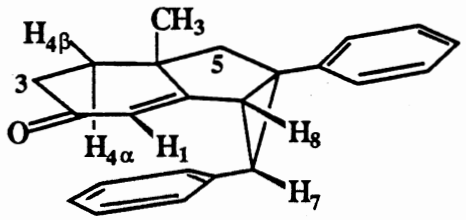
Exploratory Photochemistry and Structure Elucidation of the Products. The photochemical reactions were carried out using conditions comparable to those reported for 4,4-diphenyl-2-cyclohexen-1-one.[1] Irradiation of a 10^{-3} M solution of **4** in degassed *tert*-butanol through a Pyrex filter using a 450-W medium pressure Hanovia immersion apparatus led to the formation of two photoproducts, **8** and **9**. NMR, IR and UV indicated that both products were α,β-unsaturated cyclohexenyl ketones. Comparison of the high field ^{1}H-NMR spectrum of the compounds showed a

strong resemblance to the [3.1.0] bicyclic products isolated from the photolysis of 4,4-diphenyl-2-cyclohexen-1-one with the major product **8** resembling the isomer having trans oriented phenyls. Most notable were the coupling constants for the cis-oriented methine protons (J_{cis} = 9.7 Hz) on the three-ring of the trans diphenyl isomer **8** and for the trans-oriented protons (J_{trans}= 3.4 Hz) on the cyclopropyl of the cis diphenyl isomer **9**.[7] These coupling constants also compared well with those encountered in our previous work.[16]

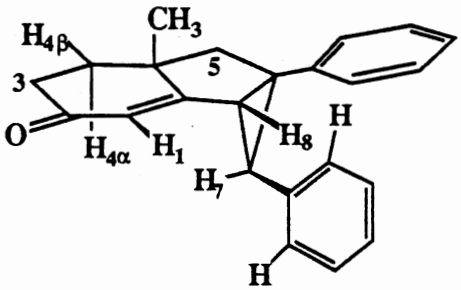
Due the complex nature of the high field ^{1}H NMR spectrum, both **8** and **9** were subjected to 2-D NMR experiments (DEPT, HETCOR, COSY), in an attempt to unequivocally assign the structures (Figures 27-30). The results of the 2-D NMR experiments were consistent with the proposed trans and cis diphenyl systems **8** and **9**. For both **8** and **9**, the DEPT experiment indicated the eight aliphatic carbon signals observed in the 1-D carbon spectra, corresponded to two quaternary, two methines, three methylenes and one methyl. The HETCOR correlated these carbon multiplicities to the proton signals (Figures 27 and 29). The methine carbons in **8** (C-7 and C-8) were assigned to the farthest downfield aliphatic signals, an AB doublet at δ 2.89 and 3.18. For **9**, the methine protons (C-7 and C-8) were assigned to the separated doublets centered at δ 3.06 and 2.31. The C-5 methylene protons in both **8** and **9** were assigned to upfield AB doublets, (δ 2.11 and 1.92 for **8**, δ 2.32 and 2.12 for **9**), based on the large geminal coupling and typical AB pattern for the isolated methylene.[121] The COSY experiment indicated coupling of one of these C-5 protons in **8** and both of the C-5 protons in **9** to the corresponding methyl protons (δ 1.33, s in **8** and δ 1.39, s in **9**, assigned by HETCOR). These couplings would seem to be the result of a W-arrangement between the C-5 proton(s) and the methyl protons.[116] It has been reported that generally, W-couplings fall in the range of 0.1-0.5 Hz and are less than the observed line width in the 1-D spectrum.[116] These couplings, however can be detected as cross peaks in COSY experiments.[116] The farthest downfield of the remaining aliphatic signals

for **8** and **9**, were assigned to the C-3 protons based on the position of these protons with respect to the carbonyl. The COSY indicated that these signals were coupled to the proton signals at δ 1.50 (1H) and 0.98 (1H) for **8**, and the signal at δ 1.97 (2H) for **9**, corresponding to the C-4 protons.

The orientation of the three-ring relative to the angular methyl was established by a series of spectroscopic observations. In a ^{1}H NOE difference experiment,[148] irradiation of H_8 in **8** led to an 11.6% enhancement in the signal intensity of H_1 and a 6.4% enhancement in the signal for H_7. In **9**, similar irradiation of H_8 resulted in a signal enhancement of 13.3% for H_1 but only 3.0% for H_7. Irradiation of the angular methyl group, on the other hand, showed no enhancement of the H_7 signal as one would expect from a syn cis isomer. A syn trans isomer was ruled out due to the absence of an upfield methyl signal which would have resulted from shielding by the endo phenyl.[7] The shielding effect of the aromatic ring was most strongly exerted on the α proton at C-4. The signal for $H_{4\alpha}$ was observed as a doublet of triplets at δ 0.98 which is consistent with the anti trans diphenyl structure. In **9**, the cis phenyl rings have a perpendicular orientation relative to one another causing shielding of one set of ortho protons to δ 6.78.



8



9

Finally, the structures of the two photoproducts were confirmed by single crystal X-ray structure determinations which clearly show the stereochemical relationships of the

phenyls and the orientation of the three-ring relative to the angular methyl. The ORTEP diagrams for (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenylcycloprop[*a*]inden-3(1*H*)-one (**8**) (molecule A of the two molecules contained in the acentric unit cell) and (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenylcycloprop[*a*]inden-3(1*H*)-one (**9**) are given in Figures 31 and 32, respectively.

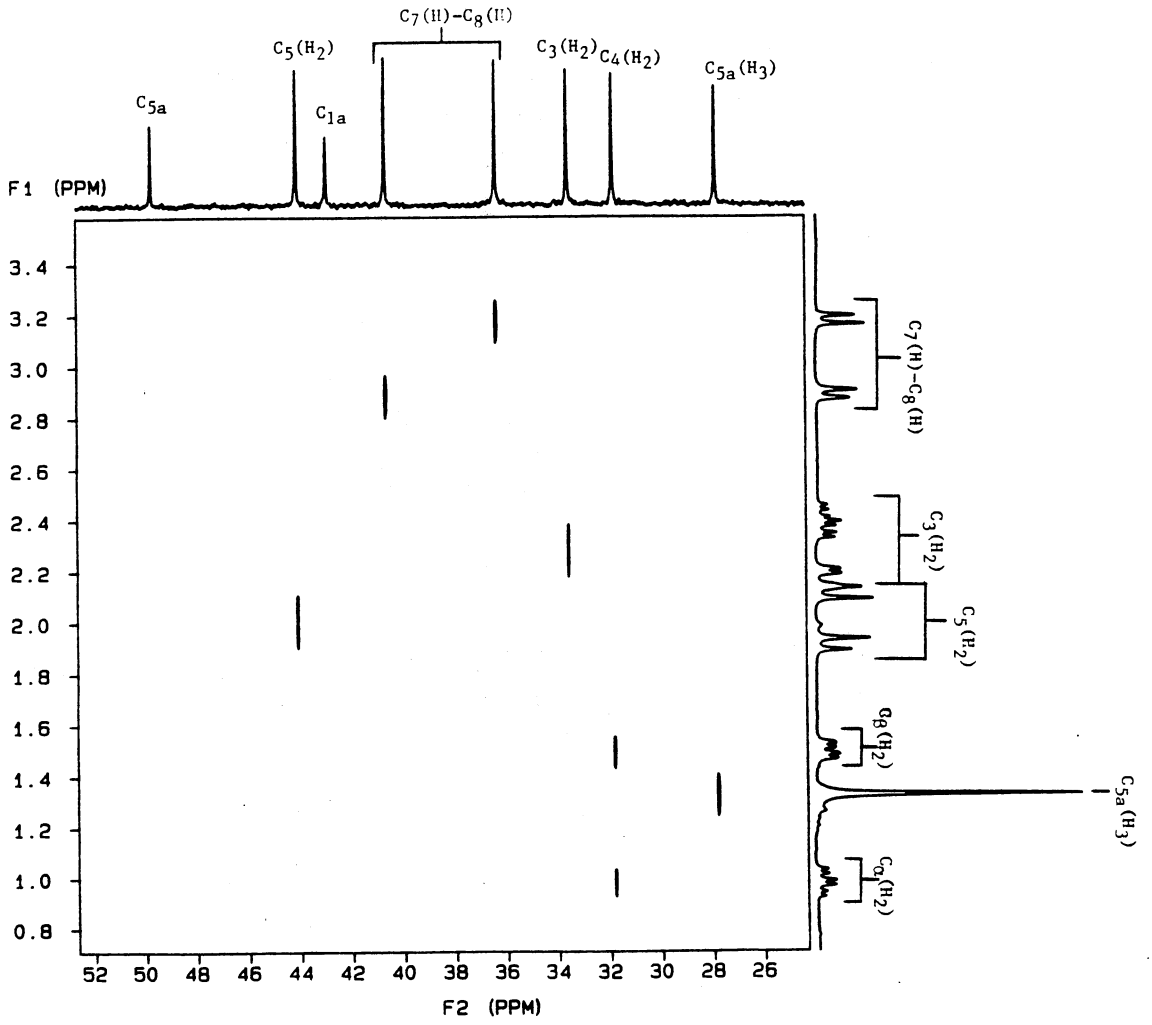


Figure 27. HETCOR of the 52-26 ppm Region for **8**.

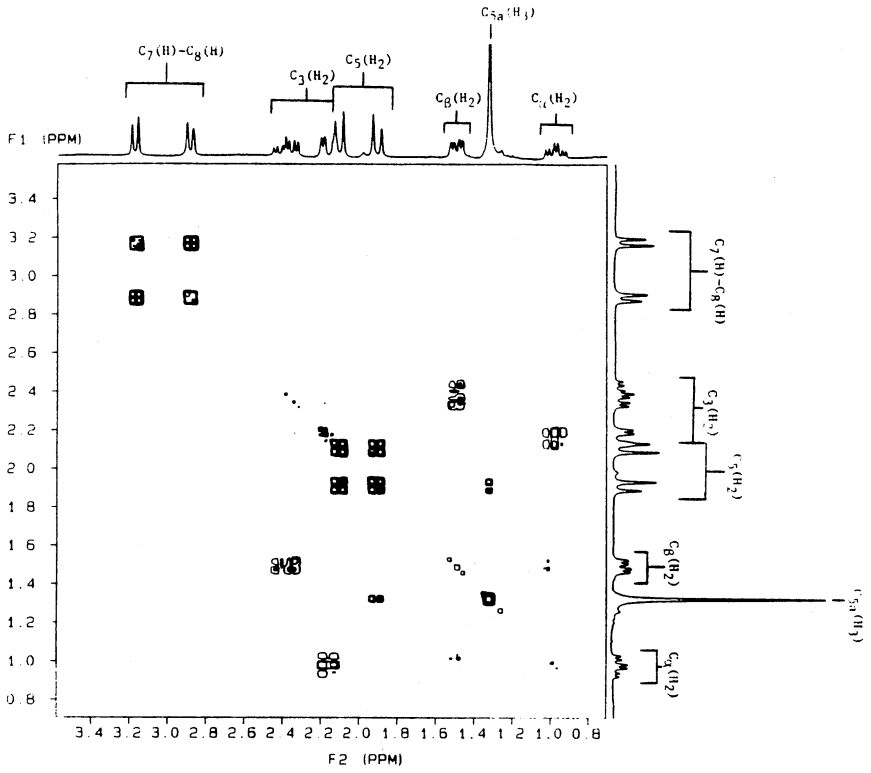


Figure 28. COSY of the δ 3.4-0.8 Region for **8**.

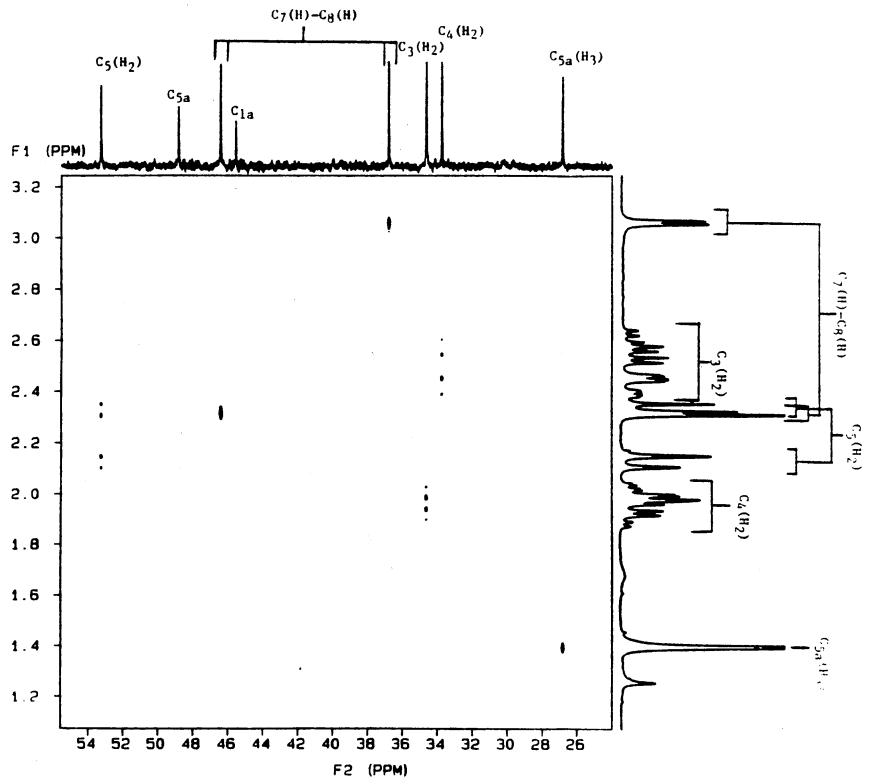


Figure 29. HETCOR of the 54-26 ppm Region for **9**.

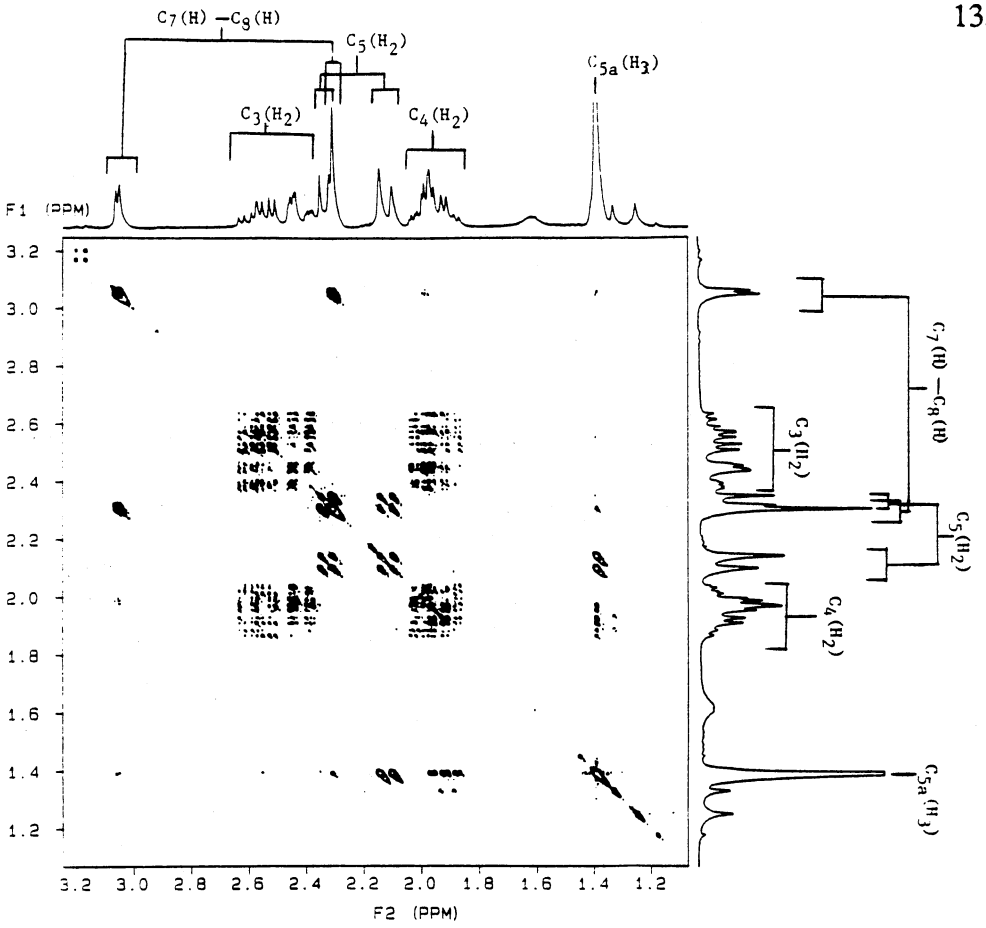


Figure 30. COSY of the δ 3.2-1.2 Region for **9**.

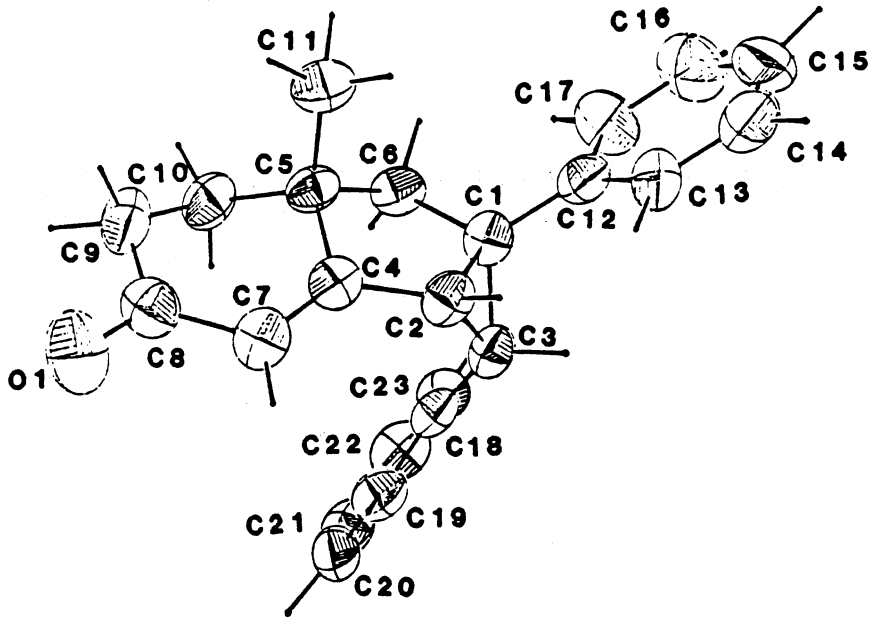


Figure 31. ORTEP Diagram for Photoproduct **8**

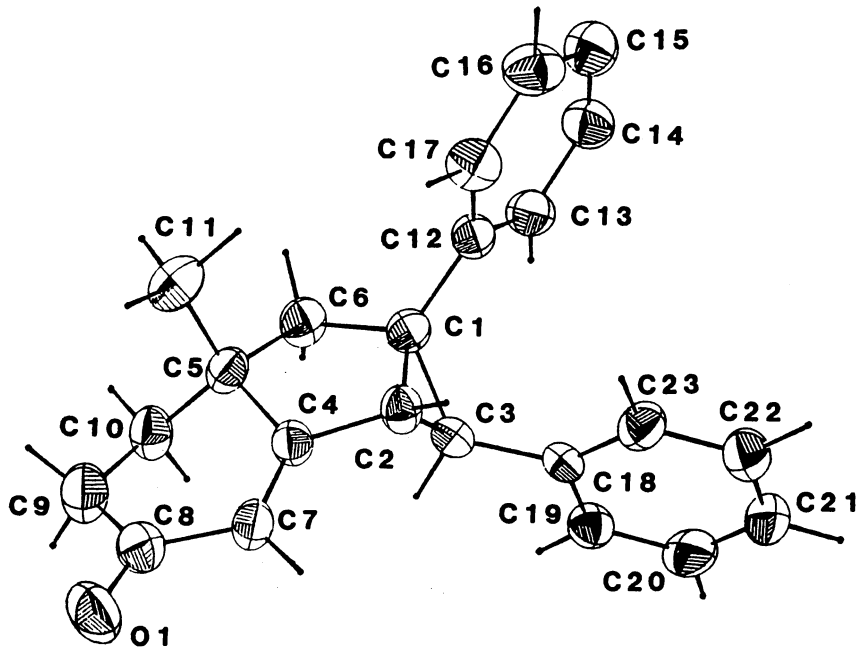


Figure 32. ORTEP Diagram for Photoproduct **9**

Compound **8**, the trans diphenyl product, was produced rapidly and appeared initially to be the only photoproduct but, at conversions greater than 30.5%, the cis diphenyl compound **9** was also observed. With longer irradiation times, it became clear that some of compound **9** was formed at the expense of **8**. Independent irradiations of **8** and **9** resulted in interconversion of the two isomers with some return to **4** occurring from **8**. The photochemistry of compound **4** is summarized in Figure 33.

Reaction Profiles and the Behavior of the Photoproducts. Figure 34 depicts the reaction profile for the irradiation of compound **4** performed as described above. Aliquots were removed every 30-90 s without interrupting the photolysis and the reaction was essentially complete (97% conversion) in 5.5 min. At this point, 83% of the product was compound **8**. Photoproduct **9** was not observed until 30.5% conversion

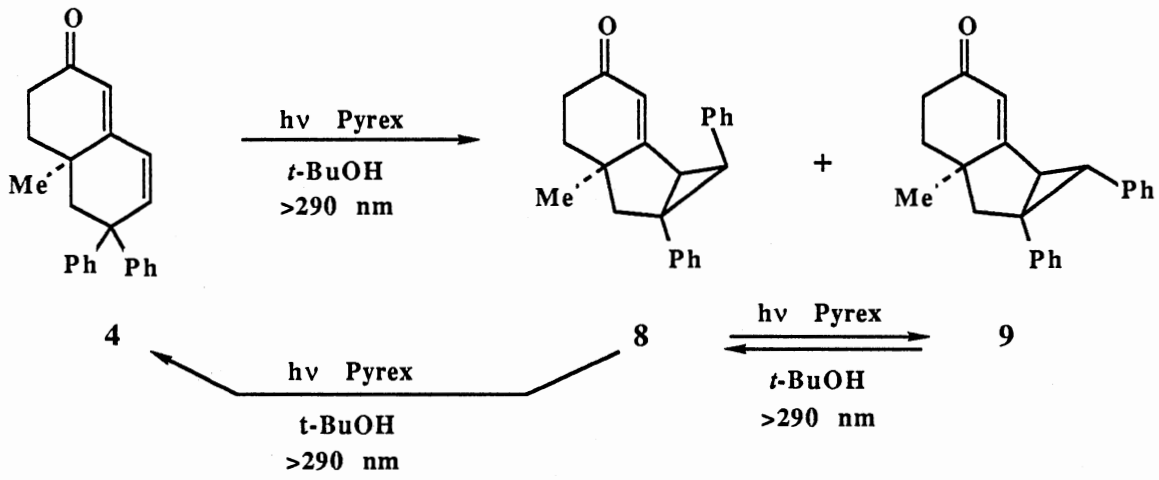


Figure 33. Photochemistry of **4**

where 0.3% could be reproducibly detected by GC. Due to this detection limit, it was not possible to unequivocally ascribe the production of **9** to a primary photoprocess. Nevertheless, the 30.2:0.3 mixture of **8**:**9** at this stage of the reaction corresponds to a *ca.* 100:1 ratio of trans:cis--very comparable to the 140:1 ratio reported for the parent case.[2,9]

Extended irradiation of **4** resulted in conversion to a photostationary mixture composed of a 76:23:1 ratio of trans:cis:dienone (**8**:**9**:**4**). This equilibrium mixture was obtained after 20 min and remained unchanged even after 6 h. A similar mixture was also formed after irradiation of either **8** or **9** for 30 min. In this latter reaction, a small amount (*ca.* 1.5%) of the dienone **4** was detected as an intermediate in the reaction of the trans but not in the reaction of the cis. Similar reactivity has been reported in the photochemistry of **1**,[9] though in the current reaction, a phenyl-migrated dienone product (e.g. **10**) could not be detected (< 0.3%). A separate plot (Figure 34) shows the reaction profile for the conversion of both **8** and **9** to the photostationary mixture. Based upon the observed rates of formation, it is clear that **8** is a primary photoproduct but the secondary interconversion of **8** and **9** makes it more difficult to comment with certainty on the origin

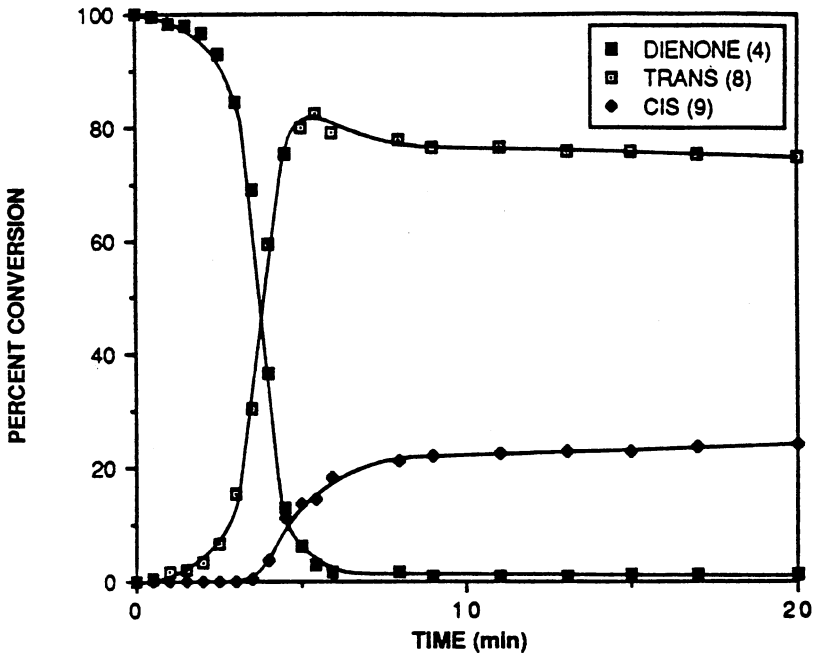
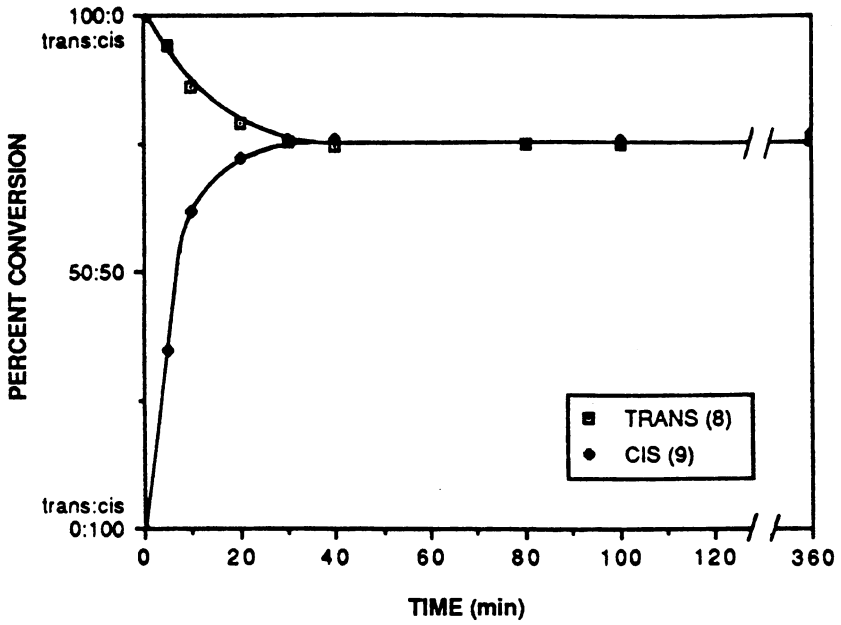


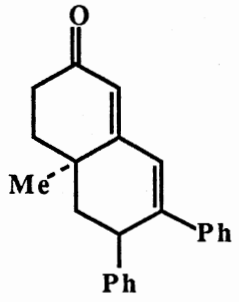
Figure 34. Reaction Profile for Irradiation of **4**



[a]*ca.* 1% of **4** was present after 25 min and remained at 360 min.

Figure 35. Reaction Profile for Irradiation of **8** and **9** through Pyrex[a]

of **9**. From our observations, it is clear that **9** arises from a secondary process but concrete evidence that it is a primary photoproduct remains elusive.



10

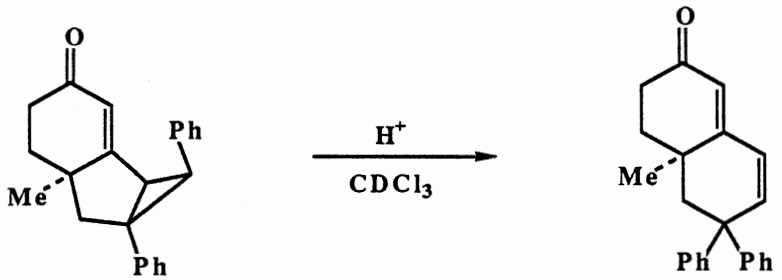
An interesting observation was made when the reaction was carried out as a series of short irradiations (< 30 s). Under these conditions, in the Hanovia apparatus with a Pyrex filter, compound **8** was the only product of the reaction, even after 90% conversion (25 min). The source of this increased stereoselectivity was intriguing and must derive from a wavelength or a light intensity effect. Several experiments were, therefore, devised to probe these possibilities.

With short irradiation times, the lamp never comes to full power. Thus, light impinging on the sample is greatly reduced and the spectral output of the lamp more closely resembles that of a low pressure mercury source (mostly 254 nm light with some low-intensity longer wavelengths).[149] These conditions could not be reproduced exactly using other means but, in a simulation, irradiating through Pyrex with a Rayonet reactor at 254 nm, no cis isomer formation was detected until 73% conversion (**8**:**9**, *ca.* 190:1). Additional experiments to evaluate this wavelength dependency were done using a series of filter solutions: (A) 0.1 *M* Na_2VO_3 in 5% NaOH (cutoff 335 nm), (B) 0.1 *M* $BiCl_3$ in 2 *M* HCl (cutoff 366 nm), and (C) 0.15 *M* $FeCl_3$ in 1*M* HCl (cutoff 445 nm). With the sodium vanadate filter, both isomers were formed as expected in a ratio similar to that

observed on extended irradiation through Pyrex. Irradiation through the bismuth chloride solution, however, gave a more stereoselective reaction (**8**:**9**, *ca.* 160:1), most likely owing to the decreased absorption of light by the photoproducts at this wavelength. Using the ferric chloride filter, no reaction was observed since none of the reactants absorb at this wavelength. These findings support a wavelength dependency in the current reaction.

Since light intensity effects have precedent in ketone photochemistry,[150] it was also necessary to evaluate this parameter. As a simple test, the distance between the light source and the dienone solution was increased from 1 cm to 40 cm. This reduced the light entering the sample since illuminating power varies inversely with the square of the distance from the source.[151] Additionally, light reaching the reaction vessel was attenuated by air and dust as well as by reflection at the Pyrex surfaces between the source and the reaction mixture. Under these conditions, the reaction, though slower, yielded approximately the same ratio of products at all conversions. Thus, light intensity appears to have little effect on the course of the reaction.

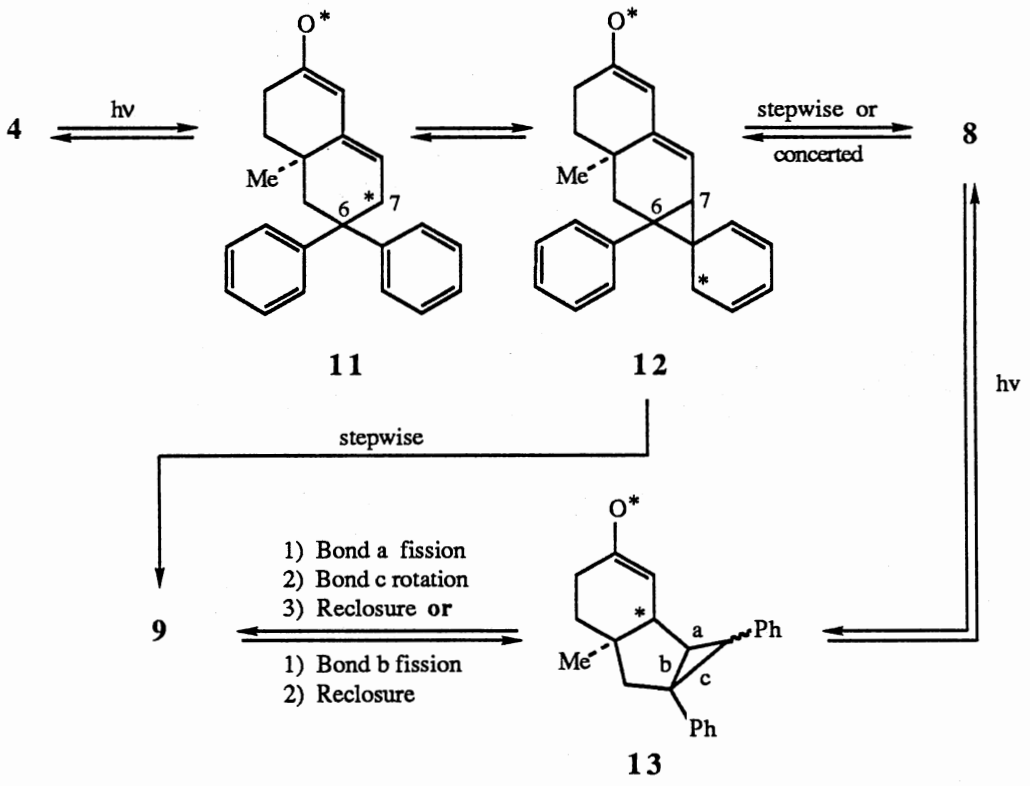
One further interesting observation was made regarding the stability of the photoproducts. Upon prolonged exposure of the product enone **8** to $CDCl_3$ (sealed NMR tube, 1 month, 0°C, no light), a quantitative reversion back to the starting dienone occurred. This was attributed to catalysis by traces of HCl normally found in



8 **4**

this NMR solvent.[152] A control experiment treating **8** with dilute HCl (0.4 mL of 1 *M* aqueous HCl) in THF (2 mL) further supported this hypothesis. The cis isomer **9**, while stable in $CDCl_3$, did react slowly under stronger acid conditions to give up to 20% of a single unidentified product (96-120 h).

Mechanistic and Interpretative Discussion. The photochemistry of **4** closely parallels that observed in the parent 4,4-diphenyl-2-cyclohexen-1-one.[1,2,9] Reaction via the triplet manifold is assumed based upon previous photochemical studies of cyclohexenones. Excitation of the dienone moiety followed by intersystem crossing to the triplet would give an intermediate analogous to that proposed for the simple enone (Figure 36). Bridging of the odd electron center at C-7 in **11** to a C-6 phenyl ring



[a] * = ·/· or +/-

Figure 36. Mechanistic Summary of the Photorearrangement of **4**[a]

followed by concerted rearomatization-three-ring formation would give the observed product **8**. The rigidity of the fused ring structure permits orbital alignment similar to that found in the parent system such that normal concerted phenyl migration may occur. An alternative mechanism[5-8] would involve stepwise rearomatization of the bridged intermediate **12** to give a phenyl-migrated diradical having an odd electron center at C-6. Closure of this species with minimization of phenyl-phenyl steric interference would then give the observed product **8**.

The presence of the angular methyl in substrate **4** introduces the possibility of products having a syn or anti relationship between the three-ring and this group. It was expected intuitively that the methyl would exert a steric effect favoring the formation of the anti product. Experimentally, this was found to be the case and only two products were observed from the reaction, even after extended irradiation times. Additionally, the methyl served to preclude complications resulting from aromatization and double bond migration.

The apparent induction period for initiation of the reaction (see Figure 34) can be attributed to the wavelength variation which occurs during lamp warm-up.[149] Repeating the reaction in the same apparatus fitted with a shutter permitted the lamp to attain full power prior to irradiation of the substrate. Under these conditions, products were produced immediately but the ratio of trans to cis at the earliest point of detection remained *ca.* 100:1. Thus, the question of whether the cis isomer is a primary photoproduct remains unresolved.

Though the present study has shown that the photochemistry of the dienone **4** bears considerable similarity to that of **1**, a difference is found in the composition of the photostationary mixture. While **1** shows a 43:57 trans:cis ratio in the photostationary state,[9,10] dienone **4** and photoproducts **8** and **9** all lead to approximately the same 76:23:1 mixture of trans:cis:dienone. Thus, the kinetic (trans) product is also the most stable product in this case. Reference to molecular models and to the X-ray data show

that there is no apparent steric bias favoring the trans over the cis stereochemistry in the final product. Thus, the preponderance of trans product likely reflects orbital overlap effects (concerted mechanism) or steric control in the phenyl-migrated diradical (stepwise mechanism).

The preference for production of the trans product at low conversions suggests that the current reaction closely approximates that observed for **1**. This seems reasonable since the skeletal rigidity of the system should permit orbital alignment comparable to that found in the parent system if the rearrangement is concerted. Additionally, if the stepwise mechanism is operating, steric interactions during the phenyl migration process would be roughly similar in both molecules. The 100:1 ratio of trans:cis products at low conversion compares well with the parent system and, in all probability, constitutes a lower limit considering the increased photolability of the γ-cyclopropyl enone products from **4** (relative to the less conjugated systems derived from **1**) and our inability to detect smaller amounts of the products at the initial stages of the reaction.

It seems reasonable that the mechanisms by which **8** and **9** interconvert also parallel those observed in the the parent compound **1**. These are summarized in Figure 36. Excitation and intersystem crossing of the enone chromophore to give **13** would be followed by fission of the external three-ring bond (bond a), rotation about bond c and reclosure to give the cis isomer. Alternatively, opening of the internal cyclopropyl bond (bond b) would generate an intermediate which could reclose to give either trans or cis. The minor pathway leading back to the starting dienone can be envisioned from the intermediate obtained from fission of the internal three-ring bond (bond b). Regeneration of the dienone would then occur with migration of the C-7 phenyl back to C-6 by a reversal of the bridging process.

Interestingly, the reaction proceeds normally despite the decreased energy requirements for excitation of **4**. Based on a simple comparison of the λ_{max} of the

$n \rightarrow \pi^*$ band in **1** and **4**, the dienone (λ_{max} ($n \rightarrow \pi^*$) = 345 nm) requires less energy for excitation than the simple enone (λ_{max} ($n \rightarrow \pi^*$) = 320 nm). Further extension of the π system might be expected to eventually afford a substrate reactive to light in the visible range. Recent studies by Zimmerman and Lamers,[8] however, have demonstrated that a linear trienone related to our system is photochemically inert.

Previous studies[2,38] have revealed significant solvent polarity effects in the photochemistry of 4,4-disubstituted cyclohexenones. For the parent case **1**, solvent polarity (benzene *vs. tert*-butanol) had little effect on the trans:cis ratio of the bicyclic products but the more polar *tert*-butanol gave a 16-fold increase in the production of phenyl-migrated enone (**3**) as well as an overall increase in quantum efficiency for the disappearance of the enone. These observations were attributed to a possible inversion of close-lying $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplets brought on by stabilization of the more polar $\pi \rightarrow \pi^*$ state by the alcohol solvent. In the current study, photolyses were run in both benzene and *tert*-butanol in an attempt to evaluate solvent effects in the extended system. As in the parent case, no significant change in trans:cis product ratio was observed; additionally, a phenyl-migrated enone **10** was not observed in either solvent.

The acid catalyzed conversion of the trans photoproduct to the starting dienone is the first case of such a reverse process.[153] This reaction presumably proceeds by protonation of the enone carbonyl by traces of HCl in the $CDCl_3$[152] to give the enol cyclopropylcarbinyl carbocation **14** followed by three-ring opening to give the phenyl-stabilized carbocation **15**. Regeneration of the dienone system with concomitant phenyl migration and loss of the proton would then regenerate **4** (Figure 37). This quantitative reversion of **8** back to **4** under mild acid conditions suggests that the current reaction represents a photoendothermic process where a considerable portion of the irradiating energy is stored in the carbon framework of the product.

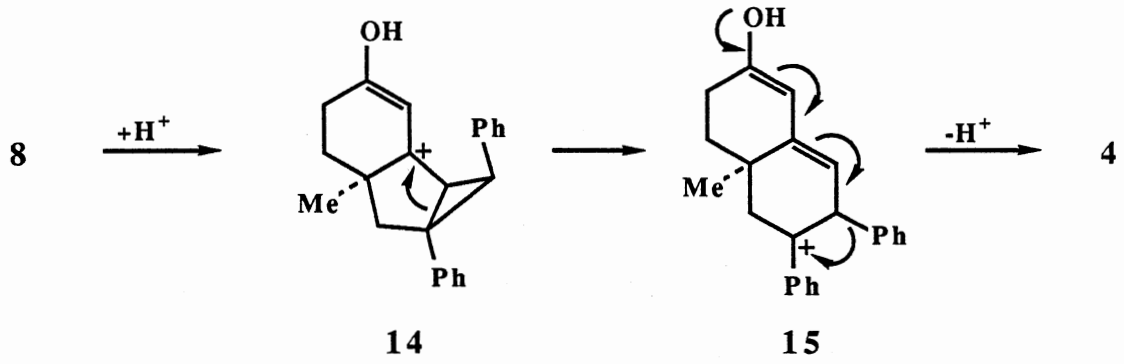


Figure 37. Acid-Catalyzed Conversion of **8** to **4**.

Experimental Section

Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded with a PE-681 instrument and are referenced to polystyrene. ^{1}H-NMR and ^{13}C-NMR were measured as solutions in $CDCl_3$ at 300 MHz and 75 MHz, respectively, on a Varian XL-300 superconducting FT instrument; chemical shifts are reported in δ units relative to internal Me_4Si. UV spectra were recorded in absolute ethanol using a Varian DMS-200 spectrophotometer. Mass spectra were recorded at 70 eV on a VG ZAB-2SE or a VG TS-250 instrument. Elemental analyses (± 0.4%) were performed by Galbraith Laboratories, Knoxville, TN. All reactions were run under an atmosphere of dry nitrogen. Solvents used in photochemical runs were purified in the following manner: *tert*-butanol was distilled from CaH_2; benzene was sequentially washed with concentrated H_2SO_4 (2x), 5% $KMnO_4$ in 10% aqueous H_2SO_4 (2x), and 10% aqueous KOH, then dried over anhydrous $MgSO_4$ and distilled from CaH_2.

All photochemical reactions were degassed with dry, oxygen-free nitrogen for 1 h prior to and during irradiation. Column chromatography was performed on silica gel (Grace, grade 62, 60-200 mesh) mixed with Sylvania 2282 phosphor and slurry packed

into Vycor columns such that band elution could be monitored with a hand-held UV lamp. Preparative thick layer chromatography (PTLC) was performed on Analtech (No. 02015) preparative silica gel uniplates with fluorescent indicator. Reactions were monitored and kinetic measurements were made on a capillary GC (Varian 3400) with FI detection on a 0.1 mm X 6 m SE-30 column programmed between 100-300°C.

6-Methyl-4,4-diphenyl-2-cyclohexen-1-one (5). The general procedure of Zimmerman[143] was used. To a 0°C solution of 8.9 g (45.4 mmol) of diphenylacetaldehyde and 6.7 g (79.8 mmol) of isopropenyl methyl ketone[154] in 70 mL of ether was added a 4.95-mL ethanol solution of 0.83 g (14.8 mmol) of potassium hydroxide dropwise during 45 min. The mixture was stirred at 23°C for 6 h, then poured onto ice and 25 mL of benzene was added to dissolve the yellow solid. The mixture was neutralized with 1M HCl to a pH of 7 and the aqueous layer was ether extracted. The organic extracts were combined, washed with saturated NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting pale yellow oil was crystallized from absolute ethanol to yield 7.67 g (29.0 mmol, 65%) of 6-methyl-4,4-diphenyl-2-cyclohexen-1-one as a white solid, mp. 96-98°C. The spectral data were: IR ($CHCl_3$) 3065, 1680, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.39-7.18 (cplx, 11 H), 6.20 (d, 1 H, J = 10.1 Hz), 2.65 (m, 1 H), 2.51 (m, 2 H), 1.15 (d, 3 H, J = 6.2 Hz); ^{13}C-NMR ($CDCl_3$) δ 201.7, 155.5, 148.1, 143.8, 129.0, 128.9, 128.8, 128.3, 128.0, 127.5, 127.3, 127.0, 50.3, 44.8, 38.7, 15.1; MS, *m/e* (%) 262 (M+, 26), 234 (18), 206 (100), 191 (24), 165 (14), 115 (17), 77 (10); HRMS, exact mass calcd for $C_{19}H_{18}O$ *m/e* 262.1357, found *m/e* 262.1358.

2-Methyl-4,4-diphenylcyclohexanone (6). The general procedure of Bordwell[146] was used. A 150 mL acetic acid solution of 11.8 g (45.0 mmol) of **5** containing 0.5 g of 10% Pd/C was shaken under 60 psi of H_2 in a Parr apparatus at 25°C for 8 h (H_2 uptake, 12 psi). The crude reaction mixture was filtered through Celite® and the solution was concentrated under vacuum. The residue was taken up in ether and the

solution was washed with $NaHCO_3$, water and saturated NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting pale yellow solid was recrystallized twice from absolute ethanol to yield 10.0 g (38.0 mmol, 84%) of 2-methyl-4,4-diphenyl-cyclohexanone as a white solid, 102-103°C, lit.[7] mp. 102-103°C. The spectal data were: IR ($CHCl_3$) 3095, 3060, 1720, 1600, 1500 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.51 (d, 2 H, J = 7.5 Hz), 7.41 (t, 2 H, J = 7.5 Hz), 7.33-7.12 (complex, 6 H), 2.95 (m, 2 H), 2.65-2.30 (complex, 4 H), 2.11 (t, 1 H, J = 13.4 Hz), 1.07 (d, 3 H, J = 6.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 212.5, 148.7, 143.5, 128.9, 128.7, 128.3, 127.3, 126.7, 126.5, 126.0, 46.4, 45.8, 41.5, 38.7, 37.3, 14.5; MS *m/e* (%) 264 (46), 207 (32), 193 (48), 180 (100), 165 (28), 115 (24), 91 (26); HRMS, exact mass calcd for $C_{19}H_{20}O$ *m/e* 264.1514, found *m/e* 264.1514.

4,4a,5,6,7,8-Hexahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (7). To a 60-mL benzene solution of 6.0 g (23.0 mmol) of **6** was added 10 mL of a 2.37 *M* solution of potassium *tert*-butoxide (23.7 mmol). The mixture was stirred for 1 h and 3.22 g (3.82 mL, 46 mmol) of methyl vinyl ketone was added dropwise. The reaction was stirred for 48 h at 23°C then diluted with ether, washed with saturated NH_4Cl, water and saturated NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The dark brown viscous oil was purified by column chromatography on an 80 cm x 2.5 cm slurry packed silica gel column eluted with increasing concentrations of ether in hexane. The compounds eluted as follows: 2% ether in hexane, 1.97 g (7.46 mmol, 32.4%) of **6**; 7.5 % ether in hexane, 2.18 g (6.90 mmol, 30%) of 4,4a,5,6,7,8-hexahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**7**) as a white solid, mp. 179-180°C. The spectral data for **7** were: IR ($CHCl_3$) 3060, 2840, 1670, 1625, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.44 (d, 2 H, J = 7.5 Hz), 7.32 (t, 2 H, J = 7.5 Hz), 7.21 (m, 6 H), 5.77 (s, 1 H), 3.01-2.78 (cplx, 3 H), 2.49-2.22 (cplx, 4 H), 1.88 (m, 3 H), 0.70 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 199.4, 169.8, 150.5, 144.9, 128.4, 128.2, 127.3, 125.9, 125.7, 125.6, 123.8, 50.3, 45.0, 38.9, 36.8, 36.7, 33.5,

30.3, 23.5; UV (abs. EtOH) λ_{max} (ε) 327 (50.3), 227 (20353) 208 (20174); MS, *m/e* (%) 316 (81), 225 (21), 193 (56), 184 (47), 180 (100), 165 (36), 115 (33), 91 (53), 77 (23); HRMS, exact mass calcd for $C_{23}H_{24}O$ *m/e* 316.1827, found *m/e* 316.1827. Anal. Calcd for $C_{23}H_{24}O$: C, 86.66; H, 7.59. Found: C, 86.98; H, 7.79.

4,4a,5,6-Tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (4). The procedure of Agnello and Laubach[147] was used. A stirred mixture of 0.20 g (0.63 mmol) of **7** and 0.90 g (3.67 mmol) of chloranil in 20 mL of *tert*-butanol was heated at reflux for 3 h. The crude reaction was filtered and concentrated *in vacuo*. The residue was dissolved in chloroform and washed with water (3x), 5% NaOH (1x), washed again with water until reappearance of yellow color, saturated NaCl, then dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was separated on a 20 cm x 20 cm PTLC plate eluted with 20% ether in hexane (6x). The fastest eluting band yielded 0.1 g (0.32 mmol, 50%) of 4,4a,5,6-tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (**4**) as a white solid, mp. 147-149°C. The slower eluting band yielded 0.03 g (0.09 mmol, 15%) of **7**, recovered starting material. The spectral data were: IR ($CHCl_3$) 1660, 1630, 1610, 1500 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.44-7.34 (cplx, 4H), 7.25 (m, 3H), 7.14 (m, 3H), 6.67 (d, 1H, J = 10.8 Hz), 6.43 (d, 1H, J = 10.8 Hz), 5.81 (s, 1H), 2.69 (A of ABd, 1H, J = 13.9 Hz), 2.57 (m, 1H), 2.45 (m, 1H), 2.38 (B of ABd, 1H, J = 13.9 Hz), 2.01-1.80 (cplx, 2H), 0.78 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 199.6, 161.1, 148.8, 145.7, 143.3, 128.4, 128.3, 128.0, 127.2, 126.9, 126.5, 126.3, 124.1, 49.0, 48.9, 37.5, 34.3, 33.8, 23.6; UV (abs. EtOH) λ_{max} (ε) 337 (500), 287 (24199) 209 (19068); MS, *m/e* (%) 314 (100), 299 (8), 286 (17), 257 (19), 243 (23), 210 (20), 195 (19), 165 (27), 115 (15), 91 (22), 77 (10); HRMS, exact mass calcd for $C_{23}H_{22}O$ *m/e* 314.1670, found *m/e* 314.1670. Anal. Calcd for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 88.09; H, 7.16.

Exploratory Direct Photolysis of 4,4a,5,6-Tetrahydro-4a-methyl-6,6-diphenyl-2(3*H*)-naphthalenone (4).

A. In *tert*-Butanol: The general procedure described by Zimmerman[1] for the photolysis of 4,4-diphenyl-2-cyclohexenone was followed. A solution of 100 mg (0.32 mmol) of **4** in 320 mL of degassed *tert*-butanol in a Kreil flask (Ace no. 6963) was irradiated through Pyrex using a 450-W medium pressure Hanovia immersion apparatus. The rearrangement was followed by GC and the source was turned off at *ca.* 98% conversion, concentrated under vacuum and purified on a 20 cm x 20 cm silica gel PTLC plate eluted with 8% ether in hexane (10x). The fastest moving of three bands yielded 70 mg (0.22 mmol, 69.7%) of (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenylcycloprop[*a*]-inden-3(1*H*)-one (**8**) as a white solid. Recrystallization from $CHCl_3$/ether/hexane afforded an analytical sample: mp. 133-134°C; IR ($CHCl_3$) 3060, 2865, 2830, 1658, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.39 (m, 4 H), 7.33-7.20 (complex, 6 H), 6.08 (s, 1 H), 3.18 (A of ABd, 1 H, J = 9.6 Hz), 2.89 (B of ABd, 1 H, J = 9.6 Hz), 2.39 (ddd, 1 H, J = 19.0, 13.6, 5.6 Hz), 2.17 (dd, 1 H, 19.0, 5.6 Hz), 2.11 (A of ABd, 1 H, J = 13.2 Hz), 1.92 (B of ABd, 1 H, J = 13.2 Hz), 1.50 (dd, 1 H, J = 12.9, 5.6 Hz), 1.33 (s, 3 H), 0.98 (dt, 1 H, J = 13.2, 5.6 Hz); ^{13}C-NMR ($CDCl_3$) δ 198.6 (C), 176.8 (C), 144.1 (C), 135.1 (C), 131.1 (CH), 128.7 (CH), 128.4 (CH), 127.0 (CH), 126.8 (CH), 126.5 (CH), 124.2 (CH), 124.2 (CH), 49.8 (C), 44.1 (CH_2), 43.0 (C), 40.7 (CH), 36.4 (CH), 33.6 (CH_2), 31.8 (CH_2), 27.8 (CH_3); UV (abs. EtOH) λ_{max} (ε) 325 (549), 258 (14381) 207 (20881); MS, *m/e* (%) 314 (M^+, 100), 257 (19), 195 (27), 165 (33), 91 (31); HRMS, exact mass calcd for $C_{23}H_{22}O$ *m/e* 314.1670, found *m/e* 314.1671. Anal. Calcd for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 87.72; H, 7.13.

The second band yielded 12 mg (0.04 mmol, 11.9%) of (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenylcycloprop[*a*]inden-3(1*H*)-one (**9**) as a white solid. Recrystallization from $CHCl_3$/ether/hexane afforded an analytical sample: mp. 212-214°C; IR ($CHCl_3$) 1660, 1605, 1500 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.25-7.00 (complex, 8H), 6.79 (dd, 2 H, J = 7.8, 2.1 Hz), 6.02 (s, 1 H), 3.06 (d, 1 H, J = 3.4

Hz), 2.56 (m, 1 H), 2.43 (m, 1 H), 2.32 (A of ABd, 1 H, J = 12.8 Hz), 2.31 (d, 1 H, J = 3.4 Hz), 2.12 (B of ABd, 1 H, J = 12.8 Hz), 1.97 (m, 2 H), 1.39 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 198.9 (C), 178.2 (C), 138.8 (C), 137.1 (C), 129.3 (CH), 128.3 (CH), 127.8 (CH), 127.4 (CH), 126.6 (CH), 126.0 (CH), 122.0 (CH), 53.3 (CH_2), 48.9 (C), 46.5 (CH), 45.6 (C), 36.9 (CH), 34.7 (CH_2), 33.8 (CH_2), 26.9 (CH_3); UV (abs. EtOH) λ_{max} (ε) 325 (463), 260 (7991) 203 (12898); MS, *m/e* (%) 314 (100), 286 (18), 258 (23), 243 (30), 203 (38), 167 (41), 115 (22), 91 (36), 77(13); HRMS, exact mass calcd for $C_{23}H_{22}O$ *m/e* 314.1670, found *m/e* 314.1670. Anal. Calcd for $C_{23}H_{22}O$: C, 87.90; H, 7.01. Found: C, 87.69; H, 6.97.

A third band, overlapping with **9**, proved to be unreacted starting material.

B. In Benzene: A solution of 100 mg (0.32 mmol) of **4** in 320 mL degassed purified benzene was photolyzed using conditions identical to those described above. After 3.5 min, there was observed a 36.0:0.40:63.6 ratio of **8**:**9**:**4**, which corresponded to a *ca.* 90:1 ratio of **8**:**9**. After 11 min a photostationary state was reached having a 75:24:1 ratio of **8**:**9**:**4**. The products:reactant ratios were all within 10% of those observed in the photolysis reaction of **4** in *tert*-butanol.

Single Crystal X-ray Structure Determination of (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenyl-cycloprop[*a*]-inden-3(1*H*)-one (8). A crystal of **8** was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table 4) were determined by least squares refinement of the best angular positions for 15 independent reflections (2θ > 15°) during normal alignment procedures using molybdenum radiation (λ = 0.71069Å). Data (3096 independent points after removal of space group forbidden and redundant data) were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every

97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. Observed reflections [2265, $I > 3.0\sigma(I)$] were used for solution of carbon and oxygen positions of the structure by direct methods using SHELX86.[155] Refinement[131] of scale factor, positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. The positions of the hydrogen atoms were located from a difference Fourier synthesis and were included (with hydrogen positional and thermal parameters fixed) in the final cycles of refinement [function minimized, $\Sigma(|F_o|-|F_c|)^2$] leading to a final agreement factor, R = 6.1% [$R = (\Sigma| |F_o| - |F_c| | / \Sigma|F_o|) \times 100$]. Scattering factors were taken from Cromer and Mann.[132] In the final stages of refinement, a weight of $1/\sigma(F)^2$ was used. $R_w = 7.7\%$.

The unit cell contains two molecules of the trans isomer which display enantiomeric chiralities at C-1, C-2, C-3 and C-5 but which are packed in the accentric cell in a manner which does not involve a crystallographic symmetry element. Appendix B, Tables 13-16 lists bonds angles and distances, positional parameters, and final anisotropic thermal parameters for **8**.

Single Crystal X-Ray Structure Determination of (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-hexahydro-5a-methyl-1,6a-diphenyl-cycloprop[*a*]inden-3(1*H*)-one (9). A crystal of **9** was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table 4) were determined by least squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$Å). Data (2237 independent points after removal of space group forbidden and redundant data) were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured every 97

TABLE 4

CRYSTAL DATA FOR **8** and **9**

	8 (trans)	**9** (cis)
formula	$C_{23}H_{22}O$	$C_{23}H_{22}O$
MWT	314.2	314.2
a, Å	9.194(3)	12.639(5)
b, Å	10.567(6)	5.680(2)
c, Å	9.867(5)	23.835(8)
α, deg	106.74(4)	90.0
β, deg	101.68(3)	90.25(3)
γ, deg	99.56(4)	90.0
V, Å^3	872.8(7)	1711.0(10)
F(000)	336	672
μ(MoKα), cm^{-1}	0.663	0.677
λ(MoKα), Å	0.71069	0.71069
D_{calcd}, g cm^{-3}	1.196	1.220
Z	2	4
obsd refl	2265	1367
R/R_w, %	6.1/7.7	5.5/7.2
space group	P1	$P2_1/c$
goodness of fit	0.38	0.33

reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. Observed reflections [1367, $I > 3.0\sigma(I)$] were used for solution of carbon and oxygen positions of the structure by direct methods using MULTAN80.[130] Refinement[131] of scale factor, positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. The positions of all hydrogen atoms, except those associated with the methyl group (C-11), were calculated and included (with hydrogen and positional and thermal parameters held fixed) in three cycles of least squares refinement. A difference Fourier synthesis then allowed location of the three hydrogens of C-11. All hydrogen parameters were included but constrained in the final cycle of refinement [function minimized, $\Sigma(|F_o| - |F_c|)^2$] leading to a final agreement factor, R = 5.5% [$R = (\Sigma| |F_o| - |F_c| | / \Sigma|F_o|) \times 100$]. Scattering factors were taken from Cromer and Mann.[132] In the final stages of refinement, a weight of $1/\sigma(F)^2$ was used. $R_w = 7.2\%$. Appendix B, Tables 17-19 lists bond angles and distances, positional parameters, and final anisotropic thermal parameters for **9**.

Reaction Profiles. Solutions of 100 mg (0.32 mmol) of **4** in 320 mL of *tert*-butanol, 50 mg (0.15 mmol) of **8** in 160 mL of *tert*-butanol and 50 mg (0.15 mmol) of **9** in 160 mL of *tert*-butanol were irradiated as before in the Hanovia apparatus. The reactions were monitored by GC analysis of 0.2 mL aliquots removed by syringe from the reaction mixture. Compound **4** was irradiated at 0.5-min intervals for the first 6 min and at 1-min intervals thereafter for a total time of 20 min. Compounds **8** and **9** were irradiated at 5-min intervals for the first 40 min and at 40-min intervals thereafter for a total time of 6 h. The samples were injected onto a 0.25 mm X 6 m SE-30 column, temperature programmed between 150-300°C; the individual compounds were found to be stable to these thermal conditions. Peak areas were determined from electronic integration of the peaks relative to internal benzophenone standard.

Control Experiment. Photostability of the Photoproducts. In a typical control run, 0.29 mmol of the photoproduct was photolyzed as a 0.001 *M* solution in *tert*-butanol using conditions identical to those described for the exploratory irradiations. The reactions were monitored by GC as above; the individual compounds were found to be stable to these thermal conditions. After 30 min, compound **8** had reached a photostationary state having a 76:23:1 ratio of **8**:**9**:**4** which remained unchanged even after 6 h. Irradiation of **9** yielded a 76:24 ratio of **8**:**9** after 30 min with no formation of **4**; this ratio remained constant after 6 h.

Acid-Catalyzed Reactions of the Photoproducts. A sealed sample of **8** (25 mg, 0.08 mmol) dissolved in 0.75 mL $CDCl_3$ for 1 month in the dark was transformed to **4** in quantitative yield. A sealed sample of **9** (25 mg, 0.08 mmol) dissolved in 0.75 mL of $CDCl_3$ for 1 month in the dark was found to be stable under these conditions. In a typical control run, 10 mg (0.03 mmol) samples of **8** and **9** were treated with 2 mL of THF containing 0.4 mL of 1.0 *M* HCl and allowed to stir at 23°C in the dark under N_2. After 2 d, **8** had undergone 80% conversion (by GC) back to **4**. After 4 d, **9** had undergone 20% conversion (by GC) to an unidentified compound; this conversion was not increased upon extended reaction.

Wavelength Dependency Experiments. The photoreaction of **4** was run in *tert*-butanol using the following filter solutions: A: 0.1 *M* $NaVO_3$ in 5% NaOH (cutoff 335 nm); B: 0.1 *M* $BiCl_3$ in 2.0 *M* HCl (cutoff 366 nm); and C: 0.15 *M* $FeCl_3$ in 1.0 *M* HCl (cutoff 445 nm). The reactions using the filter solutions were monitored by GC as above. The reaction using filter solution A was followed by removing aliquots at 0.5-min intervals for the first 6 min and at 1-min intervals for a total time of 20 min. The cis photoproduct was not observed until 38% conversion of **4**, where 0.39% of the cis isomer was detected. This corresponds to a *ca.* 100:1 ratio of **8**:**9**. After 11 min, there was obtained a 76:23:1 equilibrium ratio of **8**:**9**:**4**. The reaction using filter solution B was followed by removing aliquots at 1-min intervals for the first 10 min, 2-min intervals

for the next 30 min, and 4-min intervals for an additional 80 min. The earliest detected ratio (49% conversion) of **8**:**9**:**4** was 48.7:0.3:51 which corresponds to an **8**:**9** ratio of *ca.* 160:1. Extended irradiation of **4** resulted in a photostationary mixture composed of a 79:20:1 ratio of **8**:**9**:**4**. No reaction was seen using filter solution C, even after a 6 h photolysis time.

Irradiation using a Rayonet Reactor. The photochemical reaction of **4** (80 mg, 0.25 mmol) in 260 mL *tert*-butanol was run in a 500-mL Pyrex round bottom flask using a Rayonet reactor (254 nm lamps). The reaction was monitored by GC as above and aliquots were removed at 2-min intervals for the first 20 min and at 4-min intervals thereafter for a total time of 2 h. After 24 min, a 73.0:0.4:26.6 ratio of **8**:**9**:**4** was detected. This corresponds to *ca.* 180:1 ratio of **8**:**9.** At 95% conversion, there was observed an 88:5 ratio of **8**:**9** with 2% of an unknown product. After photolyzing 92 min there was observed a 73:24:1 ratio of **8**:**9**:**4** with 2% of an unknown product.

Irradiation using a Shutter. A solution of 50 mg (0.15 mmol) of **4** in 160 mL of *tert*-butanol was irradiated using a Hanovia apparatus fitted with an opaque cylindrical shutter between the Pyrex filter and the immersion well cooling jacket. The shutter fit snugly into a multilayered piece of aluminum foil which prevented light from passing out the bottom of the well. The lamp was turned on for 3 min. with the shutter in place to enable the lamp to warm up. Once the source was at full power, the shutter was removed and the solution was photolyzed as before. The reaction was monitored by GC; aliquots were taken at 0.5-min intervals for the first 6 min and at 1.0-min intervals thereafter, for a total photolysis time of 20 min. The earliest detected ratio of products and reactant was seen after 1 min. There was observed a 39.6:0.4:60.0 ratio of **8**:**9**:**4**, which corresponds to *ca.* 100:1 ratio of **8**:**9**. Though the production of **9** appeared to be somewhat slower, the previously encountered photostationary state of 76:23:1 (**8**:**9**:**4**) was reached after 10 min.

Light Intensity Experiment. The photochemical reaction of **4** (40 mg, 0.13 mmol) in 130 mL *tert*-butanol was run in a 250-mL Pyrex flask positioned 40 cm from the Pyrex-filtered 450-W light source. The reaction was monitored by GC, aliquots were removed at 1-min intervals for the first 40 min and at 3-min intervals for an additional 80 min. The earliest detected ratio, 36.0:0.4:63.6 of **8**:**9**:**4** occurred after 20 min. This corresponds to *ca.* 100:1 ratio. Upon extended irradiation (2 h), the equilibrium (**8**:**9**:**4**) ratio of 76:23:1 was observed.

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CHAPTER IV

THE PHOTOCHEMISTRY OF *CIS*-4,4-DI-PHENYL-2-CYCLOHEPTEN-1-ONE

Introduction

The photochemical γ to β aryl rearrangement of 4,4-diphenyl-2-cyclohexen-1-one (**1**) to give the bicyclo[3.1.0]hexanones, (**2**) and (**3**), and the 3,4-diphenyl enone (**4**) has been of considerable interest (Figure 38).[1,2,9-11] The general scope of this aryl rearrangement reaction has been presented in the photochemical studies of 4-aryl substituted cyclohexenones,[3-7,14-16,39-41] aryl-substituted 2,4-cyclohexadienones,[8,114] as well as 4-aryl substituted cyclopentenones.[42-45] In view of the generality of the reaction in five and six-ring systems, the photochemistry of *cis*-4,4-diphenyl-2-cyclohepten-1-one (**11**) was investigated to determine if comparable photochemistry would occur in a seven-ring system.

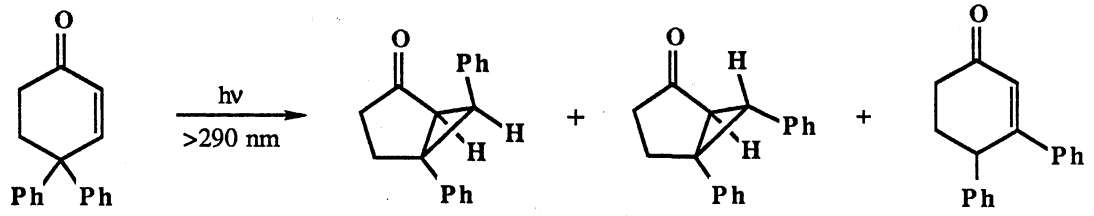


Figure 38. Photochemistry of 4,4-Diphenyl-2-cyclohexen-1-one (**1**).

Earlier photochemical studies of medium (7-9) ring α,β-enones have focused on unsubstituted systems, in an attempt to determine if photochemical [2+2] cycloadditions would occur.[46-49,53,156,157] It has been reported that in these α,β-enone systems, photochemical [2+2] reaction is not observed but instead cis-trans photoisomerization occurs to generate the ground state trans enone. These highly reactive species then undergo thermal [2+2] cycloadditions to generate head-to-head and head-to-tail dimers. In these unsubstituted systems, the intermolecular photoreaction (photochemical [2+2]) could not compete with the intramolecular photochemical process (cis-trans isomerization). In our substrate, however, the phenyls are positioned such that two intramolecular photochemical processes are possible, aryl migration and cis-trans isomerization. It was, therefore, initially expected that some aryl migration would occur. If aryl migration occurred, stable cis and trans diphenylbicyclo[4.1.0]heptanones would result. The trans diphenyl [3.1.0] system, which is generally reported in aryl migration reactions as the kinetically preferred product, may however, not predominate in the seven-ring system.[1-8,14-16] Preference for the trans isomer has previously been attributed to a concerted reaction pathway governed by orbital overlap.[1,2,16] In the larger cyclic enone, the more flexible ring may enforce poor alignment of the reactive orbitals and, thus, inhibit the concerted process and trans isomer formation.

Furthermore, we hoped this study would reveal additional information regarding the nature of the reactive excited state species for cyclic enones. It has recently been proposed that photochemical rearrangements of cyclic enones involve the intermediacy of a twisted enone triplet.[13,30-32,56,57] The planar enone triplet generated by initial photoexcitation and intersystem crossing, undergoes twisting to give a relaxed triplet species. If this proposed triplet is, in fact, the reactive intermediate, the larger ring system, which should readily accommodate excited state twisting, should exhibit some enhanced reactivity.

Results

Synthesis of the Photoreactant. The synthesis of *cis*-4,4-diphenyl-2-cyclohepten-1-one (**11**) is illustrated in Figure 39. The diphenyl enone **5** was prepared according to the synthesis of Zimmerman and coworkers.[143] Hydrogenation of **5** afforded the known cyclohexanone **6** in 95% yield.[146] Ring expansion of **6** by reaction with diazomethane gave 4,4-diphenylcyclohepten-1-one (**7**) in 58% yield along with 20% of the epoxide **8**.[158] Bromination of **7** (LDA, Br_2/CH_2Cl_2, -78°C) generated both the α- and α'-bromo regioisomers **9** and **10**.[159] Dehydrobromination of the mixture by reaction with LiBr and Li_2CO_3 in refluxing dimethylformamide then afforded the isomeric diphenyl enones **11** and **12**. Chromatography of the mixture on silica gel, yielded pure samples of both the desired starting material **11** and the 5,5-diphenyl enone **12** in 20% and 34% yield, respectively. The isomeric enones **11** and **12** were easily differentiated by ^1H NMR. In particular, the C-3 alkene proton was observed as a doublet of triplets (coupled to both the C-2 alkene proton and the C-4 protons) in **12**, while in **11** this proton corresponded to a doublet (coupled to only the C-2 alkene proton).

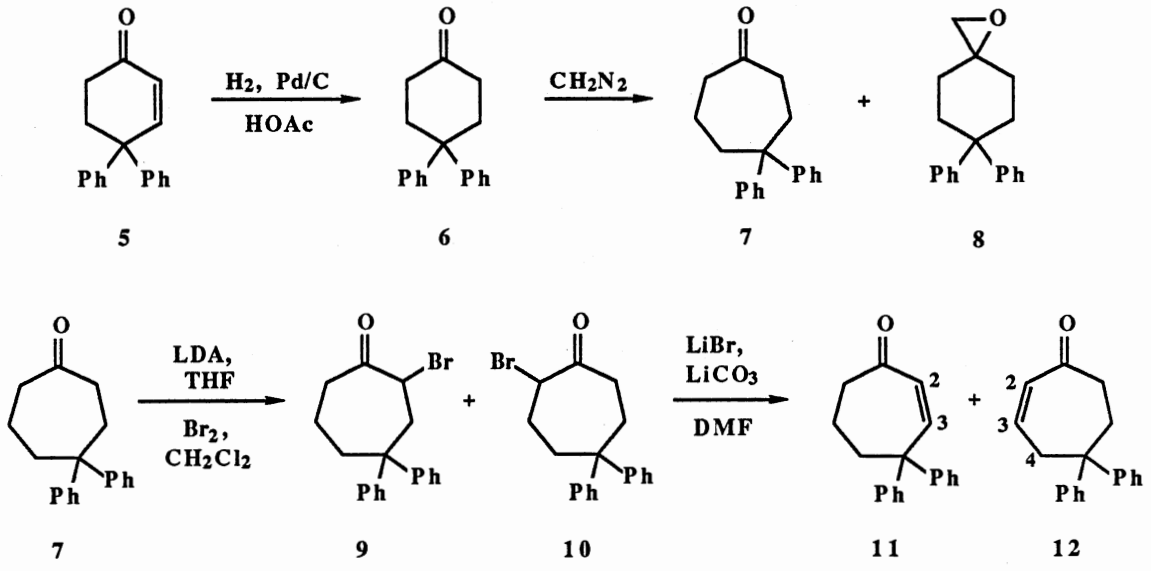


Figure 39. Synthesis of Photochemical Substrate

Despite the low yield obtained from the bromination-dehydrobromination sequence, this method proved superior to both selenation- and sulfonylation-elimination reactions for introduction of the C-2-C-3 double bond to **7**.[160-162] These other methods should, however, be noted for the anomalous yet interesting results that were observed. The selenation-elimination sequence is illustrated in Figure 40. Selenation of the seven-ring ketone **7** with phenyl selenenyl bromide afforded, after chromatography, the α- and α'-selenides **13** and **14** in 34% and 0.24% yield, respectively.[160] Surprisingly, oxidation-elimination of the α-selenide **13** with 30% H_2O_2 in pyridine lead to the 5,5-diphenyl enone **12**.[160] Only trace amounts of the expected enone **11** were produced from the reaction. In addition, oxidation-elimination of the α'-selenide **14** also generated the 5,5-diphenyl enone **12**. The unexpected result observed in the selenoxide elimination of **13** can be rationalized by a 1,3-phenylseleno migration prior to elimination. Base-catalyzed 1,3-sigmatropic rearrangements of the phenylseleno group have been reported for various α-alkylated-α-phenylselenoketones.[163,164] It has been observed that steric

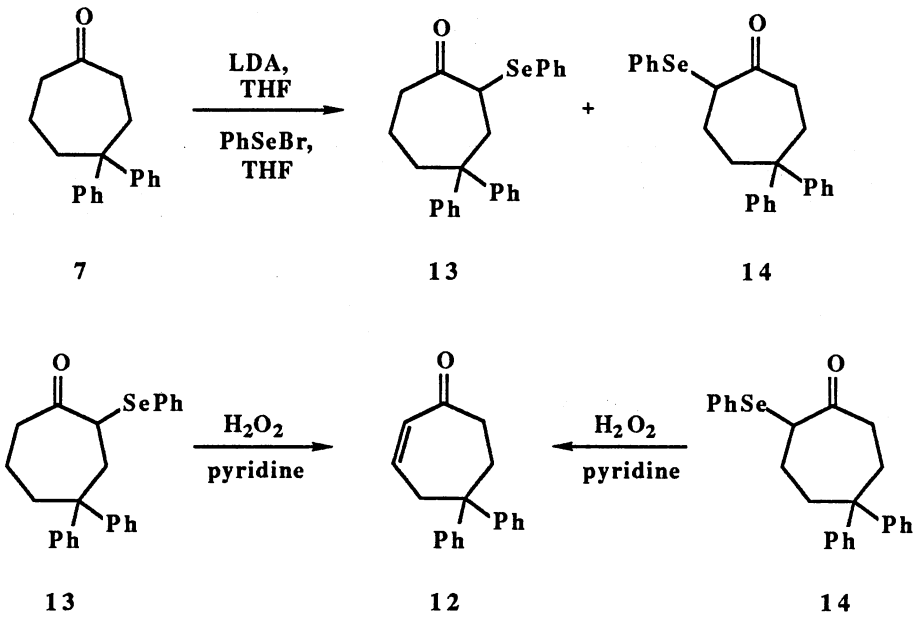


Figure 40. Phenylselenation-Elimination Sequence for **7**

crowding at or around the α-phenylseleno group accelerates the α to α' rearrangement.[163,164] An alternate suggestion[163,164] that the 1,3-migration is driven by the production of a more stabilized enolate seems less probable in the current reaction.

The sulfenylation-elimination sequence is depicted in Figure 41. Reaction of the lithium enolate of **7** with diphenyl disulfide generated the α'- and α-phenylsulfenyl ketones **15** and **16**.[161,162] Isolation of the minor phenylsulfenyl product **15**, followed by oxidation with MCPBA, yielded the sulfoxide **17**.[161,162] Thermolysis of **17** in toluene afforded only 17% of the desired enone **11** with the α-phenylsulfenylide **15** being produced in 77% (GC yield).[161,162] This apparent reduction of the phenylsulfoxide substituent, though of little utility, has not previously been reported.

Some comment is necessary concerning the regioselectivity of addition to the lithium enolates derived from **7**, by bromine, diphenyl disulfide, and phenylselenenyl bromide. Preferential reaction occurs at C-2 using phenylselenenyl bromide while

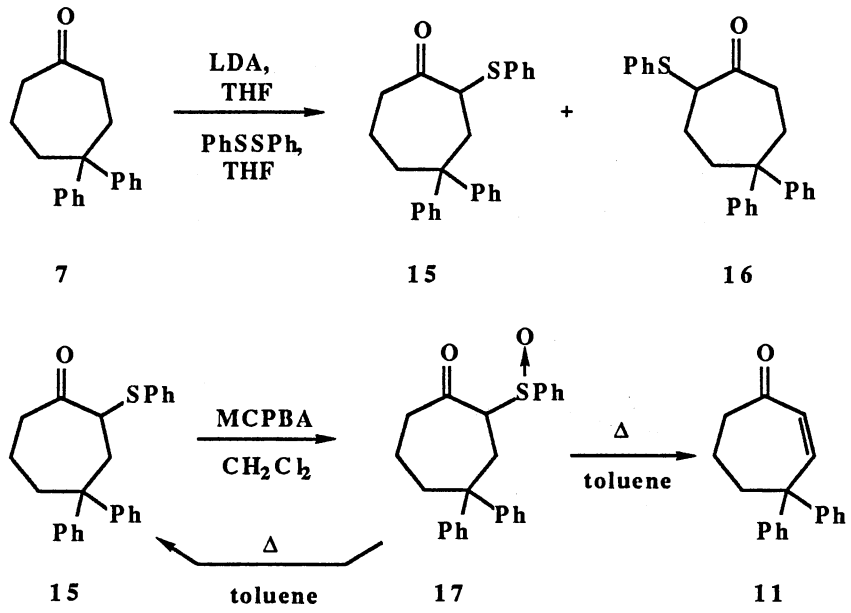


Figure 41. Phenylsulfinylation-Elimination of **7**.

substitution occurs preferentially to the C-7 enolate using bromine and diphenyl disulfide. This suggests that enolization toward C-2 is kinetically preferred since phenylselenenyl bromide is expected to be the better electrophile and should, thus, react faster than the other reagents. This preference is most intriguing and not well understood.

Exploratory Photochemistry and Structure Elucidation of the Products. The photochemical reactions were carried out using conditions comparable to those reported for 4,4-diphenyl-2-cyclohexen-1-one.[1] Irradiation of a 10^{-3} M solution of **11** in degassed *tert*-butanol through a Pyrex filter using a 450-W medium pressure Hanovia immersion apparatus led to a rapid disappearance of **11** (~30 min, monitored by TLC) and formation of two products, **18** and **19**. The products, **18** (35%) and **19** (15%) were isolated and purified by preparative thin layer chromatography on silica gel. Both products were stable to silica gel as indicated by ^{1}H NMR taken before and after the separation. The long retention times and lack of resolution on the GC programmed from 150-300°C suggested that both products were high molecular weight compounds. This was confirmed by MS, which indicated that both products were isomeric dimers of **11**. The NMR, IR and UV also supported dimeric product structures. The ^{1}H and ^{13}C NMR spectra for the major dimer **18** exhibited peak broadening and was, therefore, subjected to low temperature NMR experiments. The NMR spectra was not resolved at low temperature (-40°C) but did resolve at +50°C. Both ^{1}H and ^{13}C NMR (+50°) indicated a high degree of symmetry in the structure. The ^{1}H NMR indicated only seven different aliphatic proton signals, six of these signals corresponding to two protons each (12 total) with the farthest upfield signal corresponding to four protons. The ^{13}C NMR showed only six aliphatic signals.

The ^{1}H and ^{13}C NMR spectra (+23°C) for **19** were very similar to the high temperature spectra obtained for **18**. The ^{1}H NMR showed seven aliphatic proton signals and the ^{13}C NMR showed six aliphatic resonances. Although, the NMR spectra

for **19** did not exhibit peak broadening, high temperature NMR's were obtained for comparative purposes. The NMR's for **19** taken at 40°C were nearly identical to the room temperature spectra.

It was initially realized that from **11**, there were a total of twelve cyclobutane (head-to-tail and head-to-head) dimers possible. Based on steric arguments and symmetry considerations six of these dimers could be excluded as possibilities. Molecular models suggested that the large steric interactions between the two C-4 diphenyl substituents would preclude the formation of the head-to-head and head-to-tail dimers with cis-syn-cis geometry about the cyclobutane ring. In addition, the unsymmetrical head-to-tail and head-to-head trans-anti-cis and trans-syn-cis dimers would be eliminated as possible structures for **18** and **19**, since these dimers would show twelve aliphatic carbon signals in the ^{13}C NMR versus the six that were observed. Therefore, six total head-to-tail and head-to-head (trans-anti-trans and cis-anti-cis and trans-syn-trans) dimers were reasonable possibilities for **18** and **19**. Although, shift reagent studies would provide additional information regarding the stereochemistry about the cyclobutane ring (due to the syn and anti orientation of the carbonyls with respect to the cyclobutane protons), the regiochemistry (head-to-head or head-to-tail) was not apparent. Therefore, it was necessary to submit both isomers **18** and **19** for X-ray structure determination. The single crystal X-ray analysis revealed the structure of **18** to be (5aβ,5bβ,10aα,10bα)-dodecahydro-5,5,6,6-tetraphenylcyclobuta[1,2:3,4]dicyclo-heptene-1,10-dione and **19** to be (±)-(5aβ,5bα,10aβ,10bα)-dodecahydro-5,5,6,6-tetraphenylcyclobuta[1,2:3,4]dicycloheptene-1,10-dione. The 3-D drawings clearly illustrate the stereochemistry about the cyclobutane ring to be trans-syn-trans for **18** and trans-anti-trans for **19** (Figures 42 and 43). Interesting structural features were noted in the X-ray analysis. In particular, the C-5a-C-5b cyclobutane bond is increased from 1.58 Å in **19** to 1.61Å in **18** and the C-5-C-5a-C-5b angle is opened up from 127.4° in **19** to 140.4° in **18**. These differences are understandable since the phenyl-phenyl steric

interactions of the syn-oriented phenyl groups in **19** may be relieved by opening the angle and lengthening the bond between these substituents.

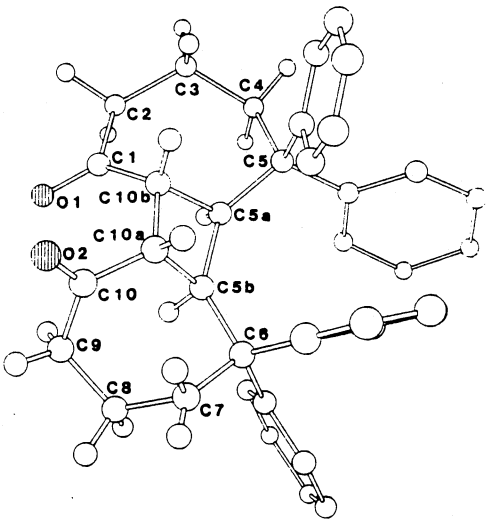


Figure 42. 3-D Drawing of the Trans-Syn-Trans Head-to-Head Dimer **18**. The 3-D Drawing Lacks the Thermal Ellipsoids Illustrated in the ORTEP Drawing.

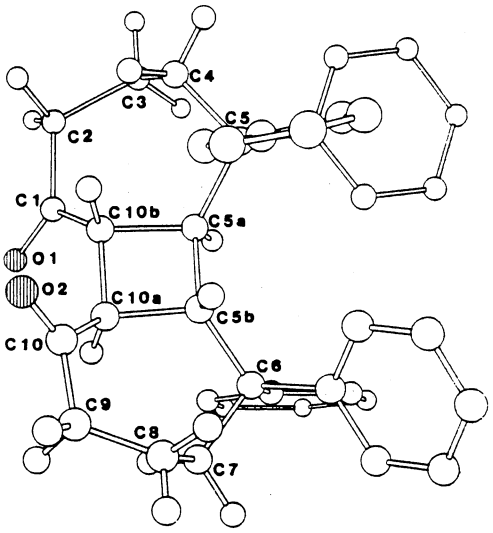
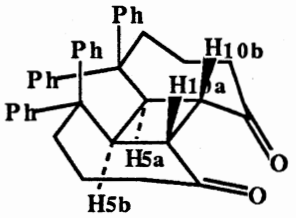
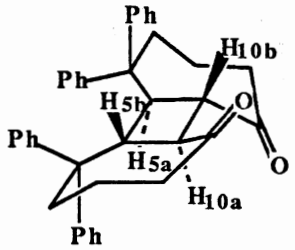


Figure 43. 3-D Drawing of the Trans-Anti-Trans Head-to-Head Dimer **19**. The 3-D Drawing Lacks the Thermal Ellipsoids Illustrated in the ORTEP Drawing.

It is interesting to note the results of the proton NMR shift reagent experiments which were found to be consistent with the stereochemistry observed from X-ray analysis.[165] In the trans-syn-trans system **18**, the syn-oriented carbonyl substituents are in a syn arrangement with the β-cyclobutyl protons (H-5a and H-5b) and in an anti arrangement with the α-cyclobutyl protons (H-10a and H-10b). Therefore, upon complexation of the carbonyl groups with shift reagent, assuming distance-dependent correlations, the β-cyclobutyl proton signal should exhibit a larger chemical shift than the α-cyclobutyl proton signal.[117-119,166] The magnitude of the β-cyclobutyl proton shift should be relatively small since the syn carbonyls are directed away from these protons. With increasing concentrations of shift reagent, the α-cyclobutyl protons, assigned to the farthest downfield aliphatic signal, and the β-cyclobutyl proton signal should move closer and closer together. The results of the shift reagent experiment are given in Figure 44 and Table 5. The slopes obtained from the response curve (Figure 44) for **19** showed the β-cyclobutyl protons to be shifted farther than the α-cyclobutyl protons.[118,119] The response curve also shows the decrease in separation for these signals with added shift reagent.



18

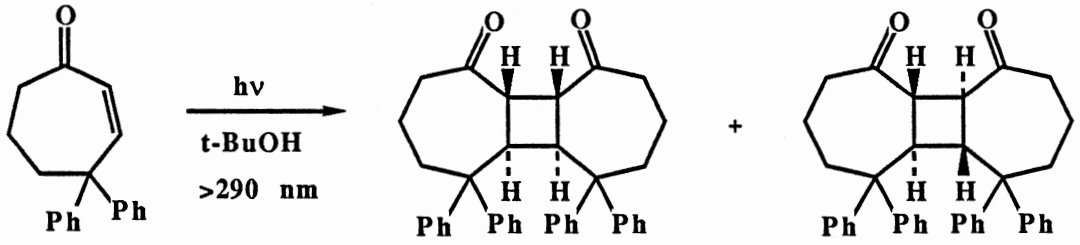


19

In the trans-anti-trans system **19**, both the α- and β-cyclobutyl protons (H-10a and H-10b and H-5a and H-5b) are in a syn arrangement with one anti-oriented carbonyl

group. The α-cyclobutyl protons are in an edge on orientation with the syn carbonyl groups while the β-cyclobutyl protons are directed away from the syn carbonyl groups. Therefore, the α-cyclobutyl protons appear to be closer to the carbonyl complexation sights. Upon addition of shift reagent the α-cyclobutyl proton signal should then experience a larger shift than the β-cyclobutyl proton signal.[117,118] With increasing concentrations of shift reagent, these signals should begin to separate. The results of the shift reagent study on the minor product **19** indicated the trans-anti-trans geometry about the cyclobutane ring (Figure 44 and Table 5). The slopes obtained from the response curve showed the larger α-cyclobutyl proton shift with respect to the β-cyclobutyl protons and increasing separation between these signals.[117,118]

The summary of the photochemistry for **11** is depicted in Figure 45. Control irradiations of **18** and **19** showed no photoisomerization between the two.



11 **18** **19**

Figure 45. Photochemical Summary for **11**.

Having established the products formed upon irradiation of **11**, it was then of interest to examine the mechanism for formation of the two dimers **18** and **19**. It has been reported that the photolysis of *cis*-2-cyclohepten-1-one (**20**) results in isomerization

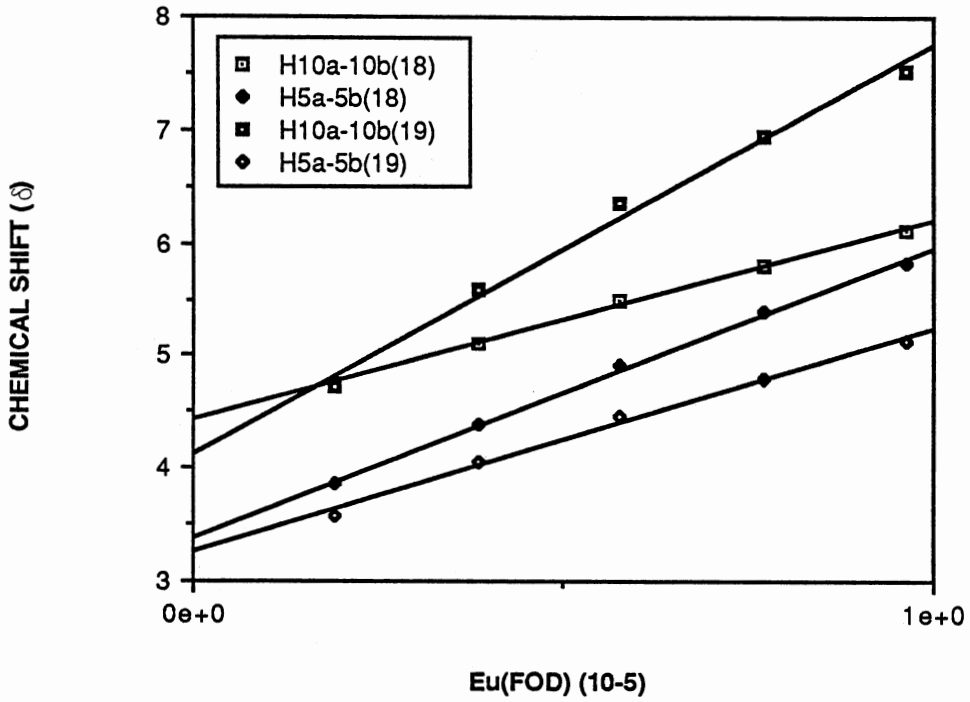


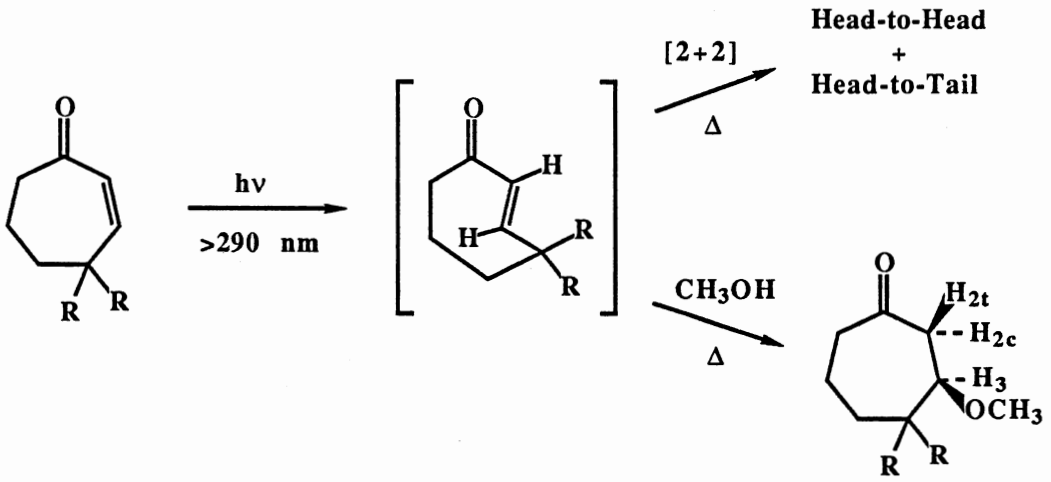
Figure 44. Chemical Shift *vs.* Moles Shift Reagent for Cyclobutane Protons of **18** and **19**.

Table 5

SLOPES AND INITIAL PROTON SHIFTS FOR **18** and **19**

Compound	Proton	Slope (Δm)	Initial Proton Shift, (IS, δ)
18	H10a-10b	1.763	4.43
18	H5a-5b	2.567	3.39
19	H-10a-10b	3.615	4.13
19	H-5a-5b	1.981	3.26

to the *trans*-2-cyclohepten-1-one (**21**). This highly reactive species then undergoes dark reactions such as [2+2] dimerizations and additions (Figure 46).[48,49] Low temperature infrared studies of **20** have confirmed the formation of the trans species as well as the thermal reactions.[48,49] Trans cyclic ketones generated from irradiation of corresponding



20 R = H
11 R = Ph

21 R = H
23 R = Ph

22 R = H
24 R = Ph

Figure 46. Reactivity of the Trans Enones Generated From **20** and **11**.

large ring cis enones have also been trapped by ground state addition reactions with dienes and nucleophiles.[50-52] For example, photoinduced additions of methanol-d_1 to **20** have been reported to lead to the mono deuterated *trans*-3-methoxy-1-cycloheptanone (**25**).[51] This result was attributed to a syn addition of methanol-d_1 to the highly strained double bond of **21** (Figure 47).[51]

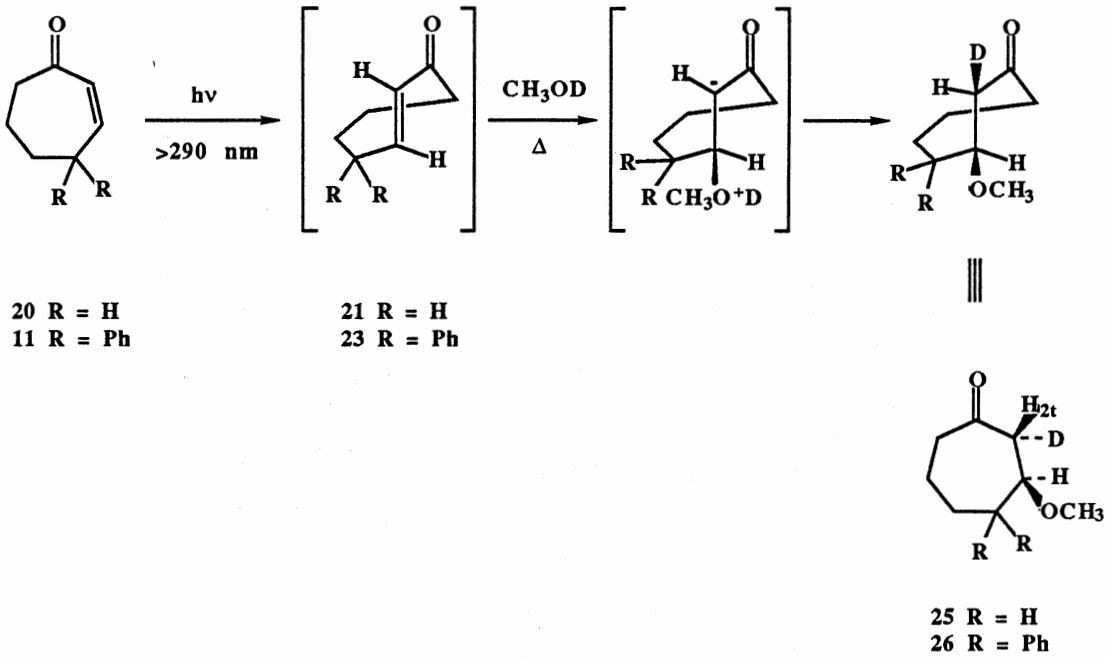


Figure 47. Photoinduced Addition of Methanol to **11** and **20**.

In accord with previous studies of seven-ring enones, it was proposed that the dimers **18** and **19** were also the result of a thermal [2+2] reaction of the strained trans enone **23**. In support of the proposed mechanism, irradiation of **11** in methanol-d_1 was found to lead to the trans-methoxy cycloheptenone system **26** (Figure 47). The assignment of **26** to the trans structure was based on proton NMR coupling constants. It has been reported that for 3-methoxy cyclic ketones, the coupling constants of H-3 with the trans and cis protons H-2t and H-2c are quite different (H-3-H-2t > H-3-H-2c).[51,167] For example, double irradiation experiments (to eliminate the H-4 coupling with H-3) on 3-methoxy-1-cycloheptenone **22** showed the H-3-H-2t coupling to be 6.5 Hz while the H-3-H-2c coupling was only 4.0 Hz.[51] The deuterated trans analog **25** showed only the larger coupling.[51] Irradiation of **11** in methanol resulted in formation of 3-methoxy-1-cycloheptanone **24**. In **24**, the coupling constants of H-3 with the H-2t and H-2c were

6.1 and 1.7 Hz, respectively. The product obtained from irradiation of **11** in methanol-d_1 showed only the larger coupling, consistent with the trans system **26.**

Discussion and Mechanistic Interpretation. The mechanism for the irradiation of *cis*-4,4-diphenyl-2-cyclohepten-1-one **11** is thought to parallel that reported for *cis*-2-cycloheptenone,[48,49] *cis*-2-cyclooctenone[47] and *cis*-2-cyclononenone[50] (Figure 48). It is proposed that the enone undergoes initial electronic excitation into the n-π^* band followed by intersystem crossing to either the n-π^* or π-π^* triplet state. The resulting planar enone triplet then undergoes a twisting motion about the C_α-C_β bond until a critical geometry is reached, followed by radiationless transition to the ground state trans enone.[168] This twisting is the favored process since rotation about the C_α-C_β bond minimizes the mutual repulsive interactions of the π and π^* electrons.[50] The twisted triplet possesses the ideal geometry for radiationless decay directly to ground state and it would appear that because of this, exclusive cis-trans isomerization occurs over the intramolecular aryl migration.[13] The ground state trans enone **23** is highly strained and very reactive and therefore undergoes thermal [2+2] cycloadditions. Thermal [2+2] cycloadditions have been reported to occur by a stepwise mechanism involving a diradical intermediate.[169] It has been suggested that any stabilizing effect on the diradical would be an important factor in determining the regiochemistry.[169] Since the more stable diradical is also thought to lead to product,[170] the initial step should involve combination of two enone double bonds and formation of the diradicals **27** and **28**, which is stabilized by the adjacent carbonyl systems.[157] The diradical precursors to the head-to-tail dimers are of only intermediate stability and if produced should not lead to product. Closure of the 1,4-diradicals **27** and **28** would then give **18** and **19.** Combination of two trans double bonds or a trans and a cis double bond would lead to the same products if we assume the diradical formed is nearly planar or slightly pyramidal with a low barrier to inversion.[171] Formation of the more strained trans-fused dimers may indicate the

combination of two trans double bonds to generate slightly pyramidal diradicals (Figure 49). Closure of the diradicals to trans product then occurs much faster than inversion and closure.

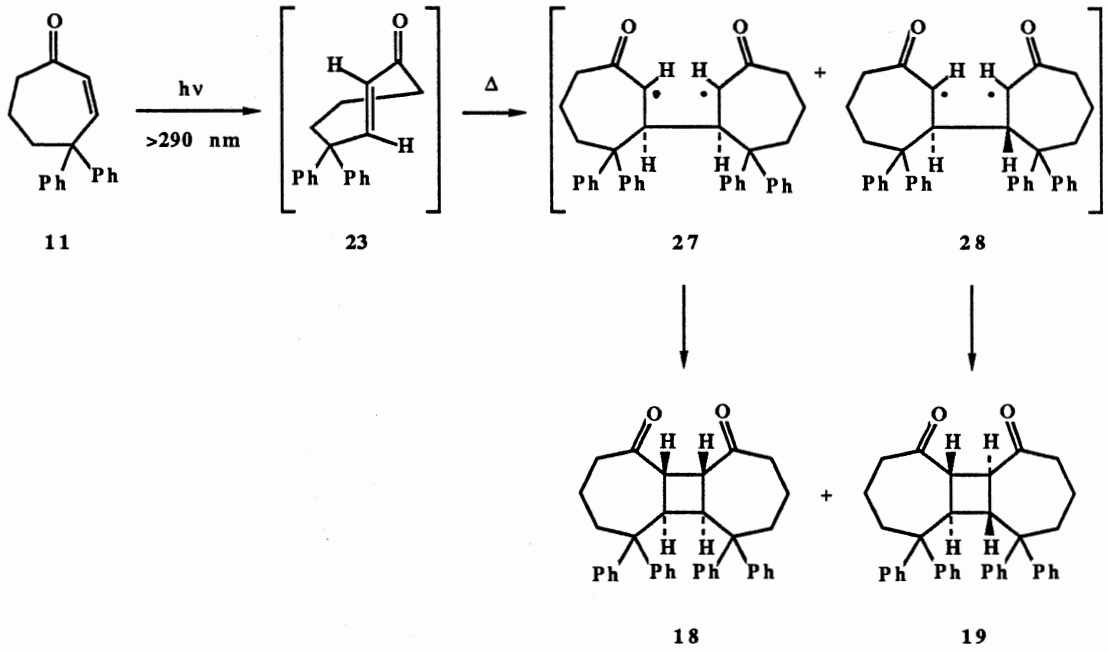


Figure 48. Proposed Mechanism for Formation of **18** and **19** from **11**.

In theory, concerted thermal [2+2] cycloadditions can proceed in a symmetry allowed fashion by a ($\pi^2_s + \pi^2_a$) process.[172] Examples of concerted thermal [2+2] reactions have been presented, generally in systems where approach of the interacting orbitals is not sterically hindered and the angle strain is minimal.[173,174] If the thermal dimerization were to proceed in a concerted fashion, a ground state trans enone **23** must react with a ground state cis enone **11**, in order to obtain the stereochemistry observed in **18**. In the concerted thermal process, three of the four carbon atoms responsible for the

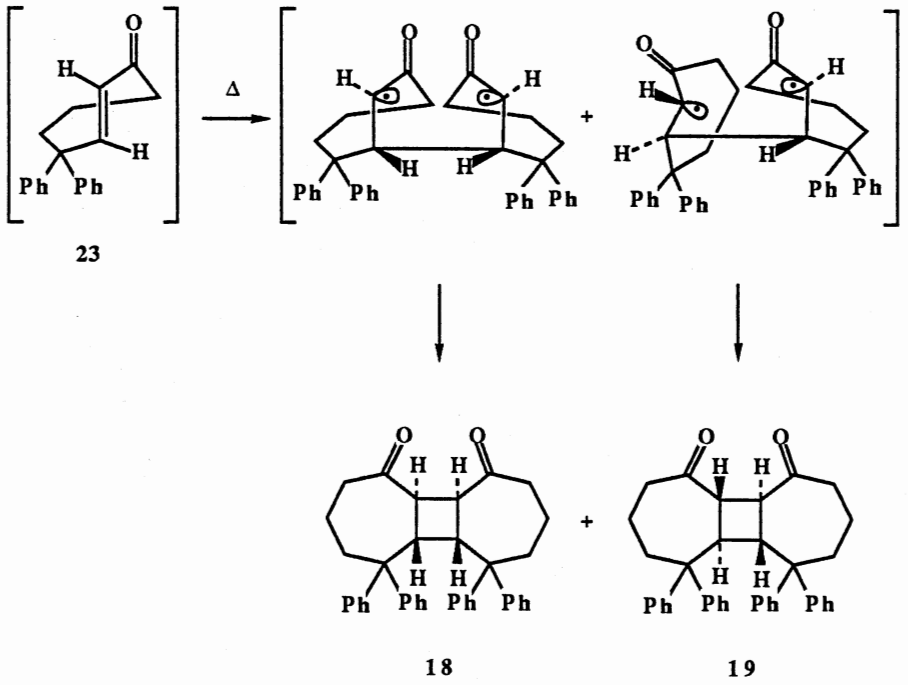
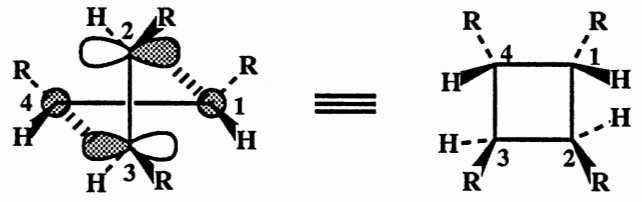


Figure 49. Formation of Trans-Fused Dimers From Pyramidal Diradicals.

cyclobutane ring will show retention of configuration and one will be inverted.[169] A concerted thermal [2+2] reaction of two ground state trans enones would lead to a product with the trans-syn-cis geometry. The concerted trans-cis addition process to give **18** does seem likely since at any given time the majority of ground state molecules will be cis enones and thus the highly reactive ground state trans species has a greater chance of colliding with one of these cis molecules.



trans-anti-trans

Ground state reaction of the highly strained trans enone **23** is also thought to account for the observed reactivity of **11** in methanol-d_1.[50,51] The photoinduced addition is thought to involve two discrete steps, in accord with previously reported low temperature studies of several medium ring α,β-enones. The first step involves photoisomerization of **11** to the trans isomer **23** and the second step is the thermal addition of methanol-d_1 to this ground state trans species. The trans double bond even though less conjugated with the carbonyl system than the cis enone, should be more polarized by strain.[51] Therefore the carbonyl group withdraws electron density effectively from C_β, encouraging regiospecific attack at this sight. Deuterium transfer to the resulting dipolar intermediate then occurs to the unblocked face, accounting for the observed stereochemistry (see Figure 47).[51]

Thermal [2+2] reactions of the ground state trans enones have been established as the mechanism responsible for dimer formation in medium ring enones. Unless the phenyls in **11** exert some influence on the reactivity, there is no evidence to the contrary. However, there is always the remote possibility that the dimers **18** and **19** are a result of a photochemical [2+2] reaction (Figure 50). This photochemical reaction has been reported to be responsible for the [2+2] dimers observed for small ring α,β-enones.[46,64] It has been reported that in photochemical [2+2] cycloadditions the mechanism involves an initial n-π^* excitation of the enone followed by intersystem to the n-π^* or π-π^* triplet state.[64,89,170,175] Corey has proposed that a π-complex between an excited state enone and a ground state enone is then formed.[176] The oriented π-complex then proceeds through a triplet 1,4-diradical, followed by spin inversion and closure to afford the cyclobutane products. The π-complex is thought to be the species largely responsible for determining the regiochemical outcome of the reaction.[64,170,175] Orientational preferences in the π-complex derive largely from charge distribution in the excited triplet state.[64,170,175] In the excited state enone species, C_β is thought to be somewhat more negative relative to C_α in contrast to the ground state species.[64] Therefore, in the 4,4-

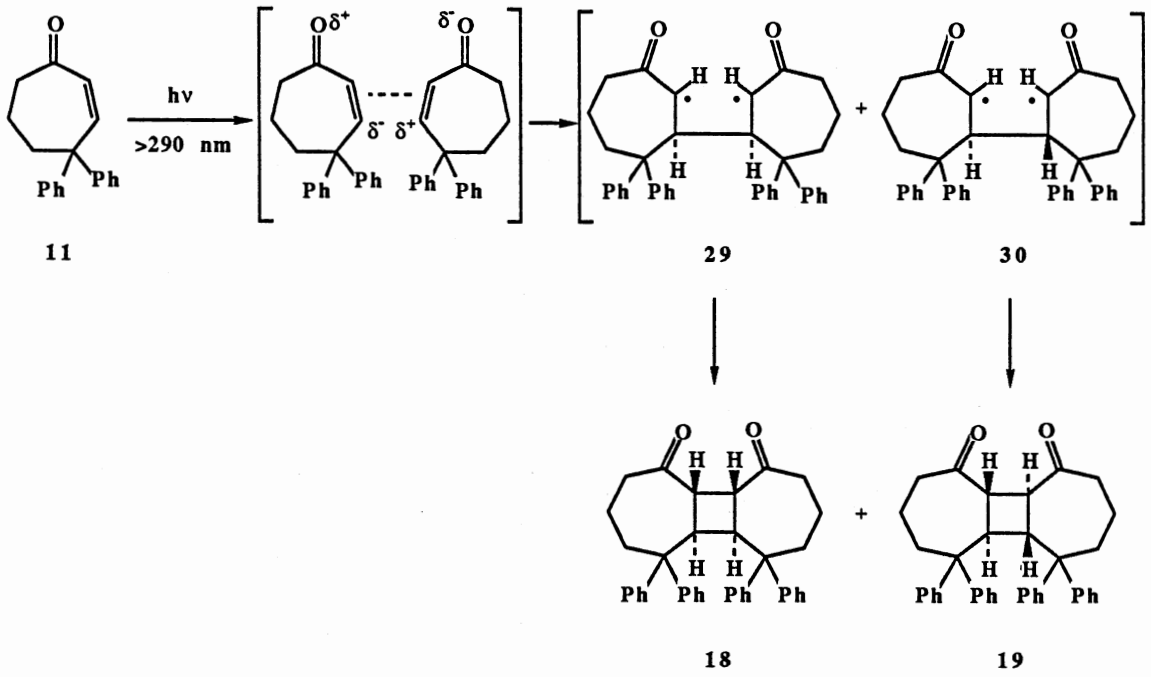


Figure 50. Photochemical [2+2] Addition Mechanism for **11**.

diphenyl cycloheptenone system **11**, dipolar interaction between the triplet enone and a ground state enone would afford the π-complex with a head-to-head orientation. Collapse of the π-complex should then lead to the 1,4-triplet diradicals **29** and **30**, followed by conversion to the singlet and ring closure.[170] The formation of the trans ring-fused products is not an obvious expectation from the π-complex. However, it is understandable if the π-complex possesses a highly twisted double bond.[170] Trans closure of the diradicals formed from this π-complex would be kinetically preferred over bond rotation and closure. Direct diradical formation, bypassing π-complex formation has also been suggested to lead to the [2+2] adducts.[64,89]

The regiochemistry of photochemical [2+2] cycloadditions has been reported to depend on solvent polarity .[46,64] There is generally a marked increase in the amount of head-to-head dimers in polar solvents as compared to nonpolar solvents. This can be

attributed to the fact that the more polar dimer is favored in the more polar solvent.[46] In the 4,4-diphenyl system **11**, a change in solvent from *tert*-butanol to benzene caused no change in the ratio of products or production of any head-to-tail adducts.

It was not initially expected that the head-to-head dimers, **18** and **19**, would prevail over the head-to-tail systems. One would expect phenyl-phenyl steric interactions to influence the course of the reaction, thus leading to a head-to-tail orientation in the products. The formation of the trans-fused head-to-head dimers is thus surprising. The lack of any apparent negative interactions in the head-to-tail dimers would suggest the possibility of positive interactions between the phenyl substituents in the head-to-head system. Additional studies of non-aromatic sterically hindered α,β-cycloheptenones would need to completed before any conclusions can be drawn.

Despite the lack of aryl migration products in the seven-ring enone system, this work has provided a definitive structural assignment of the cyclobutane dimers. Generally, the structure of the cyclodimers produced from thermal [2+2] reactions are assigned on the basis of spectral data or chemical proof and are, therefore, subject to error.[53,156,157,169] One of the major problems associated with assigning the stereochemistry about the cyclobutane ring based on NMR vicinal couplings, is that these coupling constants have been shown to be sensitive to substituent and strain effects.[177-179] The use of chemical proofs for stereochemical assignment about the cyclobutane ring, generally involves degradation to known cyclobutane products.[156,157,169] These not only assume no epimerization but also no error in original assignments of the known cyclobutane products. The crystal structures of **18** and **19** have, therefore, provided an unequivocal assignment of the stereochemistry about the cyclobutane ring.

In conclusion, the utility of the aryl migration processes seems to be limited to small ring cyclic enones and may only be possible for medium ring α,β-enones that are constrained from cis-trans isomerization.

Experimental

Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded with a PE-681 instrument and are referenced to polystyrene. ^{1}H-NMR and ^{13}C-NMR were measured as solutions in $CDCl_3$ at 300 MHz and 75 MHz, respectively, on a Varian XL-300 superconducting FT instrument; chemical shifts are reported in δ units relative to internal Me_4Si. UV spectra were recorded in absolute ethanol using a Varian DMS-200 spectrophotometer. Mass spectra were recorded at 70 eV on a VG ZAB-2SE or a VG TS-250 instrument. Elemental analyses (± 0.4%) were performed by Galbraith Laboratories, Knoxville, TN.

All reactions were run under an atmosphere of dry nitrogen. Solvents used in photochemical runs were purified in the following manner: *tert*-butanol was distilled from CaH_2; benzene was sequentially washed with concentrated concentrated H_2SO_4 (2x), 5% $KMnO_4$ in 10% aqueous H_2SO_4 (2x), and 10% aqueous KOH, then dried over anhydrous $MgSO_4$ and distilled from CaH_2. All photochemical reactions were degassed with dry, oxygen-free nitrogen for 1 h prior to and during irradiation. Column chromatography was performed on silica gel (Grace, grade 62, 60-200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored with a hand-held UV lamp. Preparative thick layer chromatography (PTLC) was performed on Analtech (No. 02015) preparative silica gel uniplates with fluorescent indicator. Reactions were monitored on a capillary GC (Varian 3400) with FI detection on a 6 mm X 0.1 m SE-30 column programmed between 100-300°C.

4,4-Diphenyl-2-cyclohexenone (5). The procedure of Zimmerman[143] was used. To a 0°C solution of 25 g (0.13 mol) of diphenylacetaldehyde and 10.6 mL (8.92 g, 0.13 mol) of methyl vinyl ketone in 187 mL of ether was added a 14-mL (95%) ethanol solution of 2.32 g (0.041 mol) of potassium hydroxide during 70 min. The mixture was stirred at 0°C for an additional 45 min, then poured onto ice. Benzene was

added to dissolve the yellow solid. The mixture was neutralized to a pH of 7 with 1 *M* HCl and the aqueous layer was ether extracted. The organic extracts were combined, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting gummy residue was crystallized and recrystallized from 95% ethanol to give 20 g (0.08 mol, 62.5%) of 4,4-diphenyl-2-cyclohexenone (**5**) as a white solid, 91-93°C, lit.[143] mp. 91-94°C. The spectral data were: IR ($CHCl_3$) 3060, 1682, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.34-7.21 (cplx, 11 H), 6.20 (d, 1 H, J = 10.2 Hz), 2.69 (t, 2 H, J = 6.3 Hz), 2.40 (t, 2 H, J = 6.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 198.9, 156.2, 145.3, 128.9, 128.8, 128.5, 127.6, 126.8, 49.2, 35.8, 34.9.

4,4-Diphenylcyclohexanone (6). The general procedure of Bordwell[146] was used. A 125 mL acetic acid solution of 20 g (0.08 mol) of 4,4-diphenyl-2-cyclohexenone (**5**) containing 0.5 g of 10% Pd/C was shaken under 60 psi of H_2 in a Parr apparatus at 25°C for 12 h (H_2 uptake, 20 psi). The crude reaction mixture was filtered through Celite® and the solution was concentrated under vacuum. The residue was taken up in a 1:1 ether:chloroform solution and washed with saturated aqueous $NaHCO_3$, water and saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting pale yellow solid was recrystallized once from absolute ethanol to yield 19.25 g (0.077 mol, 95%) of 4,4-diphenylcyclohexanone (**6**) as a white solid, 142-143°C, lit.[146] mp. 140-142°C. The spectral data were: IR ($CHCl_3$) 2950, 1707, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.32 (m, 8 H), 7.21 (m, 2 H), 2.66 (t, 4 H, J = 6.4 Hz), 2.44 (t, 4 H, J = 6.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 211.0, 145.8, 128.6, 126.7, 126.3, 45.5, 38.6, 36.4.

4,4-Diphenylcycloheptanone (7). The general procedure of Carnmalm and coworkers[158] was followed. To a stirred two phase mixture of 480 mL of ether and 240 mL of 33% NaOH was added 14.4 g (0.14 mol) of nitrosomethylurea[180] in small portions. Once addition was complete and the bubbling had ceased, the mixture was cooled to -78°C. The yellow ethereal layer of diazomethane was decanted and added

slowly with stirring to 12 g (0.048 mol) of 4,4-diphenylcyclohexanone (**6**) in 200 mL of ethanol at 23°C. After 0.5 h, 50 mL of dioxane was added and the mixture was stirred at 0°C for 24 h. To the resulting pale yellow solution was added acetic acid dropwise until all the unreacted diazomethane had decomposed. The organic solvents were removed under vacuum and the aqueous layer was extracted with ether. The combined ether extracts were washed with water, saturated aqueous $NaHCO_3$, saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting pale yellow solid was purified by column chromatography on two 80 cm x 2.5 cm slurry packed silica gel columns eluted with increasing concentrations of ether in hexane. The compounds eluted as follows: 2.5% ether in hexane, 2.53 g (9.6 mmol, 20%) of 6,6-diphenyl-1-oxaspiro-[2.5]octane (**8**); 3% ether in hexane, 0.84 g (3.4 mmol, 7%) of **6**, 7.4 g (28.0 mmol, 58%) of 4,4-diphenylcycloheptanone (**7**) as a white solid. The spectral data for **7** were: mp. 101-102°C, lit.[158] mp. 101-102°C; IR ($CHCl_3$) 2935, 1700, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.29 (m, 4 H), 7.16 (m, 6 H), 2.51 (m, 6 H), 2.39 (m, 2 H), 1.86 (quintet, 2 H, J = 5.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 214.3, 147.3, 128.3, 127.2, 126.0, 50.0, 43.2, 40.9, 39.6, 34.1, 19.8.

The spectral data for **8** were: mp. 128-129°C; IR ($CHCl_3$) 2940, 2865, 1600, 1030 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.35 (m, 3 H), 7.23 (m, 5 H), 7.16 (m, 2 H), 2.59 (s, 2 H), 2.49 (t, 4 H, J = 6.2 Hz), 1.84 (dt, 2 H, J = 7.0, 14.0 Hz), 1.50 (dt, 2 H, J = 5.0, 14.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 148.2, 145.7, 128.4, 128.3, 127.3, 126.7, 125.8, 125.7, 58.5, 54.1, 45.5, 34.7, 30.0.

4,4-Diphenyl-2-cyclohepten-1-one (11). The general procedure of Stotter and Hill[159] was followed. To a -78°C solution of 2.8 mL (2.02 g, 0.02 mol) of diisopropylamine in 25 mL THF was added 14.3 mL of a 1.4 *M* solution of *n*-BuLi in hexane. The lithium diisopropylamine was allowed to stir for 20 min and a solution of 5.0 g (0.019 mol) of 4,4-diphenylcycloheptanone (**7**) in 50 mL of THF was added. The enolate was stirred for 20 min at -78°C and a 15-mL methylene chloride solution of 1.3

mL (4.04 g, 0.025 mol) of bromine was added dropwise. There was an immediate decolorization of the bromine solution upon addition. The mixture was stirred for 5 min, added to cold saturated aqueous NH_4Cl and ether extracted. The organic layer was washed quickly with 1 *M* H_2SO_4, saturated aqueous $Na_2S_2O_3$, water and then saturated aqueous NaCl. The solution was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to yield a yellow oil. The ^{1}H-NMR ($CDCl_3$) of the crude mixture showed a 2:3 ratio (4.52, dd, 1 H, J = 3.1, 11.8 Hz and 4.34, dd, 1 H, J = 5.1, 8.9 Hz) of 2-bromo-4,4-diphenylcycloheptanone : 2-bromo-5,5-diphenylcycloheptanone. Gas chromatography of the crude mixture showed two peaks, one corresponding to **7** (ca. 28%), and the second peak with a longer retention time corresponding to the two bromides (ca. 72%). The crude mixture, thus obtained, and 3.0 g (0.04 mol) of Li_2CO_3, 3.5 g (0.04 mol) of LiBr, and 50 mL of DMF were heated to 123°C for 48 h. The mixture was taken up in ether, washed with water, saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting brown oil was purified by column chromatography on an 80 cm x 2.5 cm slurry packed silica gel column eluted with increasing concentrations of ether in hexane. Fractions (250 mL) were collected The compounds eluted as follows: 1% ether in hexane, fractions 1-2, nil; 2% ether in hexane, fractions 3-4, nil; 3.5% ether in hexane, fractions 5-6, unreacted bromide, fraction 7, nil; 4.5% ether in hexane, fractions 8-10, 4,4-diphenyl-2-cyclohepten-1-one (**11**) and a small amount of 5,5-diphenyl-2-cyclohepten-1-one (**12**), fractions 11-17, 1.68 g (6.4 mmol, 34%) of **12**, fraction 18, nil; 5% ether in hexane, fractions 19-23, .05 g (4.0 mmol, 21%) of **7**. Fractions 8-10 were combined and purified on five 20 cm x 20 cm silica gel PTLC plates eluting with 5% ethyl acetate in hexane (5x). The fastest moving band yielded compound **11**. Decolorization of **11** using activated charcoal and crystallization from ether yielded 0.99 g (3.8 mmol, 20%) of **11** as a white solid, mp. 58-60°C. The spectral data for **11** were: IR ($CHCl_3$) 2948, 1670, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.31-7.17 (cplx, 10 H), 6.69 (A of ABd, 1 H, J = 12.7 Hz), 6.12 (B

of ABd, 1 H, J = 12.7 Hz), 2.57 (2t, 4 H, J = 6.7 Hz), 1.71 (quintet, 2 H, J = 2.9 Hz); ^{13}C-NMR ($CDCl_3$) δ 203.5, 150.8, 146.2, 130.2, 128.3, 128.1, 127.9, 127.7, 126.5, 55.7, 43.7, 38.8, 18.5; UV (abs. EtOH) λ_{max} (ε) 323 (107), 230 (10250); MS, *m/e* (%) 262 (36), 234 (37), 206 (100), 191 (33), 128 (30), 91 (72); HRMS, exact mass calcd for $C_{19}H_{18}O$ *m/e* 262.1357, found *m/e* 262.1360. Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.92. Found: C, 86.60; H, 7.10.

The spectral data for **12** were: IR ($CHCl_3$) 2940, 1665, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.27 (m, 4 H), 7.23-7.12 (cplx, 6 H), 6.72 (dt, 1 H, J = 6.2, 12.1 Hz), 6.06 (d, 1 H, J = 12.1 Hz), 3.03 (d, 2 H, J = 6.2 Hz), 2.60 (m, 4 H); ^{13}C-NMR (CDCl3) δ 203.7, 148.4, 143.1, 133.1, 128.4, 127.0, 126.2, 50.4, 41.6, 40.2, 33.1; MS, m/e (%) 262 (41), 204 (46), 193 (55), 165 (43), 115 (66), 95 (100), 91 (55); HRMS, exact mass calcd for $C_{19}H_{18}O$ *m/e* 262.1357, found *m/e* 262.1356.

Exploratory Direct Photolysis of 4,4-Diphenyl-2-cyclohepten-1-one (11). A. In *tert*-Butanol: The procedure described by Zimmerman[1] for the photolysis of 4,4-diphenyl-2-cyclohexenone was followed. A solution of 100 mg (0.38 mmol) of 4,4-diphenyl-2-cyclohepten-1-one (**11**) in 305 mL of degassed *tert*-butanol in a Kreil flask (Ace no. 6963) was irradiated through Pyrex using a 450-W medium pressure Hanovia immersion apparatus. The reaction was followed by TLC analysis of concentrated aliquots taken at 10 min intervals for a total photolysis time of 30 min. The solution was concentrated *in vacuo* and the crude residue purified on a 20 cm x 20 cm silica gel PTLC plate eluted once with 50% ether in hexane. The fastest moving of three bands yielded 10 mg (0.04 mmol, 10%) of **11**. The second band yielded 30 mg (0.06 mmol, 15%) of (±)-(5aβ, 5bα, 10aβ, 10bα)-dodecahydro-5,5,6,6-tetraphenylcyclobuta-[1,2:3,4]dicycloheptene-1,10-dione (**19**) as a white solid, mp. 231-233°C; IR ($CHCl_3$) 2920, 1700, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 23°C) δ 7.28 (m, 6 H), 7.00 (m, 6 H), 6.89 (t, 4 H, J = 7.5 Hz), 6.79 (t, 4 H, J = 7.5 Hz), 4.03 (A of ABm, 2 H), 3.15 (B of ABm, 2 H), 2.66 (dd, 2 H, J = 9.0, 14.5 Hz), 2.46 (m, 4 H), 2.00 (dd, 2 H, J = 9.0,

14.5 Hz), 1.70 (A of ABm, 2 H), 1.58 (B of ABm, 2 H); ^{13}C-NMR ($CDCl_3$, 23°C) δ 210.0, 146.6, 143.9, 129.6, 129.1, 128.2, 127.3, 126.4, 125.9, 53.2, 48.1, 43.6, 43.1, 43.0, 18.5; UV (abs. EtOH) λ_{max} (ε) 260 (888), 216 (7595); MS, *m/e* (%) 524 (100), 506 (45), 313 (29), 206 (88), 193 (86), 167 (38), 91 (36); HRMS, exact mass calcd for $C_{38}H_{36}O_2$ *m/e* 524.2715, found *m/e* 524.2713. Anal. Calcd for $C_{38}H_{36}O_2$: C, 86.98; H, 6.92. Found: C, 87.06; H, 7.11.

The third band yielded 70 mg (0.13 mmol, 35%) of (5aβ, 5bβ, 10aα, 10bα)-dodecahydro-5,5,6,6-tetraphenylcyclobuta[1,2:3,4]dicycloheptene-1,10-dione (**18**) as a white solid, mp. 260-263°C; IR ($CHCl_3$) 2935, 1705, 1690, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 50°C) δ 7.06 (m, 8 H), 6.96 (m, 8 H), 6.43 (d, 4 H, J = 7.2 Hz), 4.45 (A of ABm, 2 H), 3.42 (B of ABm, 2 H), 2.98 (dt, 2 H, J = 8.8, 18.0 Hz), 2.64 (ddd, 2 H, J = 2.2, 8.8, 14.6 Hz), 2.51 (ddd, 2 H, J = 4.9, 6.4, 18.0 Hz), 1.94 (ddd, 2 H, J = 2.2, 8.8, 14.6 Hz), 1.67 (m, 4 H); ^{13}C-NMR ($CDCl_3$, 50°C) δ 211.5, 147.5, 142.2, 129.9, 128.5, 128.2, 127.5, 126.5, 126.3, 55.5, 52.0, 47.4, 43.9, 40.8, 18.6; UV (abs. EtOH) λ_{max} (ε) 260 (749), 214 (12985); MS, *m/e* (%) 524 (20), 206 (100), 194 (63), 167 (34), 115 (46), 91 (57); HRMS, exact mass calcd for $C_{38}H_{36}O_2$ *m/e* 524.2715, found *m/e* 524.2712. Anal. Calcd for $C_{38}H_{36}O_2$: C, 86.98; H, 6.92. Found: C, 87.00; H, 6.97.

B. In Benzene: A solution of 100 mg (0.38 mmol) of **11** in 305 mL degassed purified benzene was photolyzed using conditions identical to those described above. The reaction time and isolated products:reactant ratios were all within 5% of those observed in the photolysis reaction of **11** in *tert*-butanol.

Single Crystal X-ray Structure Determination of (5aβ, 5bβ, 10aα, 10bα)-dodecahydro-5,5,6,6-tetraphenylcyclobuta[1,2:3,4]dicycloheptene-1,10-dione (18) and (±)-(5aβ, 5bα, 10aβ, 10bα)-dodecahydro-5,5,6,6-tetraphenylcyclobuta[1,2:3,4]dicycloheptene-1,10-dione (19). Single crystals of **18** and **19** were mounted on a Syntex P3 automated diffractometer.

Unit cell dimensions (Table 6) were determined by least squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$Å). Data (3612 for **18**, 3685 for **19** independent points after removal of space group forbidden for **18** and redundant data for **18** and **19**) were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. Observed reflections [2119 for **18**, 2481 for **19**, $I > 3.0\sigma(I)$] were used for solution of carbon and oxygen positions of the structure by direct methods using MULTAN80.[129] Refinement[130] of scale factor, positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. The positions of the hydrogen atoms were located from a difference Fourier synthesis and were included (with hydrogen positional and thermal parameters fixed) in the final cycles of refinement [function minimized, $\Sigma(|F_o|-|F_c|)^2$] leading to a final agreement factor, R = 5.8% for **18**, 5.3% for **19** [$R = (\Sigma| |F_o| - |F_c| | / \Sigma|F_o|) \times 100$]. Scattering factors were taken from Cromer and Mann.[131] In the final stages of refinement, a weight of $1/\sigma(F)^2$ was used. R_w = 7.3% for **18** and 6.9% for **19**. Appendix C, Tables 20-24 lists bond angles and distances, positional parameters, and final anisotropic thermal parameters for **18** and **19**..

Control Experiment. Photostability of the Photoproducts. In a typical control run, 0.04 mmol of the photoproduct was photolyzed as a 10^{-4} *M* solution in cyclohexane using conditions identical to those described for the exploratory irradiations. The reactions were monitored by TLC of concentrated aliquots taken at 15 min intervals for the first hour and 1 h intervals thereafter for a total photolysis time of 5 h.

TABLE 6

CRYSTAL DATA FOR **18** AND **19**

	18 (trans-syn-trans)	**19** (trans-anti-trans)
formula	$C_{38}H_{36}O_2$	$C_{38}H_{36}O_2$
MWT	524.7	524.7
a, Å	9.629(2)	10.463(4)
b, Å	28.903(6)	10.598(5)
c, Å	10.433(6)	14.874(6)
α, deg	90.0	71.93(3)
β, deg	108.50(3)	102.45(3)
γ, deg	90.0	111.32(3)
V, Å^3	2753(2)	1450.7(10)
F(000)	1120	560
μ(MoKα), cm^{-1}	0.710	0.674
λ(MoKα), Å	0.71069	0.71069
D_{calcd}, g cm^{-3}	1.266	1.201
Z	4	2
Ind. refl. meas.	3612	3685
obsd refl	2119	2481
Octants meas.	±h, +k, +l	±h, +k, ±l
R/R_w, %	5.8/7.3	5.3/6.9
space group	$P2_1/c$	P1
goodness of fit	0.32	0.34

No photoisomerization was seen upon irradiation of either **18** or **19**, but decomposition of both photoproducts began to occur after 3 h.

^{1}H-HMR Shift Reagent Experiment. In a typical run, the ^{1}H-NMR spectra were recorded at 50°C with increasing concentrations of shift reagent. To a 0.02 *M* solution of the product (**18** and **19**) in $CDCl_3$ was added 2 mg (0.002 mmol) quantities of the solid shift reagent Resolve-Al EuFOD™ ($Eu(fod)_3$). After each 2 mg addition the NMR was taken. Sequential 2 mg additions were continued until a total of 12 mg (0.012 mmol) of shift reagent had been added. The response curve is shown in Figure 44 of Chapter 4 along with a table of the slopes (Δm) and the initial proton resonances (IS) in Table 5.

3-Methoxy-4,4-diphenylcycloheptanone (24). A solution of 21.4 mg (0.082 mmol) of 4,4-diphenyl-2-cycloheptenone (**11**) in 8.0 mL of degassed Photorex® grade methanol was irradiated through Pyrex using a 450-W medium pressure immersion apparatus. The reaction was stopped after 1 h and concentrated under vacuum. The crude residue was purified on one, 20 cm x 20 cm silica gel PTLC plate eluted with 30% ether in hexane (2x). The fastest moving of two bands yielded 6.4 mg (0.025 mmol, 30%) of **11**. The second band yielded 12.6 mg (0.043 mmol, 52%) of 3-methoxy-4,4-diphenylcycloheptanone (**24**) as a colorless oil. The spectral data for **24** were: IR ($CHCl_3$) 2930, 1700, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.29-7.12 (cplx, 9 H), 7.07 (m, 1 H), 4.24 (dd, 1 H, J = 1.7, 6.2 Hz), 3.12 (s, 3 H), 2.99 (d, 1 H, J = 6.3 Hz), 2.69-2.48 (cplx, 2 H), 2.47-2.31 (cplx, 2 H), 1.79 (m, 2 H); ^{13}C-NMR ($CDCl_3$) δ 211.8, 147.0, 144.9, 128.6, 127.9, 127.7, 127.6, 126.2, 125.8, 81.5, 57.6, 54.3, 43.3, 33.9, 19.6; MS, *m/e* (%) 294 (38), 236 (28), 180 (100), 165 (23), 103 (31); HRMS, exact mass calcd for $C_{20}H_{22}O$ *m/e* 294.1620, found *m/e* 294.1624.

***trans*-2-Deuterio-3-methoxy-4,4-diphenylcycloheptanone (26).** A solution of 21.4 mg (0.082 mmol) of 4,4-diphenyl-2-cycloheptenone (**11**) in 8.0 mL of degassed methanol-d_1 was irradiated through Pyrex using a 450-W medium pressure

immersion apparatus. The reaction was stopped after 1 h and concentrated under vacuum. The crude residue was purified on one, 20 cm x 20 cm silica gel PTLC plate eluted with 30% ether in hexane (2x). The fastest moving of two bands yielded 7.30 mg (0.028 mmol, 34%) of **11**. The second band yielded 10.4 mg (0.035 mmol, 43%) of *trans*-2-deuterio-3-methoxy-4,4-diphenylcycloheptanone (**26**) as a colorless oil. The NMR spectra of the crude and purified product were identical. The spectral data for **26** were: IR ($CHCl_3$) 2925, 2855, 1700, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.36-7.21 (cplx, 9 H), 7.14 (m, 1 H), 4.30 (d, 1 H, J = 6.6 Hz), 3.19 (s, 3 H), 3.06 (d, 1 H, J = 6.6 Hz), 2.76-2.60 (cplx, 2 H), 2.59-2.37 (cplx, 2 H), 1.86 (m, 2 H); ^{13}C-NMR ($CDCl_3$) δ 211.8, 147.0, 144.9, 128.6, 127.8, 127.8, 127.6, 126.3, 125.8, 81.6, 57.7, 54.3, 43.3, 33.9, 19.6; MS, *m/e* (%) 295 (34), 236 (27), 180 (100), 165 (24), 113 (27); HRMS, exact mass calcd for $C_{20}H_{21}DO$ *m/e* 295.1682, found *m/e* 295.1715.

4,4-Diphenyl-2-(phenylseleno)cycloheptanone (13). The general procedure of Reich and coworkers[160] was followed. To a -78°C solution of 1.40 mL (1.01 g, 10.0 mmol) of diisopropylamine in 15 mL of THF was added 7.95 mL of a 1.26 *M* solution of *n*-BuLi in hexane. The lithium diisopropylamine was allowed to stir 20 min and a solution of 2.62 g (9.9 mmol) of 4,4-diphenylcycloheptanone (**7**) in 20 mL THF was added slowly at -78°C. The enolate was stirred 20 min and phenylselenenyl bromide, prepared by treating 1.56 g (5.0 mmol) diphenyl diselenide in 10 mL THF with 0.26 mL (0.81 g, 5.0 mmol) of bromine, was added dropwise. There was immediate decolorization of the phenylselenenyl bromide solution upon addition. The mixture was stirred for 45 min at -78°C, poured into cold saturated aqueous NH_4Cl and ether extracted. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting yellow oil was purified by column chromatography on a 80 cm x 2.5 cm slurry packed silica gel column eluted with increasing concentrations of ether in hexane. Fractions (250 mL) were collected. The compounds eluted as follows: 0% ether in hexane, fractions 1-3, 0.41 g (1.3 mmol)

diphenyl diselenide, fractions 4-5, nil; 5.0% ether in hexane, fractions 6-10, crude 4,4-diphenyl-2-(phenylseleno)cycloheptanone (**13**), fraction 11, 0.01 g (.024 mmol, 0.24%) of 5,5-diphenyl-2-(phenylseleno)cycloheptanone (**14**), fractions 12-13, nil; 5.5% ether in hexane, fractions 14-17, 0.89 g (3.4 mmol, 34%) of **7**. The combined fractions 6-10 crystallized upon standing in ether to yield 1.58 g (3.8 mmol, 38%) of **13** as a pale yellow solid, mp 118-120°C. The spectral data for **13** were: IR ($CHCl_3$) 2940, 1693, 1600, 1580 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.50 (m, 1 H), 7.38-7.09 (cplx, 12 H), 6.99 (m, 2 H), 3.88 (dd, 1 H, J = 5.6, 10.8 Hz), 2.93 (ddd, 1 H, J = 1.6, 12.5, 25.0 Hz), 2.79-2.70 (cplx, 2 H), 2.43 (dd, 1 H, J = 8.2, 12.6 Hz), 2.25-2.02 (cplx, 3 H), 1.71 (m, 1 H); ^{13}C-NMR ($CDCl_3$) δ 208.9, 149.3, 144.7, 135.1, 135.1, 129.1, 128.6, 128.4, 128.3, 128.2, 127.8, 126.6, 126.0, 51.7, 49.8, 37.6, 36.7, 36.7, 25.5; MS, *m/e* (%) 420 (56), 193 (28), 167 (24), 129 (26), 115 (38), 91 (100), 77 (27); HRMS, exact mass calcd for $C_{25}H_{24}OSe$ *m/e* 420.0053, found *m/e* 420.0070. Anal. Calcd for $C_{25}H_{24}OSe$: C, 71.43; H, 5.76. Found: C, 71.55; H, 5.62.

The spectral data for **14** were: mp 197-199°C; IR ($CHCl_3$) 2875, 1692, 1602, cm^{-1}; ^{1}H-NMR ($CDCl_3$, 40°C) δ 7.59 (m, 2 H), 7.39 (m, 2 H), 7.28-7.13 (cplx, 9 H), 7.01 (d, 2 H, J = 7.3 Hz), 2.50 (m, 5 H), 2.33 (m, 2 H), 1.73 (m, 2 H); ^{13}C-NMR ($CDCl_3$) δ 206.8, 137.7, 129.5, 128.9, 128.4, 128.2, 127.3, 126.1, 67.4, 49.3, 37.6, 37.2, 34.9, 29.5; MS, m/e (%) 420 (31), 314 (28), 261 (100), 233 (34), 115 (37), 91 (84), 77 (37); HRMS, exact mass calcd for $C_{25}H_{24}OSe$ *m/e* 420.0053, found *m/e* 420.0170.

Attempted Phenylselenoxide Elimination of 4,4-Diphenyl-2-(phenylseleno)cycloheptanone. The general procedure of Reich and coworkers[160] was followed. To a cold (ice-salt bath) solution of 0.4 g (0.95 mmol) of 4,4-diphenyl-2-(phenylseleno)cycloheptanone (**13**) in 12 mL of methylene chloride containing 0.15 mL pyridine was slowly added 0.29 g (2.5 mmol) of 30% H_2O_2 in 0.25 mL of water. During addition the temperature was maintained between 30-35°C. The reaction mixture

was stirred vigorously under ice-salt bath conditions for 20 min and then allowed to warm to 23°C and stir for an additional 20 min. The solution became a dark orange color upon warming to 23°C. Methylene chloride was added and the crude mixture was washed once with 7% aqueous $NaHCO_3$ solution. The aqueous layer was washed with methylene chloride and the combined organic layers were washed with 10% aqueous HCl, saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting dark orange oil was intially chromatographed on two 20 cm x 20 cm silica gel PTLC plates, eluting with 5% ether in hexane (9x). One broad band was isolated and purified on two 20 cm x 20 cm silica gel PTLC plates, eluting with 5% ether in hexane (9x). The fastest moving of two bands yielded 8.0 mg (0.03 mmol, 3.2%) of 4,4-diphenyl-2-cyclohepten-1-one (**11**). The second band yielded 0.14 g (0.53 mmol, 56%) of 5,5-diphenyl-2-cyclohepten-1-one (**12**) as the major product of the reaction. The spectral data matched those reported above.

Elimination of **14** using conditions identical to those described above led to 5,5-diphenyl-2-cyclohepten-1-one (**12**) as the only product of the reaction.

4,4-Diphenyl-2-(phenylthio)cycloheptanone (15). The general procedure of Trost and coworkers[161] was followed. To a -78°C solution of 1.08 mL (0.78 g, 7.7 mmol) of diisopropylamine in 15 mL of THF was added 4.88 mL of a 1.6 *M* solution of *n*-BuLi in hexane. The lithium diisopropylamine was allowed to stir 20 min and a solution of 2.0 g (7.6 mmol) of 4,4-diphenylcycloheptanone (**7**) in 25 mL THF was added slowly at -78°C. The enolate was stirred 20 min and 1.32 mL (1.36 g, 7.6 mmol) of HMPA was added and stirred 10 min. To this solution was added 1.66 g (7.6 mmol) of diphenyl disulfide in 15 mL THF. The mixture was stirred for 45 min at -78°C, warmed to RT, poured into cold saturated aqueous NH_4Cl and ether extracted. The organic layer was washed with 1 *M* HCl, saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting yellow oil was purified by column chromatography on a 80 cm x 2.5 cm slurry packed silica gel column eluted with

increasing the concentrations of ether in hexane. Fractions (250 mL) were collected. The compounds eluted as follows: 0% ether in hexane, fractions 1-2, diphenyl disulfide, fractions 3-4, nil; 3.0% ether in hexane, fractions 5-8, crude 4,4-diphenyl-2-(phenylthio)cycloheptanone (**15**), fraction 9, mixture of **15** and 5,5-diphenyl-2-(phenylthio)cycloheptanone (**16**), fractions 10-15, 0.54 g (1.44 mmol, 19%) of **16**; 4.0% ether in hexane, fractions 16-19, 1.10 g (4.17 mmol, 55%) of **7**. Crystallization of the combined fractions 5-8 from ether in hexane yielded 0.28 g (0.75 mmol, 10%) of **15** as a white solid, mp. 123-125°C. The spectral data for **15** were: IR ($CHCl_3$) 2945, 1700, 1600, 1580 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.37 (m, 3 H), 7.29-7.10 (cplx, 10 H), 7.05 (m, 2 H), 3.82 (dd, 1 H, J = 5.7, 10.3 Hz), 2.99 (ddd, 1 H, J = 1.5, 12.2, 24.8 Hz), 2.74 (m, 2 H), 2.48 (m, 1 H), 2.17 (m, 3 H), 1.71 (m, 1 H); ^{13}C-NMR ($CDCl_3$) δ 208.2, 149.1, 145.2, 133.4, 132.2, 129.0, 128.9, 128.8, 128.6, 128.3, 127.8, 127.7, 126.7, 126.3, 126.1, 57.0, 49.8, 36.7, 25.4; MS, *m/e* (%) 372 (100), 163 (60), 223 (53), 151 (99), 113 (95), 91 (90); HRMS, exact mass calcd for $C_{25}H_{24}OS$ *m/e* 372.1548, found *m/e* 372.1549.

The spectral data for **16** were: IR ($CHCl_3$) 2948, 1705, 1600, 1583 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.43 (m, 2 H), 7.32-7.11 (cplx, 9 H), 7.05 (dd, 2 H, J = 1.5, 7.2 Hz), 6.95 (m, 2 H), 3.99 (dd, 1 H, J = 2.6, 11.9 Hz), 2.94 (dd, 1 H, 2.6, 14.8 Hz), 2.82-2.66 (cplx, 2 H), 2.49-2.40 (cplx, 2 H), 2.08 (cplx, 3 H); ^{13}C-NMR ($CDCl_3$) δ 208.2, 150.6, 152.7, 133.8, 133.2, 129.0, 128.6, 128.1, 128.1, 126.4, 126.2, 126.0, 55.5, 50.0, 42.2, 41.2, 39.7, 20.1; MS, *m/e* (%) 372 (91), 201 (35), 162 (73), 151 (79), 133 (48), 113 (100), 101 (43), 70 (52); HRMS, exact mass calcd for $C_{25}H_{24}OS$ *m/e* 372.1548, found *m/e* 372.1548.

4,4-Diphenyl-2-(phenylsulfinyl)cycloheptanone (17). The general procedure of Trost and coworkers[161] was followed. To a -78°C solution of 0.66 g (1.77 mmol) of 4,4-diphenyl-2-(phenylthio)cycloheptanone (**15**) in 36 mL of methylene chloride was added a 12-mL methylene chloride solution of 0.61 g (1.77 mmol) of 50-

55% MCPBA dropwise over a 5 min period. The reaction mixture was monitored by TLC and complete after 15 min. The cold solution was poured into 100 mL of 10% aqueous Na_2SO_3 and extracted with ether. The organic layer was washed with saturated aqueous $NaHCO_3$ (2x) and dried over anhydrous Na_2SO_4. Concentration under vacuum yielded 0.69 g (1.77 mmol, 100%) of 4,4-diphenyl-2-(phenylsulfinyl)cycloheptanone (**17**) as a white foam: IR 1715, 1600, 1495, 1040 cm^{-1}. The crude sulfoxide was utilized directly in the elimination step.

Attempted Phenylsulfoxide Elimination of 4,4-Diphenyl-2-(phenylsulfinyl)cycloheptanone. The general procedure of Trost and coworkers[161] was used. The crude sulfoxide 4,4-diphenyl-2-(phenylthio)cycloheptanone (**17**) (0.1 g, 0.26 mmol) in 10 mL toluene was heated to 100°C for 4 h. The reaction was followed by GC and TLC and indicated production of **11** (*ca.* 17%) and **15** (*ca.* 77%).

The reaction was also attempted in which 0.1 g (0.26 mmol) of **17** in 10 mL carbon tetrachloride was heated to 50°C for 24 h. The reaction was monitored by TLC and GC, both indicating no reaction. The thermolysis was also carried out in both solvent systems described above in the presence of added solid calcium carbonate but similar results were obtained.

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TABLE 7 (Continued)

Atoms	Distance (Å)	Atoms	Angle (°)
		C15 - C16 - C8	121.8(3)
		C11 - C17 - C18	122.1(4)
		C17 - C18 - C19	119.7(4)
		C18 - C19 - C20	120.0(4)
		C19 - C20 - C12	121.0(3)

TABLE 8

POSITIONAL PARAMETERS FOR (±)-4,4a,9,10-TETRAHYDRO-TRIBENZO[*a*,*c*,*e*]CYCLOOCTEN-2(3*H*)-ONE $C_{20}H_{18}O$ (**19**)

Atom	X(Sig(X))	Y(Sig(Y)	Z(Sig(Z)
O1	0.6870(2)	-0.2043(3)	-0.1831(3)
C1	0.7300(2)	0.0334(3)	0.0598(4)
C2	0.6948(3)	-0.0678(3)	-0.0010(4)
C3	0.7185(3)	-0.1092(4)	-0.1324(4)
C4	0.7790(3)	-0.0280(4)	-0.2064(4)
C5	0.8523(3)	0.0467(4)	-0.1078(4)
C6	0.7999(3)	0.1137(3)	-0.0068(4)
C7	0.8728(2)	0.1880(3)	0.0929(4)
C8	0.9318(3)	0.1397(3)	0.2127(4)
C9	0.9180(3)	0.0141(3)	0.2574(4)
C10	0.8423(3)	0.0034(4)	0.3555(4)
C11	0.7469(3)	0.0749(3)	0.3172(4)
C12	0.6937(3)	0.0835(3)	0.1831(4)
C13	0.8867(3)	0.3062(3)	0.0617(4)
C14	0.9551(3)	0.3764(4)	0.1428(5)
C15	1.0130(3)	0.3303(4)	0.2590(4)
C16	1.0008(3)	0.2126(4)	0.2930(4)
C17	0.7083(3)	0.1329(4)	0.4225(4)
C18	0.6200(4)	0.1939(4)	0.3978(5)
C19	0.5650(3)	0.1962(4)	0.2674(5)
C20	0.6018(3)	0.1420(3)	0.1602(4)
H2	0.6501(0)	-0.1185(0)	0.0462(0)
H41	0.8140(0)	-0.0745(0)	-0.2683(0)
H42	0.7314(0)	0.0263(0)	-0.2671(0)
H51	0.9035(0)	-0.0062(0)	-0.0538(0)
H52	0.8896(0)	0.1023(0)	-0.1585(0)
H61	0.7563(0)	0.1766(0)	-0.0610(0)
H91	0.8958(0)	-0.0347(0)	0.1742(0)
H92	0.9848(0)	-0.0172(0)	0.3015(0)
H101	0.8232(0)	-0.0815(0)	0.3608(0)
H102	0.8759(0)	0.0270(0)	0.4482(0)
H13	0.8452(0)	0.3393(0)	-0.0229(0)
H14	0.9627(0)	0.4621(0)	0.1170(0)
H15	1.0626(0)	0.3812(0)	0.3192(0)
H16	1.0431(0)	0.1772(0)	0.3765(0)
H17	0.7476(0)	0.1275(0)	0.5185(0)
H18	0.5951(0)	0.2365(0)	0.4748(0)
H19	0.4998(0)	0.2393(0)	0.2486(0)
H20	0.5628(0)	0.1437(0)	0.0650(0)

TABLE 9

ANISOTROPIC THERMAL PARAMETERS FOR (±)-4,4a,9,10-TETRAHYDRO-TRIBENZO[*a*,*c*,*e*]CYCLOOCTEN-2(3*H*)-ONE $C_{20}H_{18}O$ (**19**)

Atom	U11	U22	U33	U12	U13	U23
O1	94(2)	68(2)	56(1)	-6(1)	-11(1)	-9(1)
C1	39(2)	47(2)	36(2)	5(1)	3(1)	2(1)
C2	49(2)	45(2)	45(2)	-3(1)	3(1)	0(2)
C3	54(2)	55(2)	41(2)	8(2)	-5(2)	-8(2)
C4	65(2)	75(3)	44(2)	4(2)	11(2)	-11(2)
C5	53(2)	60(2)	47(2)	1(2)	16(2)	1(2)
C6	43(2)	48(2)	42(2)	2(1)	5(1)	3(1)
C7	36(2)	48(2)	38(2)	4(1)	9(1)	-2(1)
C8	37(2)	43(2)	51(2)	5(1)	6(1)	-1(2)
C9	47(2)	51(2)	56(2)	7(1)	-1(2)	10(2)
C10	68(2)	61(2)	50(2)	0(2)	2(2)	20(2)
C11	57(2)	46(2)	39(2)	-8(2)	13(2)	1(1)
C12	43(2)	41(2)	40(2)	-5(1)	9(1)	1(1)
C13	52(2)	49(2)	47(2)	4(2)	12(1)	5(2)
C14	63(2)	45(2)	68(2)	-2(2)	23(2)	0(2)
C15	60(2)	52(2)	59(2)	-11(2)	9(2)	-11(2)
C16	46(2)	62(2)	50(2)	4(2)	-1(2)	-2(2)
C17	85(3)	58(2)	40(2)	-13(2)	16(2)	-1(2)
C18	93(3)	48(2)	69(3)	-7(2)	46(3)	-10(2)
C19	57(2)	47(2)	86(3)	3(2)	29(2)	4(2)
C20	51(2)	52(2)	54(2)	0(2)	13(2)	2(2)

Anisotropic thermal parameters in the form:

$$\exp[\,-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)] \times 10^3$$

TABLE 10

BOND ANGLES AND DISTANCES FOR (±)-(3a*R**,13bα,13cβ)-2,3,8,9,13b,13c-HEXAHYDRO-1*H*-DIBENZO[*a*,*e*]CYCLOPENTA[1,3]CYCLOPROPA[1,2-*c*]CYCLOOCTEN-1-ONE $C_{20}H_{18}O$ (**20**)

Atoms	Distance (Å)	Atoms	Angle (°)
C1 - C2	1.57(1)	C2 - C1 - C3	59.6(6)
C1 - C3	1.52(1)	C2 - C1 - C9	116.6(9)
C1 - C9	1.48(1)	C3 - C1 - C9	117.9(9)
C2 - C3	1.53(1)	C1 - C2 - C3	58.7(6)
C2 - C10	1.48(2)	C1 - C2 - C10	112.9(10)
C3 - C4	1.48(2)	C3 - C2 - C10	107.8(8)
C3 - C12	1.52(1)	C1 - C3 - C2	61.7(6)
C4 - C5	1.40(1)	C1 - C3 - C4	120.4(8)
C4 - C13	1.42(2)	C1 - C3 - C12	111.9(10)
C5 - C6	1.51(2)	C2 - C3 - C4	121.1(9)
C5 - C16	1.37(2)	C2 - C3 - C12	104.6(8)
C6 - C7	1.53(1)	C4 - C3 - C12	121.8(8)
C7 - C8	1.47(1)	C3 - C4 - C5	121.9(9)
C8 - C9	1.43(2)	C3 - C4 - C13	120.3(8)
C8 - C20	1.38(1)	C5 - C4 - C13	117.7(9)
C9 - C17	1.38(1)	C4 - C5 - C6	120.7(9)
C10 - O1	1.22(1)	C4 - C5 - C16	120.6(10)
C10 - C11	1.48(2)	C6 - C5 - C16	118.7(9)
C11 - C12	1.52(2)	C5 - C6 - C7	117.1(8)
C13 - C14	1.38(2)	C6 - C7 - C8	120.0(9)
C14 - C15	1.38(2)	C7 - C8 - C9	122.3(8)
C15 - C16	1.42(2)	C7 - C8 - C20	120.8(8)
C17 - C18	1.39(1)	C9 - C8 - C20	116.9(8)
C18 - C19	1.38(2)	C8 - C9 - C1	117.8(8)
C19 - C20	1.37(2)	C8 - C9 - C17	119.5(8)
		C1 - C9 - C17	122.4(8)
		C2 - C10 - O1	125.6(11)
		C2 - C10 - C11	109.5(9)
		O1 - C10 - C11	124.9(12)
		C10 - C11 - C12	104.0(11)
		C11 - C12 - C3	108.2(8)
		C4 - C13 - C14	121.3(9)
		C13 - C14 - C15	120.3(11)

TABLE 10 (Continued)

Atoms	Distance (Å)	Atoms	Angle (°)
		C14 - C15 - C16	118.8(10)
		C15 - C16 - C5	121.3(9)
		C9 - C17 - C18	121.8(10)
		C17 - C18 - C19	118.1(10)
		C18 - C19 - C20	120.6(10)
		C19 - C20 - C8	123.0(9)

TABLE 11

POSITIONAL PARAMETERS FOR (±)-(3a*R**,13bα,13cβ)-2,3,8,9,13b,13c-HEXAHYDRO-1*H*-DIBENZO[*a*,*e*]CYCLOPENTA[1,3]CYCLOPROPA-[1,2-*c*]CYCLOOCTEN-1-ONE $C_{20}H_{18}O$ (**20**)

Atom	X(Sig(X))	Y(Sig(Y))	Z(Sig(Z))
O1	-0.0956(15)	0.2644(11)	0.5465(6)
C1	0.0986(15)	0.4110(12)	0.3125(6)
C2	0.0845(14)	0.2862(12)	0.3960(6)
C3	0.0014(15)	0.2218(13)	0.2971(7)
C4	0.1082(13)	0.1344(10)	0.2353(7)
C5	0.1277(15)	0.1594(11)	0.1367(7)
C6	0.0373(14)	0.2768(12)	0.0893(6)
C7	0.1450(16)	0.4655(11)	0.1081(6)
C8	0.3276(15)	0.5253(10)	0.1701(6)
C9	0.3096(14)	0.5005(10)	0.2710(6)
C10	-0.0986(20)	0.2611(13)	0.4598(8)
C11	-0.2890(19)	0.2266(17)	0.4023(9)
C12	-0.2358(18)	0.1578(14)	0.3093(8)
C13	0.1871(15)	0.0152(12)	0.2746(7)
C14	0.2838(17)	-0.0702(12)	0.2179(9)
C15	0.3083(17)	-0.0397(12)	0.1214(9)
C16	0.2240(16)	0.0746(11)	0.0812(7)
C17	0.4844(18)	0.5719(13)	0.3264(7)
C18	0.6806(18)	0.6608(13)	0.2867(9)
C19	0.6975(18)	0.6787(12)	0.1887(9)
C20	0.5247(18)	0.6128(11)	0.1333(7)
H1	-0.0472	0.4722	0.3153
H2	0.2872	0.3371	0.4057
H13	0.1621	0.0000	0.3581
H14	0.3691	-0.1558	0.2405
H15	0.3420	-0.1169	0.0417
H16	0.2134	0.0949	0.0000
H17	0.4566	0.5440	0.4045
H18	0.8339	0.7060	0.3330
H19	0.8600	0.7417	0.1522
H20	0.5600	0.6166	0.0397
H61	0.0594	0.2782	0.0000
H62	-0.1195	0.2490	0.1029
H71	0.2205	0.5255	0.0359
H72	0.0407	0.5543	0.1252
H111	-0.4580	0.1372	0.4378
H112	-0.2747	0.3800	0.3985
H121	-0.3174	0.1708	0.2344
H122	-0.3074	0.0172	0.2812

TABLE 12

ANISOTROPIC THERMAL PARAMETERS FOR (±)-(3a*R**,13bα,13cβ)-2,3,8,9,13b,13c-HEXAHYDRO-1*H*-DIBENZO[*a*,*e*]CYCLOPENTA-[1,3]CYCLOPROPA[1,2-*c*]CYCLOOCTEN-1-ONE $C_{20}H_{18}O$ (**20**)

Atom	U11	U22	U33	U12	U13	U23
O1	162(8)	155(8)	71(5)	72(6)	28(6)	31(5)
C1	73(7)	65(7)	51(6)	30(6)	-4(5)	15(5)
C2	58(6)	77(7)	50(6)	19(5)	15(5)	20(5)
C3	44(6)	70(7)	62(6)	15(5)	0(5)	17(5)
C4	44(6)	43(5)	64(6)	10(4)	-8(5)	6(5)
C5	71(7)	44(6)	67(7)	16(5)	-10(5)	9(5)
C6	62(6)	64(6)	64(6)	24(5)	-10(5)	11(5)
C7	86(8)	50(6)	61(6)	21(5)	-15(6)	11(5)
C8	63(7)	38(5)	61(6)	25(5)	-1(5)	13(4)
C9	49(6)	45(5)	62(6)	22(5)	-1(5)	9(5)
C10	111(10)	75(7)	54(7)	46(7)	-2(7)	14(6)
C11	80(9)	137(11)	84(8)	39(8)	22(7)	14(8)
C12	77(9)	88(8)	93(8)	20(6)	0(7)	4(6)
C13	61(6)	46(5)	79(7)	7(5)	-16(6)	10(5)
C14	75(7)	42(6)	113(9)	30(5)	-18(7)	3(6)
C15	82(8)	49(6)	101(9)	15(6)	-11(7)	0(6)
C16	72(7)	44(6)	78(7)	14(6)	2(6)	6(5)
C17	71(8)	61(6)	69(7)	17(6)	-18(6)	11(5)
C18	60(7)	54(6)	131(11)	8(5)	-33(8)	-3(7)
C19	77(8)	59(7)	93(9)	13(6)	21(7)	15(6)
C20	67(7)	40(5)	71(7)	11(5)	0(6)	-2(5)

Anisotropic thermal parameters in the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)] \times 10^3$$

APPENDIX B

TABLES OF CRYSTALLOGRAPHIC DATA FOR (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYLCYCLOPROP[*a*]INDEN-3(1*H*)-ONE (**8**) AND (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYLCYCLOPROP[*a*]INDEN-3(1*H*)-ONE (**9**)

TABLE 13

DISTANCES FOR (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYLCYCLOPROP[*a*]INDEN-3(1*H*)-ONE $C_{23}H_{22}O$ (**8**)

Atoms	Molecule A Distance (Å)	Molecule B Distance (Å)
C1 - C2	1.556(5)	1.537(9)
C1 - C3	1.504(8)	1.519(9)
C1 - C6	1.536(11)	1.535(11)
C1 - C12	1.493(8)	1.464(8)
C2 - C3	1.562(5)	1.527(10)
C2 - C4	1.455(5)	1.484(10)
C3 - C18	1.462(8)	1.485(8)
C4 - C5	1.532(10)	1.526(10)
C4 - C7	1.321(9)	1.335(9)
C5 - C6	1.546(10)	1.544(10)
C5 - C10	1.525(10)	1.493(9)
C5 - C11	1.532(8)	1.540(8)
C7 - C8	1.461(11)	1.425(12)
C8 - O1	1.210(9)	1.214(9)
C8 - C9	1.515(12)	1.491(12)
C9 - C10	1.499(11)	1.533(11)
C12 - C13	1.382(11)	1.396(11)
C12 - C17	1.375(11)	1.407(11)
C13 - C14	1.385(10)	1.362(10)
C14 - C15	1.343(14)	1.392(15)
C15 - C16	1.390(15)	1.358(15)
C16 - C17	1.372(11)	1.416(10)
C18 - C19'	1.422(10)	1.374(8)
C18 - C23	1.368(8)	1.373(10)
C19' - C20	1.365(9)	1.388(9)
C20 - C21	1.375(11)	1.377(13)
C21 - C22	1.378(12)	1.359(12)
C22 - C23	1.382(9)	1.388(9)

TABLE 14

ANGLES FOR (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYLCYCLO-PROP[*a*]INDEN-3(1*H*)-ONE $C_{23}H_{22}O$ (8)

Atoms	Molecule A Angle (°)	Molecule B Angle (°)
C2 - C1 - C3	61.4(4)	59.9(4)
C2 - C1 - C6	106.6(5)	105.0(5)
C2 - C1 - C12	121.6(4)	123.7(6)
C3 - C1 - C6	116.9(5)	114.3(5)
C3 - C1 - C12	119.0(6)	118.6(6)
C6 - C1 - C12	118.2(5)	120.5(6)
C1 - C2 - C3	57.7(5)	59.4(4)
C1 - C2 - C4	107.0(4)	108.0(6)
C3 - C2 - C4	118.2(3)	118.4(5)
C1 - C3 - C18	125.1(6)	126.0(6)
C2 - C3 - C18	124.5(5)	124.9(6)
C1 - C3 - C2	60.9(5)	60.6(4)
C2 - C4 - C5	108.6(5)	108.8(5)
C2 - C4 - C7	127.2(5)	128.8(7)
C5 - C4 - C7	124.0(7)	122.4(6)
C4 - C5 - C6	103.7(5)	102.5(6)
C4 - C5 - C10	109.1(5)	110.0(5)
C4 - C5 - C11	107.8(5)	106.9(5)
C6 - C5 - C10	115.2(6)	115.8(6)
C6 - C5 - C11	108.5(4)	107.4(4)
C10 - C5 - C11	111.9(6)	113.4(6)
C1 - C6 - C5	104.9(6)	107.2(6)
C4 - C7 - C8	120.2(7)	121.8(7)
C7 - C8 - O1	121.3(8)	122.0(8)
C9 - C8 - O1	120.4(8)	119.7(8)
C7 - C8 - C9	118.2(6)	118.3(6)
C8 - C9 - C10	115.0(7)	114.8(7)
C9 - C10 - C5	111.0(6)	110.6(6)
C1 - C12 - C13	122.7(6)	120.2(6)
C1 - C12 - C17	120.5(7)	121.8(6)
C13 - C12 - C17	116.8(6)	117.9(6)
C12 - C13 - C14	120.6(8)	122.3(8)
C13 - C14 - C15	121.2(9)	119.2(8)
C14 - C15 - C16	119.8(7)	120.4(7)
C15 - C16 - C17	118.4(8)	120.3(9)

TABLE 14 (Continued)

Atoms	Molecule A Angle (°)	Molecule B Angle (°)
C16 - C17 - C12	123.2(8)	119.3(8)
C3 - C18 - C19	119.6(5)	121.8(6)
C3 - C18 - C23	122.8(6)	120.4(5)
C19 - C18 - C23	117.3(5)	117.6(5)
C18 - C19 - C20	119.7(6)	120.6(7)
C19 - C20 - C21	122.0(8)	121.4(6)
C20 - C21 - C22	118.7(6)	117.9(6)
C21 - C22 - C23	119.8(6)	121.0(8)
C22 - C23 - C18	122.4(7)	121.5(6)

TABLE 15

POSITIONAL PARAMETERS FOR (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYLCYCLO-PROP[*a*]INDEN-3(1*H*)-ONE $C_{23}H_{22}O$ (**8**)

Atom	X(Sig(X))	Y(Sig(Y)	Z(Sig(Z)
O1	-0.2024(7)	-0.4494(5)	0.4731(6)
O19	0.3072(7)	0.0109(6)	0.0274(6)
C1	-0.3217(7)	0.0718(6)	0.7965(7)
C2	-0.2659	0.0057	0.6601
C3	-0.4249(7)	0.0421(6)	0.6461(7)
C4	-0.2582(6)	-0.1312(6)	0.6579(7)
C5	-0.2566(7)	-0.1399(6)	0.8105(6)
C6	-0.3480(7)	-0.0362(7)	0.8707(6)
C7	-0.2450(7)	-0.2314(7)	0.5480(7)
C8	-0.2297(7)	-0.3611(7)	0.5670(8)
C9	-0.2470(8)	-0.3823(7)	0.7089(9)
C10	-0.3244(8)	-0.2866(7)	0.7956(8)
C11	-0.0907(8)	-0.0889(8)	0.9049(8)
C12	-0.2538(7)	0.2164(7)	0.8920(7)
C13	-0.1530(9)	0.3052(7)	0.8556(8)
C14	-0.0947(10)	0.4391(9)	0.9467(10)
C15	-0.1330(11)	0.4861(8)	1.0730(9)
C16	-0.2363(11)	0.4004(10)	1.1119(10)
C17	-0.2930(9)	0.2680(8)	1.0207(9)
C18	-0.5721(7)	-0.0576(6)	0.5834(7)
C19*	-.6885(7)	-.0472(7)	0.6586(7)
C20	-0.8299(8)	-0.1339(8)	0.5952(9)
C21	-0.8653(8)	-0.2304(8)	0.4582(9)
C22	-0.7544(8)	-0.2394(7)	0.3830(8)
C23	-0.6101(8)	-0.1536(7)	0.4468(7)
C19	0.2008(7)	0.3623(6)	0.5706(7)
C29	0.2593(7)	0.2342(6)	0.5139(7)
C39	0.1051(7)	0.2232(6)	0.5505(7)
C49	0.2620(6)	0.2152(6)	0.3595(7)
C59	0.2489(6)	0.3469(6)	0.3287(7)
C69	0.1612(7)	0.4108(6)	0.4382(7)
C79	0.2747(7)	0.1055(6)	0.2582(8)
C89	0.2805(7)	0.1054(7)	0.1150(8)
C99	0.2514(9)	0.2254(8)	0.0728(8)
C109	0.1726(8)	0.3161(7)	0.1702(7)
C119	0.4120(8)	0.4384(7)	0.3782(8)
C129	0.2623(7)	0.4609(6)	0.7193(7)
C139	0.2170(9)	0.5833(8)	0.7569(9)
C149	0.2718(10)	0.6785(8)	0.8935(10)
C159	0.3713(12)	0.6508(10)	1.0019(10)
C169	0.4178(10)	0.5327(10)	0.9718(9)
C179	0.3643(9)	0.4348(8)	0.8292(8)
C189	-0.0455(7)	0.1537(6)	0.4424(6)
C199	-0.0763(7)	0.0201(6)	0.3543(7)
C209	-0.2219(9)	-0.0460(7)	0.2636(8)
C219	-0.3399(8)	0.0190(9)	0.2595(8)
C229	-0.3094(8)	0.1508(9)	0.3474(9)

TABLE 15 (Continued)

Atom	X(Sig(X))	Y(Sig(Y)	Z(Sig(Z)
C239	-0.1636(8)	0.2180(7)	0.4372(8)
H2	-0.1744	0.0725	0.6353
H3	-0.4002	0.1400	0.6499
H7	-0.2508	0.2300	0.4527
H13	-0.1223	0.2618	0.7540
H14	-0.0196	0.5009	0.9187
H15	-0.0838	0.5771	1.1624
H16	-0.2971	0.4600	1.1859
H17	-0.3731	0.1982	1.0570
H19*	-.6592	0.0276	0.7668
H20	-0.9238	-0.1400	0.6392
H21	-0.9700	-0.2931	0.4115
H22	-0.7875	-0.3206	0.2857
H23	-0.5152	-0.1628	0.3891
H29	0.3705	0.1977	0.5663
H61	-0.3070	0.0122	0.9832
H62	-0.4610	-0.0884	0.8544
H79	0.2852	0.0200	0.2832
H91	-0.1163	-0.3800	0.7296
H92	-0.2698	-0.4800	0.6901
H101	-0.3170	-0.3150	0.8841
H102	-0.4527	-0.3151	0.7392
H111	0.0000	-0.1408	0.8858
H112	-0.0378	0.0000	0.9089
H113	-0.0662	-0.0597	1.0168
H139	0.1515	0.5800	0.6617
H149	0.2024	0.7600	0.9513
H159	0.4057	0.7172	1.1010
H169	0.5066	0.5016	1.0428
H179	0.4612	0.3773	0.7767
H199	0.0206	-0.0262	0.3677
H209	-0.2496	-0.1529	0.2019
H219	-0.4437	-0.0473	0.1670
H229	-0.4025	0.2030	0.3542
H239	-0.1316	0.3222	0.4972
H391	0.1213	0.2008	0.6455
H591	0.4035	0.4983	0.3135
H592	0.4658	0.4642	0.4792
H593	0.4940	0.4172	0.3253
H691	0.1884	0.5060	0.4612
H692	0.0434	0.3938	0.3965
H991	0.1983	0.2067	-0.0393
H992	0.3628	0.2790	0.0793
H1091	0.0536	0.2660	0.1478
H1092	0.1673	0.3807	0.1130

TABLE 16

ANISOTROPIC THERMAL PARAMETERS FOR (±)-(1α,1aβ,5aβ,6aβ)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYL-CYCLOPROP[*a*]INDEN-3(1*H*)-ONE $C_{23}H_{22}O$ (**8**)

Atom	U11	U22	U33	U12	U13	U23
O1	97(4)	66(3)	96(3)	33(2)	41(3)	16(2)
O19	98(4)	75(3)	80(3)	32(3)	37(3)	13(3)
C1	50(3)	49(3)	52(3)	17(2)	23(2)	19(3)
C2	54(3)	55(3)	48(3)	18(3)	24(3)	25(3)
C3	56(3)	46(3)	50(3)	18(2)	21(3)	24(3)
C4	35(3)	50(3)	49(3)	7(2)	16(2)	21(3)
C5	38(3)	55(3)	43(3)	8(2)	9(2)	25(2)
C6	51(3)	60(3)	37(3)	17(3)	22(2)	19(2)
C7	45(3)	58(4)	61(4)	19(3)	25(3)	23(3)
C8	47(3)	57(4)	58(4)	18(3)	16(3)	10(3)
C9	69(4)	50(3)	81(5)	27(3)	19(3)	28(3)
C10	63(4)	59(4)	61(4)	14(3)	20(3)	36(3)
C11	45(3)	73(4)	58(4)	15(3)	3(3)	24(3)
C12	54(3)	57(3)	48(3)	22(3)	11(3)	22(3)
C13	84(5)	44(4)	66(4)	16(3)	14(3)	18(3)
C14	83(5)	73(5)	91(5)	11(4)	1(4)	46(4)
C15	101(6)	61(5)	70(5)	27(4)	-15(4)	-3(4)
C16	101(6)	82(6)	79(5)	36(5)	25(4)	-2(4)
C17	72(5)	77(5)	64(4)	18(4)	31(4)	4(4)
C18	49(3)	52(3)	50(3)	25(3)	18(2)	29(3)
C19*	52(3)	64(4)	54(3)	23(3)	19(3)	19(3)
C20	40(3)	86(5)	86(5)	21(3)	27(3)	41(4)
C21	45(3)	68(4)	87(5)	11(3)	4(3)	36(4)
C22	62(4)	45(4)	67(4)	8(3)	2(3)	16(3)
C23	52(4)	64(4)	56(3)	23(3)	15(3)	27(3)
C19	46(3)	44(3)	63(4)	20(2)	23(3)	21(3)
C29	51(3)	43(3)	56(3)	21(2)	19(3)	24(3)
C39	53(3)	47(3)	52(3)	18(3)	18(3)	23(3)
C49	34(3)	42(3)	55(3)	14(2)	17(2)	17(2)
C59	37(3)	35(3)	57(3)	10(2)	18(2)	18(2)
C69	55(3)	44(3)	67(4)	26(3)	28(3)	28(3)
C79	47(3)	44(3)	73(4)	20(2)	19(3)	25(3)
C89	47(3)	59(4)	63(4)	15(3)	24(3)	8(3)
C99	74(4)	57(4)	56(4)	12(3)	21(3)	18(3)
C109	62(4)	62(4)	59(4)	24(3)	21(3)	33(3)
C119	48(3)	56(4)	65(4)	0(3)	15(3)	18(3)
C129	55(3)	37(3)	59(4)	5(2)	21(3)	12(3)
C139	79(5)	66(5)	67(4)	21(4)	23(4)	14(4)
C149	77(5)	68(5)	74(5)	11(4)	23(4)	0(4)
C159	96(6)	70(6)	84(6)	-24(5)	38(5)	0(5)
C169	89(6)	81(6)	68(5)	-2(5)	10(4)	21(4)
C179	74(5)	70(4)	54(4)	10(4)	18(3)	25(3)
C189	48(3)	46(3)	44(3)	7(2)	18(2)	21(2)
C199	57(4)	43(3)	51(3)	9(3)	20(3)	19(3)
C209	81(5)	56(4)	50(4)	-2(4)	23(3)	20(3)
C219	51(4)	98(6)	57(4)	3(4)	15(3)	38(4)
C229	52(4)	76(5)	71(4)	23(3)	17(3)	36(4)
C239	48(4)	66(4)	75(4)	20(3)	29(3)	28(3)

TABLE 17

BOND ANGLES AND DISTANCES FOR (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYLCYCLO-PROP[*a*]INDEN-3(1*H*)-ONE $C_{23}H_{22}O$ (**9**)

Atoms	Distance (Å)	Atoms	Angle (°)
C1 - C2	1.510(6)	C2 - C1 - C3	60.9(3)
C1 - C3	1.513(6)	C2 - C1 - C6	106.3(3)
C1 - C6	1.548(6)	C2 - C1 - C12	122.9(4)
C1 - C12	1.497(6)	C3 - C1 - C6	112.4(4)
C2 - C3	1.532(6)	C3 - C1 - C12	122.6(4)
C2 - C4	1.478(6)	C6 - C1 - C12	119.0(4)
C3 - C18	1.495(6)	C1 - C2 - C3	59.6(3)
C4 - C5	1.517(6)	C1 - C2 - C4	108.7(4)
C4 - C7	1.327(6)	C3 - C2 - C4	114.7(4)
C5 - C6	1.546(6)	C1 - C3 - C2	59.4(3)
C5 - C10	1.534(7)	C1 - C3 - C18	124.4(4)
C5 - C11	1.541(7)	C2 - C3 - C18	120.4(4)
C7 - C8	1.466(6)	C2 - C4 - C5	109.3(4)
C8 - O1	1.226(6)	C2 - C4 - C7	127.8(4)
C8 - C9	1.505(8)	C5 - C4 - C7	123.0(4)
C9 - C10	1.527(7)	C4 - C5 - C6	104.4(4)
C12 - C13	1.381(7)	C4 - C5 - C10	108.7(4)
C13 - C14	1.405(7)	C4 - C5 - C11	107.5(4)
C14 - C15	1.385(8)	C6 - C5 - C10	114.5(4)
C15 - C16	1.392(8)	C6 - C5 - C11	109.6(4)
C16 - C17	1.376(7)	C10 - C5 - C11	111.7(4)
C17 - C12	1.395(7)	C1 - C6 - C5	106.6(4)
C18 - C19	1.390(7)	C4 - C7 - C8	120.3(4)
C19 - C20	1.396(7)	C7 - C8 - C9	118.5(4)
C20 - C21	1.362(8)	C8 - C9 - C10	115.4(4)
C21 - C22	1.382(7)	C9 - C10 - C5	110.6(4)
C22 - C23	1.379(7)	C1 - C12 - C13	120.6(4)
C23 - C18	1.383(7)	C1 - C12 - C17	121.6(4)
		C13 - C12 - C17	117.8(4)
		C12 - C13 - C14	121.8(5)
		C13 - C14 - C15	119.3(5)
		C14 - C15 - C16	119.2(5)
		C15 - C16 - C17	120.8(5)

TABLE 17 (Continued)

Atoms	Distance (Å)	Atoms	Angle (°)
		C16 - C17 - C12	121.2(4)
		C3 - C18 - C19	117.5(4)
		C3 - C18 - C23	124.6(4)
		C19 - C18 - C23	117.8(4)
		C18 - C19 - C20	121.2(4)
		C19 - C20 - C21	119.3(5)
		C20 - C21 - C22	120.7(4)
		C21 - C22 - C23	119.6(5)
		C22 - C23 - C18	121.4(4)

TABLE 18

POSITIONAL PARAMETERS FOR (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYLCYCLOPROP[*a*]INDEN-3(1*H*)-ONE $C_{23}H_{22}O$ (**9**)

Atom	X(Sig(X))	Y(Sig(Y))	Z(Sig(Z))
O1	0.5100(3)	0.3191(7)	-0.0782(1)
C1	0.8152(3)	-0.0068(8)	0.0957(2)
C2	0.7268(3)	0.1681(8)	0.0866(2)
C3	0.7087(3)	-0.0530(8)	0.1221(2)
C4	0.6897(3)	0.1497(8)	0.0278(2)
C5	0.7667(3)	-0.0001(9)	-0.0053(2)
C6	0.8273(4)	-0.1427(9)	0.0398(2)
C7	0.6036(4)	0.2446(8)	0.0052(2)
C8	0.5768(4)	0.2002(9)	-0.0537(2)
C9	0.6332(4)	0.0046(10)	-0.0839(2)
C10	0.7040(4)	-0.1505(9)	-0.0472(2)
C11	0.8436(4)	0.1684(10)	-0.0352(2)
C12	0.9121(3)	0.0482(8)	0.1296(2)
C13	0.9509(4)	-0.1116(9)	0.1682(2)
C14	1.0442(4)	-0.0688(10)	0.1988(2)
C15	1.0995(4)	0.1383(11)	0.1898(2)
C16	1.0603(4)	0.3008(9)	0.1513(2)
C17	0.9684(4)	0.2569(9)	0.1219(2)
C18	0.6865(3)	-0.0327(9)	0.1835(2)
C19	0.6250(4)	-0.2075(9)	0.2079(2)
C20	0.6000(4)	-0.2011(10)	0.2649(2)
C21	0.6355(4)	-0.0184(10)	0.2969(2)
C22	0.6959(4)	0.1587(10)	0.2736(2)
C23	0.7211(4)	0.1499(9)	0.2174(2)
H2	0.7291	0.3243	0.1052
H3	0.6473	-0.1359	0.1048
H7	0.5577	0.3469	0.0290
H13	0.9117	-0.2567	0.1749
H16	1.0992	0.4577	0.1463
H17	0.9379	0.3740	0.0943
H19	0.5975	-0.3382	0.1844
H20	0.5559	-0.3297	0.2805
H21	0.6167	-0.0103	0.3370
H22	0.7237	0.2838	0.2977
H23	0.7620	0.2788	0.1997
H61	0.9028	-0.1568	0.0298
H62	0.7987	-0.3012	0.0432
H91	0.6760	0.0627	-0.1143
H92	0.5788	-0.1039	-0.1011
H101	0.7524	-0.2426	-0.0695
H102	0.6595	-0.2618	-0.0254
H111	0.8943	0.0770	-0.0532
H112	0.8128	0.2939	-0.0617
H113	0.8932	0.2602	-0.0036

TABLE 19

ANISOTROPIC THERMAL PARAMETERS FOR (±)-(1α,1aα,5aα,6aα)-1a,4,5,5a,6,6a-HEXAHYDRO-5a-METHYL-1,6a-DIPHENYL-CYCLOPROP[*a*]INDEN-3(1*H*)-ONE $C_{23}H_{22}O$ (**9**)

Atom	U11	U22	U33	U12	U13	U23
O1	59(2)	72(2)	46(2)	15(2)	-13(1)	4(2)
C1	33(2)	37(2)	36(2)	5(2)	2(2)	-3(2)
C2	40(2)	33(2)	30(2)	6(2)	0(2)	-3(2)
C3	30(2)	47(3)	34(2)	1(2)	-4(2)	0(2)
C4	35(2)	36(2)	30(2)	2(2)	0(2)	-2(2)
C5	37(2)	41(3)	33(2)	5(2)	7(2)	1(2)
C6	45(2)	41(3)	43(3)	10(2)	3(2)	-7(2)
C7	44(2)	43(3)	28(2)	4(2)	4(2)	0(2)
C8	45(3)	50(3)	39(2)	3(2)	0(2)	5(2)
C9	66(3)	64(3)	38(3)	3(3)	1(2)	-2(3)
C10	56(3)	48(3)	35(2)	6(2)	2(2)	-4(2)
C11	52(3)	52(3)	54(3)	4(2)	18(2)	-1(2)
C12	34(2)	39(3)	34(2)	5(2)	0(2)	-2(2)
C13	40(2)	47(3)	45(3)	-1(2)	0(2)	1(2)
C14	41(3)	64(3)	51(3)	5(3)	-4(2)	-2(2)
C15	47(3)	63(4)	53(3)	2(3)	0(2)	-10(3)
C16	44(3)	41(3)	72(3)	-9(2)	5(2)	-13(3)
C17	44(2)	39(3)	51(3)	5(2)	-1(2)	0(2)
C18	30(2)	43(3)	32(2)	0(2)	-6(2)	-2(2)
C19	42(2)	40(3)	41(3)	-5(2)	0(2)	-1(2)
C20	48(3)	62(4)	48(3)	-5(2)	8(2)	16(3)
C21	51(3)	60(3)	32(2)	1(3)	3(2)	0(2)
C22	51(3)	54(3)	40(3)	-8(2)	0(2)	-9(2)
C23	43(2)	46(3)	39(2)	-5(2)	8(2)	0(2)

Anisotropic thermal parameters in the form:

$$\exp[-2\pi^2(U11h^2a^{*2} + U22k^2b^{*2} + U331^2c^{*2} + 2U12hka^*b^* + 2U13h1a^*c^* + 2U23k1b^*c^*0] \times 10^3$$

APPENDIX C

TABLES OF CRYSTALLOGRAPHIC DATA FOR (5aβ,5bβ,10aα,10bα)-DODECA-HYDRO-5,5,6,6-TETRAPHENYLCYCLOBUTA[1,2:3,4]DICYCLO-HEPTENE-1,10-DIONE (**18**) AND (±)-(5aβ,5bα,10aβ,10bα)-DODECAHYDRO-5,5,6,6-TETRAPHENYLCYCLOBUTA-[1,2:3,4]DICYCLOHEPTENE-1,10-DIONE (**19**)

TABLE 20

BOND ANGLES AND DISTANCES FOR (5aβ,5bβ,10aα,10bα)-DODECAHYDRO-5,5,6,6-TETRAPHENYLCYCLOBUTA[1,2:3,4]DICYCLOHEPTENE-1,10-DIONE $C_{36}H_{38}O_2$ (**18**) AND (±)-(5aβ, 5bα,10aβ,10bα)-DODECAHYDRO-5,5,6,6-TETRAPHENYLCYCLOBUTA[1,2:3,4]DICYCLOHEPTENE-1,10-DIONE $C_{36}H_{38}O_2$ (**19**)

Atoms	Distance (Å) **18**	Distance (Å) **19**	Atoms	Angle (°) **18**	Angle (°) **19**
C1 - O1	1.221(6)	1.211(5)	C10b - C1 - O1	123.0(5)	121.2(4)
C1 - C2	1.513(9)	1.507(7)	C10b - C1 - C2	115.6(4)	117.2(4)
C1 - C10b	1.491(7)	1.490(7)	O1 - C1 - C2	121.2(5)	121.6(5)
C2 - C3	1.524(8)	1.528(5)	C1 - C2 - C3	117.6(5)	115.1(4)
C3 - C4	1.537(8)	1.541(7)	C2 - C3 - C4	117.8(4)	115.1(3)
C4 - C5	1.565(7)	1.554(6)	C3 - C4 - C5	118.2(5)	114.2(3)
C5 - C5a	1.568(6)	1.581(4)	C4 - C5 - C5a	102.8(4)	107.2(3)
C5 - C11	1.533(7)	1.541(6)	C4 - C5 - C11	110.5(4)	107.5(3)
C5 - C17	1.523(8)	1.538(4)	C4 - C5 - C17	105.6(4)	109.6(3)
C5a - C5b	1.610(7)	1.587(6)	C5a - C5 - C11	114.2(4)	112.9(3)
C5a - C10b	1.570(7)	1.566(5)	C5a - C5 - C17	113.5(3)	109.6(2)
C5b - C6	1.552(6)	1.571(5)	C11 - C5 - C17	109.6(4)	109.9(3)
C5b - C10a	1.546(7)	1.569(5)	C5 - C5a - C5b	140.4(4)	127.4(3)
C6 - C7	1.553(7)	1.563(5)	C5 - C5a - C10b	111.9(3)	115.3(3)
C6 - C23	1.538(6)	1.538(6)	C5b - C5a - C10b	85.7(4)	87.8(2)
C6 - C29	1.546(7)	1.557(6)	C5a - C5b - C6	137.6(4)	127.3(3)
C7 - C8	1.536(7)	1.531(6)	C5a - C5b - C10a	90.1(3)	88.0(3)
C8 - C9	1.536(7)	1.528(6)	C6 - C5b - C10a	117.4(4)	115.4(3)
C9 - C10	1.501(6)	1.505(7)	C5b - C6 - C7	103.9(4)	106.8(2)
C10 - O2	1.211(7)	1.214(5)	C5b - C6 - C23	114.2(3)	113.2(4)
C10 - C10a	1.517(7)	1.499(5)	C5b - C6 - C29	112.2(4)	111.3(3)
C10a - C10b	1.536(7)	1.522(6)	C7 - C6 - C23	110.0(4)	107.9(3)
C11 - C12	1.389(8)	1.400(5)	C7 - C6 - C29	107.0(3)	106.6(4)
C12 - C13	1.385(7)	1.394(7)	C23 - C6 - C29	108.8(4)	110.7(3)
C13 - C14	1.391(7)	1.383(7)	C6 - C7 - C8	115.5(5)	115.3(3)
C14 - C15	1.359(9)	1.374(8)	C7 - C8 - C9	116.7(4)	114.6(4)
C15 - C16	1.390(8)	1.370(8)	C8 - C9 - C10	116.6(4)	116.1(3)
C16 - C11	1.396(6)	1.401(6)	C9 - C10 - O2	122.0(5)	122.0(4)
C17 - C18	1.382(7)	1.388(6)	C9 - C10 - C10a	119.6(4)	116.6(3)
C18 - C19	1.395(9)	1.393(5)	O2 - C10 - C10a	118.4(4)	121.3(4)
C19 - C20	1.378(8)	1.363(6)	C10 - C10a - C10b	119.7(4)	118.0(3)
C20 - C21	1.350(10)	1.379(7)	C10 - C10a - C5b	117.1(3)	117.8(4)
C21 - C22	1.389(9)	1.385(6)	C5b - C10a - C10b	89.2(4)	90.0(2)
C22 - C17	1.396(7)	1.386(6)	C10a - C10b - C5a	92.0(3)	90.5(2)

TABLE 20 (Continued)

Atoms	Distance (Å) **18**	Distance (Å) **19**	Atoms	Angle (°) **18**	Angle (°) **19**
C23 - C24	1.367(8)	1.408(7)	C10a - C10b - C1	121.9(4)	119.2(3)
C24 - C25	1.401(7)	1.379(7)	C5a - C10b - C1	107.8(4)	113.9(3)
C25 - C26	1.375(9)	1.370(7)	C5 - C17 - C18	120.6(4)	120.2(3)
C26 - C27	1.374(9)	1.377(8)	C5 - C17 - C22	121.8(4)	122.9(3)
C27 - C28	1.396(7)	1.400(7)	C18 - C17 - C22	117.5(5)	116.8(3)
C28 - C23	1.402(7)	1.396(5)	C17 - C18 - C19	121.7(5)	121.7(4)
C29 - C30	1.400(6)	1.382(5)	C18 - C19 - C20	119.2(5)	120.4(4)
C30 - C31	1.365(8)	1.392(7)	C19 - C20 - C21	120.0(6)	118.9(4)
C31 - C32	1.378(9)	1.386(7)	C20 - C21 - C22	121.4(5)	120.7(4)
C32 - C33	1.374(8)	1.380(6)	C21 - C22 - C17	120.2(5)	121.4(4)
C33 - C34	1.397(8)	1.380(7)	C5 - C11 - C12	120.6(4)	121.4(3)
C34 - C29	1.371(8)	1.403(6)	C5 - C11 - C16	122.3(5)	121.4(3)
			C12 - C11 - C16	117.0(4)	117.2(4)
			C11 - C12 - C13	121.6(4)	121.1(4)
			C12 - C13 - C14	119.9(5)	119.6(4)
			C13 - C14 - C15	119.7(4)	119.7(5)
			C14 - C15 - C16	120.2(4)	120.9(5)
			C15 - C16 - C11	121.6(5)	121.2(4)
			C6 - C23 - C24	123.5(4)	120.7(3)
			C6 - C23 - C28	118.3(4)	123.3(4)
			C24 - C23 - C28	118.2(4)	116.0(4)
			C23 - C24 - C25	121.5(5)	122.0(4)
			C24 - C25 - C26	119.9(6)	121.0(5)
			C25 - C26 - C27	119.6(5)	118.9(5)
			C26 - C27 - C28	120.6(5)	120.7(4)
			C27 - C28 - C23	120.2(5)	121.4(4)
			C6 - C29 - C30	117.4(5)	123.1(4)
			C6 - C29 - C34	124.3(4)	119.4(3)
			C30 - C29 - C34	118.3(5)	117.5(4)
			C29 - C30 - C31	121.0(5)	118.9(5)
			C30 - C31 - C32	120.4(5)	120.4(4)
			C31 - C32 - C33	119.6(5)	119.9(5)
			C32 - C33 - C34	120.0(5)	120.6(4)
			C33 - C34 - C29	120.7(4)	121.2(4)

TABLE 21

POSITIONAL PARAMETERS FOR (5aβ,5bβ,10aα,10bα)-DODECA-HYDRO-5,5,6,6-TETRAPHENYLCYCLOBUTA[1,2:3,4]-DICYCLOHEPTENE-1,10-DIONE $C_{36}H_{38}O_2$ (18)

Atom	X(Sig(X))	Y(Sig(Y)	Z(Sig(Z)
O1	0.2579(5)	0.7885(1)	0.7124(5)
O2	0.0548(5)	0.7457(2)	0.8737(4)
C1	0.3649(6)	0.7641(2)	0.7629(5)
C2	0.5156(7)	0.7785(2)	0.7618(6)
C3	0.6437(6)	0.7468(2)	0.8316(6)
C4	0.6506(5)	0.6995(2)	0.7668(5)
C5	0.5494(5)	0.6599(2)	0.7881(5)
C5A	0.3921(5)	0.6806(2)	0.7248(4)
C5B	0.2226(5)	0.6657(2)	0.6863(4)
C6	0.1306(5)	0.6207(2)	0.6489(5)
C7	-0.0231(5)	0.6351(2)	0.6535(6)
C8	-0.0885(5)	0.6787(2)	0.5721(5)
C9	-0.0387(6)	0.7254(2)	0.6413(5)
C10	0.0714(6)	0.7240(2)	0.7803(5)
C10A	0.2077(5)	0.6944(2)	0.8063(5)
C10B	0.3554(5)	0.7174(2)	0.8200(5)
C11	0.5888(5)	0.6477(2)	0.9385(5)
C12	0.4918(5)	0.6229(2)	0.9862(5)
C13	0.5296(6)	0.6084(2)	1.1194(5)
C14	0.6667(6)	0.6192(2)	1.2092(6)
C15	0.7629(6)	0.6440(2)	1.1656(6)
C16	0.7254(6)	0.6579(2)	1.0314(6)
C17	0.5796(5)	0.6184(2)	0.7107(5)
C18	0.5218(6)	0.6164(2)	0.5715(5)
C19	0.5507(6)	0.5793(2)	0.4980(6)
C20	0.6400(7)	0.5440(2)	0.5660(7)
C21	0.6990(7)	0.5456(2)	0.7017(7)
C22	0.6690(6)	0.5819(2)	0.7762(5)
C23	0.1906(5)	0.5800(2)	0.7458(5)
C24	0.1436(6)	0.5697(2)	0.8531(5)
C25	0.2029(6)	0.5326(2)	0.9396(6)
C26	0.3070(6)	0.5047(2)	0.9145(6)
C27	0.3554(5)	0.5143(2)	0.8069(5)
C28	0.2978(5)	0.5516(2)	0.7216(5)
C29	0.1114(5)	0.6047(2)	0.5029(5)
C30	0.0351(5)	0.5634(2)	0.4595(5)
C31	0.0128(6)	0.5471(2)	0.3317(6)
C32	0.0636(6)	0.5714(2)	0.2421(5)
C33	0.1388(6)	0.6121(2)	0.2825(5)
C34	0.1605(5)	0.6290(2)	0.4128(5)
H2(1)	0.4923	0.7829	0.6479
H2(2)	0.5202	0.8143	0.8058
H3(1)	0.7309	0.7652	0.8180
H3(2)	0.6514	0.7431	0.9340
H4(1)	0.7601	0.6927	0.8009
H4(2)	0.6143	0.7028	0.6505
H5A	0.4048	0.6966	0.6430

TABLE 21 (Continued)

Atom	X(Sig(X))	Y(Sig(Y)	Z(Sig(Z)
H5B	0.1719	0.6840	0.5972
H7(1)	-0.0223	0.6405	0.7585
H7(2)	-0.1117	0.6254	0.6365
H8(1)	-0.2088	0.6804	0.5440
H8(2)	-0.0783	0.6777	0.4742
H9(1)	-0.1255	0.7430	0.6576
H9(2)	0.0151	0.7465	0.5751
H10A	0.2201	0.6732	0.9016
H10B	0.4221	0.7172	0.9229
H12	0.3853	0.6169	0.9124
H13	0.4538	0.5861	1.1537
H14	0.6937	0.6012	1.3014
H15	0.8687	0.6460	1.2451
H16	0.8049	0.6776	0.9995
H18	0.4426	0.6410	0.5275
H19	0.4866	0.5771	0.3969
H20	0.6492	0.5179	0.4989
H21	0.7609	0.5183	0.7437
H22	0.7322	0.5811	0.8923
H24	0.0543	0.5862	0.8857
H25	0.1417	0.5179	1.0019
H26	0.3510	0.4786	0.9858
H27	0.4559	0.4973	0.7781
H28	0.3282	0.5594	0.6359
H30	0.0152	0.5419	0.5411
H31	-0.0418	0.5186	0.3028
H32	0.0510	0.5587	0.1409
H33	0.1507	0.6374	0.2185
H34	0.2198	0.6614	0.4581

TABLE 22

POSITIONAL PARAMETERS FOR (±)-(5aβ,5bα,10aβ,10bα)DODECA-HYDRO-5,5,6,6-TETRAPHENYLCYCLOBUTA[1,2:3,4]-DICYCLOHEPTENE-1,10-DIONE $C_{36}H_{38}O_2$ (**19**)

Atom	X(Sig(X))	Y(Sig(Y)	Z(Sig(Z)
O1	0.5446(4)	0.3325(4)	0.0551(2)
O2	0.6288(3)	0.5810(3)	0.2471(3)
C1	0.5380(4)	0.2686(4)	0.1379(3)
C2	0.5801(4)	0.1385(4)	0.1783(3)
C3	0.4848(4)	0.0195(4)	0.2462(3)
C4	0.4706(4)	0.0551(4)	0.3357(3)
C5	0.3405(4)	0.0977(4)	0.3276(2)
C5A	0.3409(4)	0.2193(4)	0.2334(2)
C5B	0.3043(4)	0.3575(4)	0.2191(2)
C6	0.1681(4)	0.3897(4)	0.1663(2)
C7	0.2114(4)	0.5483(4)	0.1123(3)
C8	0.3051(4)	0.6487(4)	0.1723(3)
C9	0.4593(4)	0.6906(4)	0.1649(3)
C10	0.5202(4)	0.5730(4)	0.1961(3)
C10A	0.4359(4)	0.4416(4)	0.1657(2)
C10B	0.4873(4)	0.3155(4)	0.2042(2)
C11	0.3497(4)	0.1437(4)	0.4181(2)
C12	0.4572(4)	0.2596(4)	0.4397(3)
C13	0.4604(5)	0.3057(5)	0.5185(3)
C14	0.3576(6)	0.2342(6)	0.5779(3)
C15	0.2553(6)	0.1163(6)	0.5600(3)
C16	0.2513(4)	0.0707(5)	0.4825(3)
C17	0.2097(4)	-0.0285(4)	0.3207(2)
C18	0.0840(4)	-0.0079(4)	0.2803(3)
C19	-0.0377(4)	-0.1198(4)	0.2772(3)
C20	-0.0361(5)	-0.2541(4)	0.3140(3)
C21	0.0879(5)	-0.2773(4)	0.3530(4)
C22	0.2088(4)	-0.1661(4)	0.3570(3)
C23	0.0921(4)	0.3047(4)	0.0925(3)
C24	0.1554(4)	0.3203(4)	0.0134(3)
C25	0.0900(5)	0.2454(5)	-0.0538(3)
C26	-0.0413(6)	0.1529(5)	-0.0468(3)
C27	-0.1070(5)	0.1344(5)	0.0294(4)
C28	-0.0416(4)	0.2099(4)	0.0980(3)
C29	0.0696(4)	0.3692(4)	0.2383(3)
C30	0.0895(4)	0.3059(4)	0.3343(3)
C31	0.0014(5)	0.2939(5)	0.3967(3)
C32	-0.1086(4)	0.3462(5)	0.3637(3)
C33	-0.1298(4)	0.4090(5)	0.2680(3)
C34	-0.0437(4)	0.4192(4)	0.2059(3)
H2(1)	0.6827	0.1567	0.2325
H2(2)	0.5871	0.1059	0.1228
H3(1)	0.3809	-0.0190	0.2054
H3(2)	0.5153	-0.0647	0.2641
H4(1)	0.4690	-0.0302	0.3965
H4(2)	0.5609	0.1289	0.3569
H5A	0.2792	0.1684	0.1813

TABLE 22 (Continued)

Atom	X(Sig(X))	Y(Sig(Y)	Z(Sig(Z)
H5B	0.3223	0.3830	0.2833
H7(1)	0.1188	0.5771	0.0785
H7(2)	0.2624	0.5564	0.0524
H8(1)	0.2754	0.6097	0.2481
H8(2)	0.2768	0.7358	0.1578
H9(1)	0.4776	0.7376	0.0939
H9(2)	0.5225	0.7732	0.1988
H10A	0.4103	0.4549	0.0921
H10B	0.5558	0.3232	0.2753
H12	0.5335	0.3182	0.3847
H13	0.5499	0.3889	0.5418
H14	0.3418	0.2625	0.6422
H15	0.1685	0.0464	0.6161
H16	0.1655	-0.0244	0.4608
H18	0.0841	0.0965	0.2556
H19	-0.1258	-0.0829	0.2394
H20	-0.1289	-0.3429	0.3053
H21	0.0896	-0.3854	0.3833
H22	0.2983	-0.1802	0.3930
H24	0.2486	0.4029	0.0000
H25	0.1372	0.2567	-0.1170
H26	-0.1083	0.0721	-0.0903
H27	-0.2127	0.0593	0.0401
H28	-0.0848	0.1857	0.1606
H30	0.1792	0.2671	0.3638
H31	0.0164	0.2391	0.4749
H32	-0.1653	0.3503	0.4205
H33	-0.2263	0.4397	0.2540
H34	-0.0630	0.4661	0.1265

TABLE 23

ANISOTROPIC THERMAL PARAMETERS FOR (5aβ,5bβ,10aα,10bα)-DODECAHYDRO-5,5,6,6-TETRAPHENYLCYCLOBUTA[1,2:3,4]-DICYCLOHEPTENE-1,10-DIONE $C_{36}H_{38}O_2$ (**18**)

Atom	U11	U22	U33	U12	U13	U23
O1	78(3)	42(2)	134(4)	7(2)	25(2)	20(2)
O2	96(3)	101(3)	60(2)	44(2)	30(2)	-13(2)
C1	64(3)	26(2)	49(3)	0(2)	5(2)	-8(2)
C2	72(4)	37(3)	62(3)	-12(3)	20(3)	-1(3)
C3	59(3)	44(3)	61(3)	-17(3)	20(3)	-9(3)
C4	38(3)	40(3)	56(3)	-13(2)	13(2)	-13(2)
C5	34(2)	40(3)	33(3)	-3(2)	12(2)	-6(2)
C5A	38(2)	24(2)	35(2)	-7(2)	14(2)	-4(2)
C5B	36(2)	28(2)	27(2)	3(2)	11(2)	1(2)
C6	31(2)	31(2)	32(2)	-1(2)	10(2)	1(2)
C7	25(2)	45(3)	60(3)	0(2)	16(2)	9(2)
C8	42(3)	50(3)	39(3)	7(2)	8(2)	2(2)
C9	49(3)	40(3)	53(3)	13(2)	19(2)	8(2)
C10	62(3)	40(3)	38(3)	4(2)	26(2)	0(2)
C10A	42(2)	33(2)	31(2)	4(2)	17(2)	-4(2)
C10B	45(3)	28(2)	37(3)	-2(2)	8(2)	-5(2)
C11	34(2)	32(3)	36(3)	0(2)	8(2)	-9(2)
C12	43(3)	34(3)	40(3)	1(2)	8(2)	-5(2)
C13	63(3)	38(3)	40(3)	3(2)	15(2)	2(2)
C14	68(4)	49(3)	42(3)	17(3)	4(3)	3(2)
C15	49(3)	71(4)	40(3)	21(3)	-2(2)	-11(3)
C16	41(3)	49(3)	55(3)	1(2)	12(2)	-8(2)
C17	34(2)	39(3)	50(3)	-11(2)	17(2)	-8(2)
C18	43(3)	65(3)	48(3)	-1(2)	20(2)	-12(3)
C19	58(3)	77(4)	56(3)	-11(3)	20(3)	-22(3)
C20	71(4)	61(4)	83(5)	-17(3)	42(3)	-31(3)
C21	74(4)	44(3)	82(5)	9(3)	37(3)	-5(3)
C22	55(3)	40(3)	57(3)	0(2)	23(2)	1(2)
C23	32(2)	28(2)	35(2)	-2(2)	5(2)	0(2)
C24	56(3)	37(3)	42(3)	1(2)	20(2)	1(2)
C25	60(3)	46(3)	52(3)	3(2)	24(2)	10(2)
C26	61(3)	37(3)	50(3)	0(2)	6(2)	15(2)
C27	44(3)	34(3)	53(3)	-1(2)	8(2)	6(2)
C28	34(2)	36(3)	38(3)	-4(2)	9(2)	-1(2)
C29	30(2)	25(2)	41(3)	1(2)	8(2)	0(2)
C30	48(3)	33(3)	40(3)	-3(2)	1(2)	0(2)
C31	61(3)	37(3)	53(3)	-7(2)	1(3)	-9(3)
C32	63(3)	52(3)	41(3)	7(3)	8(2)	-14(3)
C33	63(3)	46(3)	36(3)	0(2)	17(2)	1(2)
C34	38(3)	38(3)	42(3)	-3(2)	10(2)	-2(2)

Anisotropic thermal parameters in the format:

$\exp[-2\pi^2(U11h^2a^{*2} + U22k^2b^{*2} + U33l^2c^{*2} + 2U12hka^*b^* + 2U13hla^*c^* + 2U23klb^*c^*)] \times 10^3$

TABLE 24

ANISOTROPIC THERMAL PARAMETERS FOR (±)-(5aβ,5bα,10aβ,10bα)-DODECAHYDRO-5,5,6,6-TETRAPHENYLCYCLOBUTA[1,2:3,4]-DICYCLOHEPTENE-1,10-DIONE $C_{36}H_{38}O_2$ (**19**)

Atom	U11	U22	U33	U12	U13	U23
O1	149(3)	84(2)	64(2)	65(2)	56(2)	5(1)
O2	47(1)	66(2)	127(2)	23(1)	-18(1)	-47(2)
C1	48(2)	52(2)	54(2)	17(2)	20(2)	-9(2)
C2	65(3)	53(2)	69(3)	31(2)	20(2)	-16(2)
C3	60(2)	43(2)	54(2)	27(2)	5(2)	-13(2)
C4	43(2)	37(2)	41(2)	21(1)	-4(1)	-7(1)
C5	37(2)	35(2)	33(2)	18(1)	1(1)	-4(1)
C5A	34(2)	35(2)	32(2)	14(1)	5(1)	-9(1)
C5B	36(2)	36(2)	31(2)	16(1)	3(1)	-7(1)
C6	41(2)	44(2)	27(1)	23(1)	2(1)	-5(1)
C7	49(2)	42(2)	43(2)	24(2)	2(1)	-3(1)
C8	60(2)	40(2)	55(2)	29(2)	6(2)	-11(2)
C9	54(2)	34(2)	57(2)	11(1)	9(2)	-14(2)
C10	39(2)	43(2)	53(2)	13(1)	9(1)	-11(2)
C10A	37(2)	34(2)	37(2)	11(1)	7(1)	-8(1)
C10B	36(2)	37(2)	38(2)	14(1)	9(1)	-6(1)
C11	52(2)	45(2)	32(2)	31(2)	-5(1)	-8(1)
C12	66(2)	45(2)	37(2)	28(2)	-9(2)	-11(2)
C13	103(3)	62(3)	50(2)	45(2)	-24(2)	-28(2)
C14	124(4)	108(4)	36(2)	78(3)	-4(2)	-21(2)
C15	94(3)	104(4)	37(2)	55(3)	5(2)	-13(2)
C16	65(2)	70(3)	33(2)	31(2)	5(2)	-11(2)
C17	42(2)	41(2)	32(2)	14(1)	5(1)	-8(1)
C18	44(2)	42(2)	45(2)	12(1)	5(1)	-11(1)
C19	48(2)	56(2)	52(2)	11(2)	3(2)	-17(2)
C20	53(3)	52(2)	67(3)	-1(2)	15(2)	-22(2)
C21	70(3)	37(2)	100(4)	5(2)	9(3)	-13(2)
C22	55(2)	39(2)	80(3)	15(2)	-4(2)	-4(2)
C23	46(2)	40(2)	41(2)	28(1)	-4(1)	-4(1)
C24	60(2)	58(2)	40(2)	22(2)	-2(2)	-16(2)
C25	87(3)	80(3)	45(2)	47(3)	-11(2)	-27(2)
C26	81(3)	65(3)	66(3)	39(3)	-21(2)	-31(2)
C27	59(3)	59(3)	77(3)	25(2)	-19(2)	-25(2)
C28	54(2)	52(2)	49(2)	23(2)	-8(2)	-15(2)
C29	38(2)	42(2)	48(2)	19(1)	5(1)	-12(1)
C30	49(2)	57(2)	50(2)	23(2)	17(2)	-2(2)
C31	62(3)	78(3)	61(3)	26(2)	23(2)	-7(2)
C32	50(2)	72(3)	83(3)	14(2)	27(2)	-29(2)
C33	36(2)	63(3)	93(3)	20(2)	8(2)	-32(2)
C34	42(2)	52(2)	63(2)	26(2)	0(2)	-17(2)

Anisotropic thermal parameters in the format:

$\exp[-2\pi^2(U11h^2a^{*2} + U22k^2b^{*2} + U33l^2c^{*2} + 2U12hka^*b^* + 2U13hla^*c^* + 2U23klb^*c^*)] \times 10^3$

VITA

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