SECONDARY α-DEUTERIUM ISOTOPE EFFECTS AS A PROBE TO THE RELATIONSHIP BETWEEN STRUCTURE AND MECHANISM OF PYROLYSIS OF SECONDARY AZOALKANES

By

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1971

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
December, 1975

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ACKNOWLEDGEMENTS

I wish to extend my appreciation to my major adviser, Dr. Stuart E. Scheppele for his guidance, encouragement, and friendship throughout the course of this study. I would also like to thank my advisory committee: Drs. E. J. Eisenbraun, L. M. Raff, and R. E. Koeppe. Appreciation is also extended to D. W. Miller and T. D. Marriott for assistance in rate determinations and M. W. Adkins for construction and maintenance of equipment for kinetic studies. I wish also to acknowledge my fellow graduate students for their helpful suggestions and especially for their friendship.

I am indebted to Continental Oil Company, Phillips Petroleum Company, Gulf Oil Company, and Oklahoma State University Department of Chemistry for financial assistance during the course of my graduate study.

Finally, I wish to extend my special appreciation to my wife and daughter, Connie and Cassandra, for their patience, encouragement, and many sacrifices.

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CHAPTER I

INTRODUCTION

Within the framework of the Born-Oppenheimer approximation, interatomic electronic forces are independent of the nuclear masses. Thus, the potential-energy surface describing the motions of the nuclei is independent of isotopic substitution. Detailed theoretical studies within the framework of transition-state (absolute-rate) theory have shown that isotope effects reflect the changes in force constants associated with isotopic nuclei upon passing from the reactant state to the transition state.[1] Kinetic isotope effects are extremely useful as a qualitative tool in the elucidation of reaction mechanisms. Furthermore the measurement of a sufficient number of isotope effects increases the information about the potential-energy reaction hypersurface. A sufficient number of isotope effects permits one to obtain a reasonably complete and self-consistent transition-state force field.

One method for probing the nature of the potential-energy reaction hypersurface is to investigate substituent effects. However, a change in molecular structure itself perturbs the potential-energy reaction hypersurface. Clearly, kinetic isotope effects constitute a powerful tool in the investigation of molecular structure on the potential-energy reaction hypersurface.[2]

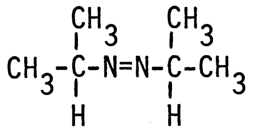
Kinetic isotope effects, in general, and α-secondary deuterium isotope effects, specifically, have been extensively utilized in the investigation of the mechanism and of the effect of molecular structure on the potential-energy hypersurface for thermolysis of azo compounds. The mechanism for azoalkane thermolysis has generally been considered to involve either a concerted, one-step, (eq 1) or stepwise, two-step, (eq 2) rupture of both carbon-nitrogen bonds in the rate controlling step.

$$R\text{-}N{=}N\text{-}R \longrightarrow R\cdots N{=}N\cdots R^{\ddagger} \longrightarrow R\cdot + N_2 + \cdot R \qquad (1)$$

$$R\text{-}N{=}N\text{-}R \xrightarrow{\text{slow}} R\cdots N{=}N\text{-}R^{\ddagger} \longrightarrow R\cdot + \cdot N{=}N\text{-}R$$

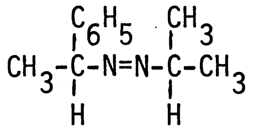
$$\cdot N{=}N\text{-}R \xrightarrow{\text{fast}} N_2 + \cdot R \qquad (2)$$

For a one-step thermolysis mechanism, Ramsperger[3] originally suggested that the activation energy, E_a, of an unsymmetrical compound should be the average of the activation energies for the corresponding symmetrical compounds. In light of this suggestion, Cohen and Wang[4] and Overberger and Digiuilo[5] considered in detail the effect of the variation of the alkyl substituents (R) on the mechanism of azoalkane thermolysis. Their experimental results[4,5] were consistent with Ramsperger's suggestion. For example, in the series 1,1'-dimethylazoethane (I), 1-methyl-1'-phenylazoethane (II), and 1,1'-diphenylazoethane (III) the activation energies are 40.9, 36.5, and 32.6 kcal/mole, respectively.[5]



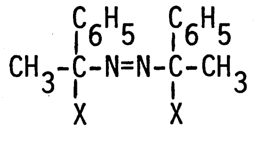
$CH_3\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}N{=}N\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}CH_3$

I



$CH_3\text{-}\underset{H}{\overset{C_6H_5}{C}}\text{-}N{=}N\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}CH_3$

II



$CH_3\text{-}\underset{X}{\overset{C_6H_5}{C}}\text{-}N{=}N\text{-}\underset{X}{\overset{C_6H_5}{C}}\text{-}CH_3$

III; X = H III-d_2; X = D

Thus, symmetrical substitution of two methyl groups by two phenyl groups decreases E_a by about 8 kcal/mole and E_a for **II** approximates closely the average of the E_a for the symmetrical compounds **I** and **III**. Furthermore a one-step mechanism suggests a ratio of 2:1 for the rate constants for thermolysis of **III** and **II**.[5] The experimental ratio (k_{III}/k_{II}) of 36.7 at 120°[5] strongly suggests that a one-step thermolysis mechanism attains. The increase in the rate constant for **III** reflects the ability of the phenyl group to delocalize the odd incipient electron.

Using kinetic isotope effects Seltzer[6] and Seltzer and Dunne[7] confirmed a one-step thermolysis mechanism for **III** and demonstrated a change in mechanism from symmetrical to unsymmetrical one-step cleavage to a two-step cleavage in the series **III**, **II**, and (1-phenylethyl)azomethane (**IV**). For **III**, the α-secondary deuterium isotope effect is 1.27.[6a] For typical unimolecular reactions, the α-effect per D is approximately 1.12-1.15.[6a] Also, detailed model calculations by Wolfsberg and Stern[1a] indicate that the magnitude of the α-effect principally reflects the change in the H-C-N bending force constant upon passing from the reactant state to the transition state. Hence, the magnitude of k_H/k_D for **III** most reasonably requires a decrease in the force constants associated with the two benzylic hydrogens upon passing from the reactant state to the transition state. Thus, the α-effect for **III** is entirely consistent with the rupture of both C-N bonds in the rate determining step (eq 1). The α-secondary deuterium and primary nitrogen[8] effects in the thermolysis of **II**, **III**, and **IV** are presented in Table I. Assuming that a direct relationship exists between the magnitude of the decrease in the H-C-N bending force constant, f_{HCN},[9] and the C-N stretching force constant, f_{CN},[9] upon

TABLE I

ISOTOPE EFFECTS AND ACTIVATION ENERGIES FOR THERMAL DECOMPOSITION OF II, III AND IV

Compound	T,°C	k_H/k_D	Position	k_{14}/k_{15}	E_a,kcal/mole
II	143.20	1.148^a	benzyl	1.0152^b	36.5^c
		1.036^a	propyl		
III	105.28	1.27^d	benzyl	1.0229^b	32.6^c
IV	161.00	1.13^e	benzyl	1.0132^b	38.6^e
		0.97^e	methyl		

[a] See reference 6b.

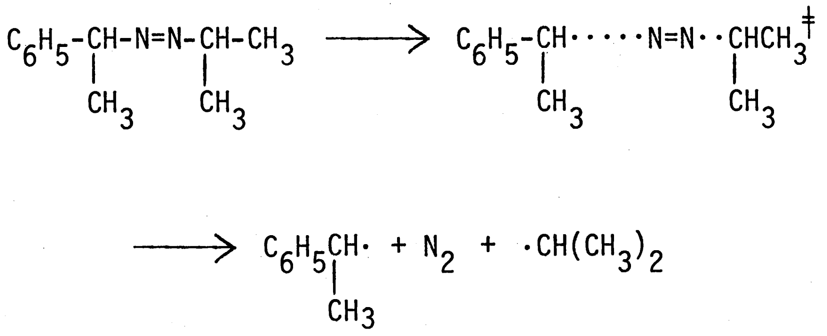
[b] See reference 8.

[c] See reference 5.

[d] See reference 6a.

[e] See reference 7.

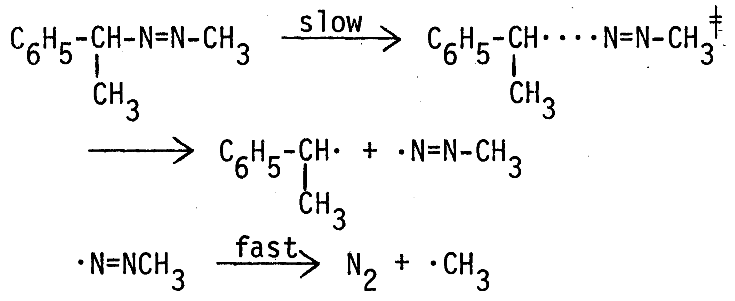
passing from the reactant state to the transition state, the α-effect at the benzylic and propyl positions in II indicate a simultaneous but unequal homolysis of both C-N bonds[6b] (eq 3).



$$C_6H_5\text{-}\underset{\displaystyle CH_3}{CH}\text{-}N{=}N\text{-}\underset{\displaystyle CH_3}{CH}\text{-}CH_3 \longrightarrow C_6H_5\text{-}\underset{\displaystyle CH_3}{CH}\cdots\cdots N{=}N\cdot\cdot\underset{\displaystyle CH_3}{CH}CH_3^{\ddagger}$$

$$\longrightarrow C_6H_5\underset{\displaystyle CH_3}{CH}\cdot + N_2 + \cdot CH(CH_3)_2 \qquad (3)$$

For IV, the α-effects[7] at the benzylic and methyl positions are consistent with stretching and tightening of the benzylic carbon to nitrogen and methyl carbon to nitrogen bonds, respectively, (eq 4) as the

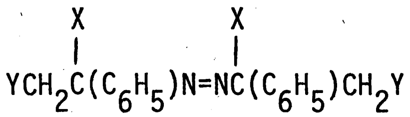


$$\underset{\displaystyle CH_3}{C_6H_5\text{-}\underset{|}{CH}}\text{-}N{=}N\text{-}CH_3 \xrightarrow{\text{slow}} \underset{\displaystyle CH_3}{C_6H_5\text{-}\underset{|}{CH}}\cdot\cdot\cdot N{=}N\text{-}CH_3^{\ddagger}$$
$$\longrightarrow \underset{\displaystyle CH_3}{C_6H_5\text{-}\underset{|}{CH}}\cdot + \cdot N{=}N\text{-}CH_3$$
$$\cdot N{=}NCH_3 \xrightarrow{\text{fast}} N_2 + \cdot CH_3 \qquad (4)$$

reactant is converted to the activated complex.[7] A change of mechanism in the series is qualitatively consistent with the primary nitrogen[8] effects in pyrolysis of III, II, and IV and with the carbon effect[7] ($\underline{k}_{12}/\underline{k}_{13}$ = 1.0068 at 161.00°) in IV. Using the deuterium and heavy atom isotope effects, consistent transition-state force fields have been calculated for each reactant by Seltzer and Mylonakis.[8] Also, the deuterium isotope effect in thermolysis of III-*methyl*-$\underline{d}_6$[10] and III-*ring*-$\underline{d}_{10}$[11] demonstrates for the transition state of III that hyperconjugative stabilization is of little importance[10] and that delocalization of the incipient odd electron produces a negligible perturbation of the aromatic C-H force constants.[11]

Similar studies by Crawford and coworkers[12] indicate that pyrazoline thermolysis proceeds via a concerted (one-step) mechanism.

To investigate the influence of molecular structure on the potential-energy reaction hypersurface for azo compound pyrolysis, α-effects were measured in the decomposition of *meso*- and *dℓ*-1,1',2,2'-tetraphenylazoethane[13] (V), 1,1'-diphenylazobutane[14] (VI), and 2,2-dimethoxy-1,1'-diphenylazoethane[14] (VII); the data are presented in



$$\mathrm{YCH_2\overset{X}{\overset{|}{C}}(C_6H_5)N{=}N\overset{X}{\overset{|}{C}}(C_6H_5)CH_2Y}$$

meso- and *dℓ*-**V**; Y = C_6H_5 X = H

meso- and *dℓ*-**V**-d_2; Y = C_6H_5 X = D

VI; Y = CH_3CH_2 X = H

VI-d_2; Y = CH_3CH_2 X = D

VII; Y = CH_3O X = H

VII-d_2; Y = CH_3O X = D

Table II. Since the magnitude of the α-effect reflects the decrease in force constants upon passing from the reactant state to the transition state[1], α-effects have been used to probe the reactant-like:product-like character of the transition state.[2,13,14] Since for the one-step mechanism the reaction coordinate involves extension of both carbon-nitrogen bonds, a large decrease in both f_{HCN} (large k_H/k_D) can be interpreted as reflecting appreciable C-N bond homolysis in the transition state; thus, the transition state is described as being product-like. Conversely, isotope effects smaller than the one for **III** reflect less cleavage of the C-N bonds and a more reactant-like transition state. For thermolysis of *meso*- and *dℓ*-**V** a decrease in k_H/k_D as compared to the one for **III** is indicative of a more reactant-like transition state for the first two than for the third one.[13] Participation between the π electrons of the β-phenyl and the incipient odd electron in the transition state and nonbonded interactions in the ground state of **V** were presented as possible explanations for the decrease in the α-effect for both diasteromers of **V**.[13] Consideration

TABLE II

ISOTOPE EFFECTS AND ACTIVATION ENERGIES FOR THERMAL DECOMPOSITION OF V, VI, AND VII

Compound	Temp.,°C	k_H/k_D	$(k_H/k_D)^a$ 105.28°C	E_a,kcal/mole
meso-V	106.47	1.224^b	1.225	33.1^b
dℓ-V	106.47	1.202^b	1.203	33.2^b
VI	106.68	1.194^c	1.201^d	33.5^c
	107.35	1.206^c		
VII	118.09	1.188^c	1.195	34.0^c

[a] Extrapolated from other temperatures assuming $A_H/A_D = 1$.

[b] See reference 13.

[c] See reference 14.

[d] Average of two extrapolated values, 1.195 and 1.208.

of all data led the authors to conclude that the former explanation is preferable to the latter. Hence, isotope effects may be a sensitive tool for probing the possibility of neighboring-group effects in reactions of structurally related compounds.[13]

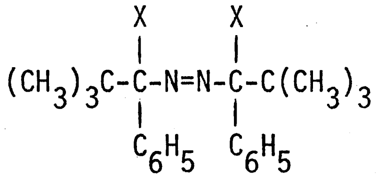
To further investigate the effects of anchimeric assistance and steric hindrance on the reaction energetics for azoalkane thermolysis, the α-effect was determined for VI.[14] Based upon the strain energies for R = CH_3CH_2 and C_6H_5 in the molecule RCH_2X, V and VI were judged to possess comparable strain energy.[14] Hence, if steric hindrance in the ground state influences the reaction energetics for V, the α-effect for VI was predicted to be comparable in magnitude. Conversely, since participation is not possible in thermolysis of VI, a k_H/k_D for it was predicted to be ca. 1.27 if anchimeric assistance to bond homolysis is significant in pyrolysis of meso- and dℓ-V. The very similar α-effects for thermolysis of VI and both diasteromers of V supported the hindered reactant hypothesis.[14]

For VII, the α-effect is considerably smaller in magnitude than for III. Hence, the transition state for the former was interpreted to be more reactant-like than the transition state of the latter.[14] Various explanations involving structure-reactivity relationships were advanced in view of the "abnormal" α-effect for VII.[2,14] Stabilization of the transition state by interaction of the incipient odd electron on C-α with an unoccupied orbital on oxygen constituted one argument. However, this explanation is not consistent with the observation that the 2-hydroxyethyl radical exists in a bisected form. On the other hand, a more reactant-like transition state was considered plausible with a transition state for thermolysis of VII in which the methoxy group is in a similarly bisected conformation. Although seemingly implausible, a crossover in the mechanism from symmetrical to two-step cleavage was considered as an explanation for the "abnormal" effect for VII.[14]

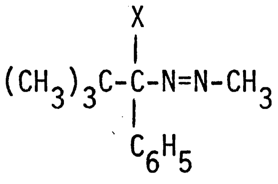
Because the magnitude of the α-effect for III is of singular importance in interpreting the ones obtained for related compounds we have redetermined its value. Furthermore, since the extent of pyrolysis could affect the magnitude of k_H/k_D, the percent decomposition of samples of III, meso-V, VI, VII and III-ring-d_{10} used in the isotope effect determinations has been obtained.

To further study the mechanism of azoalkane thermolysis and the effect of molecular structure on the potential energy hypersurface for pyrolysis, the α-effect and activation parameters in the thermolysis of 2,2,2',2'-tetramethyl-1,1'-diphenylazopropane (VIII) have been determined. Severn and Kosower[15] postulated that the difference in λ_{max} of the n-π* transitions for a given class of azo compounds reflects differences in nonbonded interactions in their ground state. Thus, VIII (λ_{max}= 369 nm) should possess 2.2 kcal/mole of strain energy compared to III (λ_{max} = 359 nm). Assuming that a simultaneous mechanism attains for VIII and that the strain energy is effective in reducing the activation energy, the transition state for VIII is qualitatively predicted by the Hammond postulate[16] to be more reactant-like than that for III. Thus, k_H/k_D for VIII should be less than that for III. However, inspection of molecular models of the 2,2-dimethyl-1-phenylpropyl radical suggests that interaction between the methyl groups of the t-butyl and ortho hydrogens of the ring prevents maximum overlap between the p orbitals on C-α and the π system of the aromatic ring. Hence, steric inhibition of resonance could influence the reaction energetics for thermolysis of VIII. Qualitatively the consequence of this phenomena would be to increase the radical-like character of the transition state for VIII as compared to III; k_H/k_D for the former would be greater than the latter. Clearly, the magnitude of the α-effect for pyrolysis of VIII will aid in the assessment of the importance of steric inhibition of resonance and reactant state nonbonded interactions on the potential-energy surface for decomposition.

To aid in the interpretation of k_H/k_D for **VIII** the α-effect and activation parameters were also determined in the thermolysis of (2,2-dimethyl-1-phenylpropyl)azomethane (**IX**). The inability to prepare **VIII** and **IX** by conventional methods necessitated the development of a new method for synthesis of secondary azo compounds.



$(CH_3)_3C-\overset{X}{\underset{C_6H_5}{C}}-N=N-\overset{X}{\underset{C_6H_5}{C}}-C(CH_3)_3$



$(CH_3)_3C-\overset{X}{\underset{C_6H_5}{C}}-N=N-CH_3$

VIII; X = H

VIII-d_2; X = D

IX; X = H

IX-d; X = D

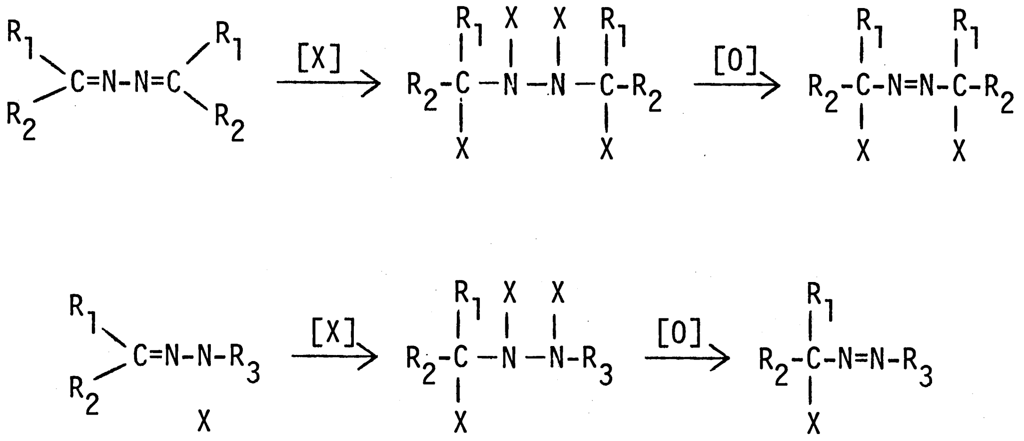
CHAPTER II

A CONVENIENT SYNTHESIS OF PROTIATED AND SPECIFICALLY DEUTERATED SECONDARY AZOALKANES

Results and Discussion

The classical method (Scheme I) for the synthesis of symmetrical (eq 5) or unsymmetrical (eq 6) secondary azoalkanes involves catalytic

Scheme I



$$\begin{matrix}R_1\\ R_2\end{matrix}\!\!>C=N-N=C<\!\!\begin{matrix}R_1\\ R_2\end{matrix} \xrightarrow{[X]} R_2-\underset{X}{\overset{R_1}{C}}-\overset{X}{N}-\overset{X}{N}-\underset{X}{\overset{R_1}{C}}-R_2 \xrightarrow{[O]} R_2-\underset{X}{\overset{R_1}{C}}-N=N-\underset{X}{\overset{R_1}{C}}-R_2 \quad (5)$$

$$\begin{matrix}R_1\\ R_2\end{matrix}\!\!>C=N-\underset{X}{N}-R_3 \xrightarrow{[X]} R_2-\underset{X}{\overset{R_1}{C}}-\overset{X}{N}-\overset{X}{N}-R_3 \xrightarrow{[O]} R_2-\underset{X}{\overset{R_1}{C}}-N=N-R_3 \quad (6)$$

X = H or D

reduction of the corresponding azine or hydrazone to the hydrazine followed by oxidation; usual oxidizing reagents are yellow mercuric oxide,[6a,12c,13,17] hydrogen peroxide,[17a,18] and cupric chloride.[17b]

However, a number of complications have been observed with Scheme I. Rather vigorous conditions have been required for the reduction of some azines to the hydrazines,[17a,c;18a] e.g., ring-substituted acetophenone azines.[17c,18a] Reduction of t-butyl phenyl ketazine (X) in ethanol with Pd at room temperature gave only hydrazone; reduction of the hydrazone in glacial acetic acid yielded both the hydrazine and 2,2-dimethyl-1-phenylpropylamine. All attempts to reduce 2,2-dimethylpropiophenone methylhydrazone (XI) and phenylhydrazone (XII) failed. Similarly low-pressure hydrogenation of benzophenone phenylhydrazone was unsuccessful.[4] Difficulties have also been encountered with the oxidation step in reaction rate and product yield.[19]

Scheme I imposes limitations on the synthesis of specifically deuterated azo compounds. Generally some fraction of the sample is not specifically labelled because some exchange of aliphatic protium (deuterium) normally accompanies reduction with $D_2(H_2)$;[6a,7,10,13,14] exchange of aromatic protium (deuterium) in the reduction is usually negligible.[6a,7,10,11,13,14,20] Furthermore in catalytic deuteration the number of atoms of D introduced is variable and less than the maximum.[6a,7,13,14,21] This result presumably reflects catalytic exchange between the deuterium gas and hydroxylic protium; water present in the solvent or absorbed on the walls of the hydrogenation vessel and exchangeable protium in the solvent constitute sources of the latter.

Lithium aluminum hydride and deuteride are ideal reagents to obviate problems in the reduction step of Scheme I. Although some success has been realized in the reduction of hydrazones (eq 5) with these reagents,[4,6b] the $LiAlH_4$ reduction of azines to hydrazines (eq 6) has been remarkably unsuccessful[17a] except in the case of simple aliphatic azines.[22]

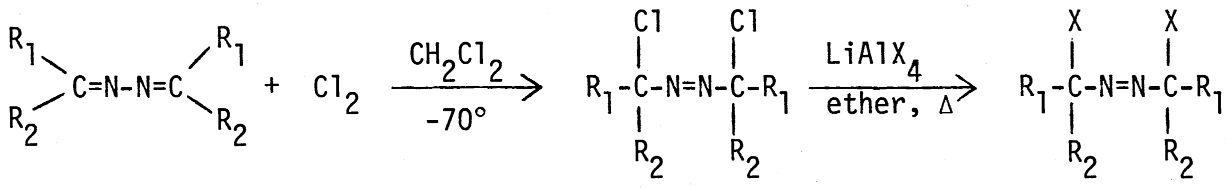
Consequently, a chlorine addition:metal-hydride reduction method was developed. The general reaction scheme and the azoalkanes so prepared are given in Table III. The addition-reduction method bypasses the oxidation step in Scheme I and incorporates a) the desirable properties of $LiAlH_4$ ($LiAlD_4$), b) the propensity of ketazines to undergo 1,4-addition of Cl_2 to form 1,1'-dichloroazoalkanes,[26] and c) the facileness with which the latter undergo nucleophilic substitution.[26b,c;27] Azine and excess Cl_2 were combined in CH_2Cl_2, usually at -70°. After removal of the CH_2Cl_2 the 1,1'-dichloroazoalkane, depending upon its stability, was either purified before reaction with the metal hydride or immediately treated with the hydride in refluxing diethyl ether. The general utility of this approach is demonstrated by the variety of azines which were converted to the corresponding azoalkanes; see Table III.

The structures of 1,1'-dichloro-1,1'-diphenylazobutane and 1,1'-dichloro-1,1',3,3,3',3'-hexaphenylazopropane were confirmed by nmr and ms; their reduction to **VI** and **XVII** also provides confirmation of structure.

As reported[26d] **X** smoothly added Cl_2 (3 hrs) to give 1,1'-dichloro-2,2,2',2'-tetramethyl-1,1'-diphenylazopropane (**XVIII**). In contrast to the reaction of **X** with H_2/Pd (see eq 5), reaction of **XVIII** with $LiAlH_4$ ($LiAlD_4$) for four hours gave **VIII** (**VIII**-$\underline{d}_2$). 4-Bromoacetophenone azine (**XIX**) and 3,3-diphenylpropiophenone azine (**XX**) were smoothly and rapidly converted to **XIII** and **XVII** analogously. It is noteworthy that **XIII** could not be prepared via eq 5 because attempts to reduce **XIX** were unsuccessful. Furthermore in the synthesis of **XVII** via eq 5, low-pressure hydrogenation (Pd to azine ratio in grams was 3:1) required

TABLE III

SYMMETRICAL AZOALKANES SYNTHESIZED VIA CHLORINE ADDITION:METAL-HYDRIDE REDUCTION



$$(R_1)(R_2)C{=}N{-}N{=}C(R_1)(R_2) + Cl_2 \xrightarrow[-70°]{CH_2Cl_2} R_1{-}C(Cl)(R_2){-}N{=}N{-}C(Cl)(R_2){-}R_1 \xrightarrow[\text{ether, }\Delta]{LiAlX_4} R_1{-}C(X)(R_2){-}N{=}N{-}C(X)(R_2){-}R_1$$

Compound	X	R_1	R_2	mp or bp;°C(mm)[a]	atom D	% Yield[b]
III[c]	H	CH_3	C_6H_5	72-73		52
III-d_2[d]	D	CH_3	C_6H_5	72-73	1.960 ± 0.002[e]	64
XIII	H	CH_3	p-Br-C_6H_4	107.5-108		41
XIV[f]	H	CH_3	p-CH_3-C_6H_4	78-79		48
XV	H	CH_3	2-$C_{10}H_7$	144-144.5		58
XVI[g]	H	CH_3	C_2H_5	48-49(25)		63

TABLE III (Continued)

Compound	X	R_1	R_2	mp or bp;°C(mm)[a]	atom **D**	% Yield[b]
VI[h]	H	C_3H_7	C_6H_5	60-61		42
XVII	H	$(C_6H_5)_2CHCH_2$	C_6H_5	146.5-147.5		60
VIII	H	t-C_4H_9	C_6H_5	155.5-156.5		61
VIII-d_2[d]	D	t-C_4H_9	C_6H_5	156-156.5	1.998 ± 0.003[e]	63

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[a] Melting points and boiling points are not corrected.

[b] Yield based on azine.

[c] See reference 23.

[d] See reference 24.

[e] Determined by duplicate combustion analysis; uncertainty is average deviation.

[f] See reference 18a.

[g] See reference 25.

[h] See reference 14.

from 15 to 48 hours depending upon the solvent, and oxidation of the hydrazine with yellow mercuric oxide required 24 hours. Pure XV was easily obtained via chlorine addition:metal-hydride reduction but not via eq. 5. The low-pressure catalytic hydrogenation of methyl 2-naphthyl ketazine continued after uptake of two moles of H_2 per mole of azine; one or more of the double bonds in the 2-naphthyl moiety evidently underwent reduction. The applicability of the chlorine addition:metal-hydride reduction method to the preparation of aliphatic secondary azoalkanes was demonstrated by the conversion of 2-butanone azine to XVI.

If substitution of Cl_2 competed appreciably with its addition, the chlorine addition:metal-hydride reduction method would not be a satisfactory route to deuterated azo compounds because the $LiAlD_4$ cleavage of carbon-chlorine bonds other than the C-1--Cl and C-1'--Cl bonds would result in substitution of deuterium for protium. Similarily in the conversion of deuterated azines to the corresponding azo compounds use of $LiAlH_4$ would result in substitution of protium for deuterium. The hydrogenolysis of bonds linking chlorine to an aromatic ring with metal hydride would not be expected.[28]

The following evidence reveals that such substitution is negligible. The chemical shifts observed in and the proton ratios obtained upon integration of the nmr spectra of the chloroazoalkanes were consistent with the presence of chlorine only at C-1 and C-1'. Mass spectra were obtained for the chloroazoalkane precursors to III (III-d_2), VI, XIV, XV, and XVII. These spectra were characterized by ions formally derived from formation and subsequent fragmentation of the substituted alkyl radicals from C-N bond homolysis. Neither the ion intensities nor the high resolution data showed any evidence for the presence of chlorine at positions other than C-1 and C-1'. Finally III-d_2 and VIII-d_2 containing 1.960 and 1.998 atoms of D, respectively, were obtained upon $LiAlD_4$ reduction of 1,1'-dichloro-1,1'-diphenylazoethane (XXI) and XVIII. The same $LiAlD_4$ was used in preparation of VIII-d_2 and benzyl alcohol-α,α-d_2.[29] It is thus noteworthy that the atom %-D of the former as determined by combustion, 99.9 ± 0.3, is in good agreement with the value for the latter as determined by low-voltage mass spectrometry,[29] 99.3 ± 0.3. Different $LiAlD_4$ was used in synthesis of III-d_2. Since III-d_2 and VIII-d_2 do not contain in excess of 2 atoms of D either the formation of or the reduction of chlorine-substituted 1,1'-dichloroazoalkanes must be negligible. These conclusions concerning the extent to which substitution of chlorine accompanies its addition to azines are supported by the results of Malament and McBride.[26d]

Pyrolysis of recrystallized VIII in ethylbenzene yielded only 81.6% of the theoretical quantity of nitrogen gas.[30] This result was attributed to the presence of a trace amount of XVIII in the sample. Although the thermal decomposition of 1,1'-dichloroazoalkanes proceeds predominately by C-N bond homolysis,[26,31] there may be some C-Cl bond cleavage, which under our conditions would lead to formation of traces of HCl. The HCl would catalyze the isomerization of VIII to hydrazone; the uv spectrum of the residue from pyrolysis displayed absorption characteristics of the hydrazone. The 99.1% yield of nitrogen obtained upon heating a mixture of pyridine[32] and VIII (6:1 mole ratio) in ethylbenzene supports this explanation.

Since 1,1'-dichloroazoalkanes undergo hydrolysis,[26b-d;33] the crude azoalkanes were solvolyzed homogeneously in ether-acetone-water containing equimolar amounts of $AgNO_3$; in all cases formation of traces of AgCl was observed. The azoalkane was then purified by column chromatography over silica gel followed by recrystallization. The chromatography step, which is not unique to the chlorine addition: metal-hydride reduction method, and which may have been unnecessary, was introduced to facilitate removal of colloidal silver and silver salts. After purification, a 99.2 and 99.7% yield of nitrogen was obtained upon pyrolysis of **VIII** and **VIII**-*d*$_2$, respectively, in ethylbenzene. Similar results were obtained for decomposition of **III** and **III**-*d*$_2$ prepared by both chlorine addition:metal-hydride reduction and eq 5.[30]

(Secondary-alkylazo)benzenes cannot be prepared by chlorine addition:metal-hydride reduction because substitution of chlorine for aromatic hydrogen is known to accompany its addition to phenylhydrazones.[34] However, (2,2-dimethyl-1-phenylpropyl)azomethane (**IX**), ($R_1 = C_6H_5$, $R_2 = (CH_3)_3C$ and $R_3 = CH_3$) and (2,2-dimethyl-1-phenylpropyl-1-*d*)azomethane (**IX**-*d*) were prepared from **XI** via chlorine addition:metal-hydride reduction. Deuterium analysis of **IX**-*d* yielded 1.072 atoms of **D**, indicating that 0.092 atoms of **H** (1.072-1.960/2) had been replaced by chlorine in the addition step. This extent of deuterium-protium exchange is in almost all cases less than that observed in the catalytic deuteration of azines or hydrogenation of deuterated azines. Thus it appears that chlorine addition:metal-hydride reduction is applicable to the synthesis of (*sec*-alkylazo)-alkanes and (*sec*-alkylazo)2,4,6-trichlorobenzenes since Moon[34] has demonstrated that 2,4,6-trichlorophenylhydrazones react with Cl_2 to form [(1-chloroalkyl)azo]-2,4,6-trichlorobenzenes.

Experimental Section

General

NMR spectra were recorded on a Varian XL-100 spectrometer. Chemical shifts are reported with respect to tetramethylsilane. Mass spectra were obtained using a CEC 21-110B spectrometer at 70 eV. Elemental and deuterium analysis were performed by Galbraith Laboratories, Inc. and Mr. Josef Nemeth, Urbana, Illinois, respectively.

Butyrophenone (Aldrich), 4-bromoacetophenone (Aldrich), 4-methylacetophenone (Aldrich), methyl 2-naphthyl ketone (Eastman), acetophenone (Baker), and 2-butanone (Mallinckrodt) were commercial samples and used without further purification. 3,3-Diphenylpropiophenone was prepared by the procedure of Vörlander and Friedberg.[35]

Preparation of 2,2-Dimethylpropiophenone

In a 1-ℓ four-necked flask equipped with an addition funnel, mechanical stirrer, reflux condenser, and a section of Gooch tubing for solid introduction were placed 60 ml of dry ether and 36 ml of an ethereal solution of phenylmagnesium bromide (Arapaho, 0.1082 mol). The flask was cooled to 0° and anhydrous cadmium chloride (10.35 g, 0.0565 mol) was slowly added via the Gooch tubing to the stirred solution. The mixture was allowed to warm to room temperature and refluxed for 20 min. The major portion of the ether was removed by distillation and 120 ml of dry benzene was added. Distillation was continued until the distillate was ether-free, as analyzed by gas chromatography. The flask and its contents were then cooled to 10°, 2,2-dimethylpropanoyl chloride (10.0 g, 0.0833 mol, Aldrich) in 30 ml of dry benzene was slowly added, and the resulting mixture stirred for 4 hr. The reaction mixture was hydrolyzed at 5-7° by addition of 140 ml of 20% sulfuric acid. The organic phase was separated, washed twice with a saturated solution of sodium bicarbonate, and repeatedly with water, and dried over anhydrous magnesium sulfate. The solution was filtered and the benzene distilled. Distillation at 91-93° (6.5 mm) [lit. bp 103-104° (13 mm)][36] afforded 11 g, 82% of product.

Preparation of Ketazines

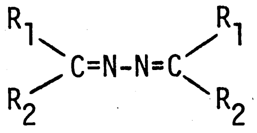
All ketazines were prepared by the method of Cohen, et al.[18a] Acetophenone azine,[37] 4-bromoacetophenone azine,[38] 4-methylacetophenone azine,[39] methyl 2-naphthyl ketazine,[40] 2-butanone azine,[25] 2,2-dimethylpropiophenone azine,[26d] and butyrophenone azine[14] have been previously described. Table IV presents the physical constants of the ketazines.

Preparation of 3,3-Diphenylpropiophenone Azine

3,3-Diphenylpropiophenone (30 g, 0.105 mol) and 95% hydrazine (1.71 g, 0.0525 mol) were refluxed for 6 hr in absolute ethanol (50 ml) containing 10 drops of glacial acetic acid. The reaction mixture was cooled to room temperature and filtered. The crude azine was recrystallized twice from a 9:1 mixture of absolute ethanol and benzene; 26.8 g (90%), mp 137.5-138°; mass spectrum, M^+ at m/e 568.288 (calcd for $C_{42}H_{36}N_2$, 568.288); nmr ($CDCl_3$) δ 3.33 (d, 4H), 4.34 (t, 2H), 6.92-7.38 (m, 30H).

TABLE IV

PHYSICAL CONSTANTS OF THE KETAZINES



R_1	R_2	mp or bp;°C(mm)[a]	mp or bp;°C(mm)(Lit)
CH_3	C_6H_5	120.5-121.5	121[b]
CH_3	p-Br-C_6H_4	164-165	159-160[c]
CH_3	p-CH_3-C_6H_4	136-137	137-138[d]
CH_3	2-$C_{10}H_7$	212-213	212-213[e]
CH_3	C_2H_5	65-66.4(20)	73-78(25)[f]
C_3H_7	C_6H_5	40-41	40-41[g]
$(C_6H_5)_2CHCH_2$	C_6H_5	137.5-138	--
t-C_4H_9	C_6H_5	80.5-81.5	79[h]

[a] Melting points and boiling points are not corrected.

[b] See reference 37.

[c] See reference 38.

[d] See reference 39.

[e] See reference 40.

[f] See reference 25.

[g] See reference 26d.

[h] See reference 14.

Preparation of 2,2-Dimethylpropiophenone Methylhydrazone

2,2-Dimethylpropiophenone (10 g, 0.0617 mol) and methylhydrazine (3.5 g, 0.0761 mol) were refluxed for 5 days in absolute ethanol (30 ml) containing 5 drops of glacial acetic acid. The crude product, obtained upon removal of the ethanol at reduced pressure, was taken up in ether, washed with a saturated solution of sodium bicarbonate and with water, dried over anhydrous magnesium sulfate, and filtered. Removal of the ether at reduced pressure and recrystallization of the crude product from hexanes yielded 7.0 g (60%) of product, mp 54.5-55°; mass spectrum, M^+ at m/e 190.147 (calcd for $C_{12}H_{18}N_2$, 190.147); nmr ($CDCl_3$) δ 1.14 (s, 9 H), 2.76 (s, 3 H), 4.25 (broad, 1 H), 7.05 and 7.36 (m, total 5 H).

General Procedure for the Addition of Chlorine to Ketazine

The method was essentially the one described by Moon.[34] A 5% solution of the ketazine in methylene chloride was cooled to -70° in a dry ice-acetone bath. Liquid chlorine (2 moles/mole ketazine) at -70° was rapidly added in the dark to the stirred solution. The mixture was stirred at -70° for 2 hr and then at -40° for an additional hour. The excess chlorine and the methylene chloride were removed at reduced pressure. The crude chloroazo compounds were purified when possible by recrystallization from acetone, hexanes, or a binary acetone-hexanes solvent.

The preparation of 1,1'-dichloro-1,1'-diphenylazoethane,[26a] 1,1'-dichloro-1,1'-bis-(4-bromophenyl)azoethane,[26b] 1,1'-dichloro-1,1'-bis-(4-methylphenyl)azoethane,[26b] 1,1'-dichloro-1,1'-di-(2-naphthyl)azoethane,[26d] 1,1'-dichloro-2,2'-azobutane,[26c] and 1,1'-dichloro-2,2,2',2'-tetramethyl-1,1'-diphenylazopropane[26d] have been reported previously. The following new 1,1'-dichloroazoalkanes were prepared. Table V presents the physical constants of the 1,1'-dichloroazoalkanes.

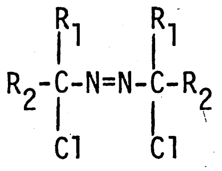
1,1'-Dichloro-1,1'-diphenylazobutane. Butyrophenone azine was quantitatively converted to this azo compound by the above procedure. The crude product was recrystallized from hexanes, mp 85.5-86.0° with decomposition; nmr ($CDCl_3$) δ 0.81 (t, 6H), 1.29 (m, 4H), 2.47 (m, 4H), 7.37 and 7.65 (m, total 10H).

1,1'-Dichloro-1,1',3,3,3',3'-hexaphenylazopropane. Addition of liquid chloride to 3,3-diphenylpropiophenone azine by the general procedure afforded a quantitative yield. Recrystallization from hexanes yielded material melting with decomposition at 227-228°; nmr ($CDCl_3$) δ 3.26 (m, 4H), 4.07 (t, 2H), 6.80-7.36 (m, 30H).

(2,2-Dimethyl-1-chloro-1-phenylpropyl)azomethane. Addition of liquid chlorine to 2,2-dimethylpropiophenone methylhydrazone by the general procedure yielded an unstable yellow viscous oil. The nmr spectrum of the product in $CDCl_3$ changed rapidly with time. Short exposure to the atmosphere resulted in the rapid evolution of gas. Owing to instability of this product no quantitative data were obtained.

TABLE V

PHYSICAL CONSTANTS OF 1,1'-DICHLOROAZOALKANES



$$R_2\text{-}\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}\text{-}N{=}N\text{-}\overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}\text{-}R_2$$

R_1	R_2	mp or bp;°C(mm)[a]	mp or bp;°C(mm)(lit)
CH_3	C_6H_5	108.5-109	108[b]
CH_3	p-Br-C_6H_4	119.5-120	120[c]
CH_3	p-CH_3-C_6H_4	129-130	130[c]
CH_3	2-$C_{10}H_7$	137-138	137[d]
CH_3	C_2H_5	--	40-42(0.005)[e]
C_3H_7	C_6H_5	85.5-86	--
$(C_6H_5)_2CHCH_2$	C_6H_5	227-228	--
t-C_4H_9	C_6H_5	121.5-122.5	122[d]

---

[a] Melting points and boiling points are not corrected.

[b] See reference 26a.

[c] See reference 26b.

[d] See reference 26d.

[e] See reference 26c.

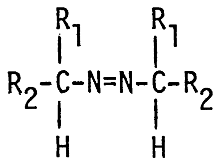
General Procedure for the $LiAlH_4$ Reduction of the 1,1'-Dichloroazoalkanes

Each of the 1,1'-dichloroazoalkanes were reduced with excess lithium aluminum hydride to the corresponding secondary azoalkanes (Table III). The reflux time varied with the compound; completion of the reaction was taken as the disappearance of the green color in the reaction mixture. Elemental composition of azoalkanes not previously prepared are presented in Table VI. The preparation of 2,2'-azobutane illustrates the general procedure.

In a 500-ml three-necked flask equipped with an addition funnel, condenser, and mechanical stirrer were placed 2.5 g (0.066 mol) of lithium aluminum hydride and 50 ml of dry ether. The stirred solution was cooled to 0° and 11 g (0.052 mol) of 1,1'-dichloro-2,2'-azobutane in 200 ml of dry ether was added in *ca.* 15 min. The mixture was allowed to warm to room temperature and then refluxed for 19 hr. The aqueous and organic phases obtained upon hydrolysis of the ice-cooled mixture by the slow addition of a saturated solution of sodium potassium tartrate (100 ml) with vigorous stirring were separated. The former phase was removed and extracted three times with ether, and the ether extracts were combined with the latter phase. The ethereal solution was washed twice with water, dried over anhydrous magnesium sulfate, filtered, and freed of ether under reduced pressure. Distillation of the crude yellow oil yielded 4.8 g (63%) of XVI bp 48.5-49.0° (25 mm) [lit. bp 49-52° (27 mm)].[25]

TABLE VI

ELEMENTAL COMPOSITION DATA FOR AZOALKANES



$$R_2-\overset{\displaystyle R_1}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-N=N-\overset{\displaystyle R_1}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-R_2$$

			Carbon, %		Hydrogen, %		Nitrogen, %		Bromine, %	
Compound	R_1	R_2	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
XIII	CH_3	p-Br-C_6H_4	48.51	48.61	4.07	4.11	7.07	7.13	40.34	40.32
XV	CH_3	2-$C_{10}H_7$	85.17	85.22	6.55	6.74	8.28	8.06		
XVII	$(C_6H_5)_2CHCH_2$	C_6H_5	88.38	87.94	6.71	6.60	4.91	5.38		
VIII	t-C_4H_9	C_6H_5	81.94	81.81	9.38	9.07	8.69	9.06		

1,1'-Bis-(4-bromophenyl)azoethane (XIII). Using a reflux time of 19 hr, XIII was prepared by the general procedure. A 41% yield was obtained after recrystallization from methanol, mp 107.5-108°; nmr ($CDCl_3$) δ 1.46 (D, 6 H), 4.52 (q, 2 H), 7.22 (d, 4 H), 7.44 (d, 4 H).

1,1'-Di-(2-naphthyl)azoethane (XV). Using a reflux time of 20 hr, XV was prepared by the general procedure. A 58% yield was obtained after recrystallization from a 3:1 mixture of methanol and acetone, mp 144-144.5°; nmr ($CDCl_3$) δ 1.60 (d, 6 H), 4.84 (q, 2 H), 7.48 (m, 6 H), 7.80 (m, 8 H).

1,1',3,3,3',3'-Hexaphenylazopropane (XVII). Using a reflux time of 18 hr, XVII was prepared by the general procedure. A 60% yield was obtained after recrystallization from methanol, mp 146.5-147.5° with decomposition; nmr ($CDCl_3$) δ 2.78 (m, 4 H), 3.53 (m, 2 H), 4.42 (m, 2 H), 6.82-7.50 (m, 30 H).

1,1'-Diphenyl-2,2,2',2'-tetramethylazopropane (VIII). Using a reflux time of 4 hr, VIII was prepared by the general procedure. A 61% yield was obtained after recrystallization from methanol, mp 155.5-156.5°; nmr ($CDCl_3$) δ 1.00 (s, 18 H), 4.17 (s, 2 H), 7.11 (s, 10 H).

1,1'-Diphenyl-2,2,2',2'-tetramethylazopropane-1,1'-d_2 (VIII-d_2). Using lithium aluminum deuteride instead of lithium aluminum hydride in the general procedure, VIII-d_2 was prepared with a reflux time of 4 hr. A 63% yield was obtained upon recrystallization from methanol, mp 156-156.6°; nmr ($CDCl_3$) δ 1.00 (s, 18 H), 7.11 (s, 10 H).

(2,2-Dimethyl-1-phenylpropyl)azomethane (IX). Using the procedure for the reduction of 1,1'-dichloroazolakanes, IX was prepared with a reflux time of 15 hr. Crude IX was purified by column chromatography (column dimensions, 4.7 x 60 cm) using Baker AR grade silica gel as the substrate and a 2:1 mixture of benzene and hexanes as the eluting solvent followed by distillation, yield 56%, bp 52-54° (0.7 mm); nmr ($CDCl_3$) δ 0.94 (s, 9H), 3.70 (s, 3H), 4.10 (s, 1H), 7.29 (m, 5H).

Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.75.
Found: C, 75.76; H, 9.56; N, 14.38.

(2,2-Dimethyl-1-phenylpropyl-1-*d*)azomethane (**IX**-*d*). Using lithium aluminum deuteride, **IX**-*d* was prepared and purified by the procedure described for **IX**, yield 60%, bp 50-51° (0.6 mm); nmr ($CDCl_3$) δ 0.94 (s, 9H), 3.70 (s, 3H), 7.29 (m, 5H).

Purification Procedure for Secondary Azo Compounds

Azo compounds and silver nitrate (mole ratio 1:1) were added to a ternary solution of ether, acetone, and water. The resulting solution was stirred in the dark for 24 hr. The ether and acetone were removed under reduced pressure and the azo compound taken up in ether. The ether solution was washed twice with a saturated solution of sodium carbonate and then with water, dried over anhydrous magnesium sulfate, filtered, and freed of ether at reduced pressure. The crude product was purified by column chromatography (column dimensions, 4.7 x 60 cm) using silica gel as the substrate and either benzene, hexanes, or a binary mixture of benzene-hexanes as an eluting solvent, followed by distillation or recrystallization.

CHAPTER III

REEXAMINATION OF THE SECONDARY α-DEUTERIUM ISOTOPE EFFECT IN THERMOLYSIS OF 1,1'-DIPHENYLAZOETHANE

Results

Excellent first-order kinetics were observed for decomposition a) of III-1 and III-d_2-1 prepared by reduction of 1,1'-dichloro-1,1'-diphenylazoethane with $LiAlH_4$ and $LiAlD_4$,[41] respectively, and b) of III-2 and III-d_2-2 prepared by catalytic hydrogenation and deuteration, respectively, of acetophenone azine. At the completion of all kinetic determinations the samples exhibited no absorption in the region centered around 360 nm. The rate constant $4.50 \pm 0.03 \times 10^{-3}$ min^{-1} for decomposition of III-1 in ethylbenzene at 103.90 ± 0.04° is in good agreement with the value $4.56 \pm 0.09 \times 10^{-3}$ min^{-1} obtained for III-2 at 103.9 ± 0.2° (Appendix A).

Table VII presents the observed and corrected (2 atoms of α-D) isotope effects and the deuterium content of III-d_2-1 determined by combustion and of III-d_2-2 determined by both combustion and nmr (proton ratios determined by integration following repetitive scanning with a Varian C-1024). For III-d_2-2 the value for atoms of deuterium by combustion, 1.810 ± 0.003, differs on the average by only 1.1% from the nmr value 1.830 ± 0.106 (1.585 ± 0.016 atoms of α- and 0.245 ± 0.105

TABLE VII

ISOTOPE EFFECT IN THE DECOMPOSITION OF 1,1'-DIPHENYLAZOETHANE-*1*,*1*'-d_2 IN ETHYLBENZENE AT 103.90°[a]

Compound	Atoms of α-*d*	$< k_H/k_D >_{\text{obs.}}$[b]	$< k_H/k_D >_{\text{cor.}}$[c]
III-*1*/**III**-d_2-*1*	1.960 ± 0.002[d]	1.1912 ± 0.0062[e,f]	1.195 ± 0.006
III-*2*/**III**-d_2-*2*	1.585 ± 0.016[g]	1.1590 ± 0.0104[h,i]	1.198 ± 0.014

[a] Deviations are standard deviations except where noted. Column 3 is not rounded for computation purposes.

[b] Measured simultaneously.

[c] k_H/k_D observed corrected to 2 atoms of α-*d*.

[d] Calculated from average atom % *D* obtained from duplicate combustion analysis; atom % *D* found: 10.88 and 10.90. Deviation is average deviation.

[e] Average of six determinations.

[f] ΔT = ± 0.04°.

[g] Determined by nmr. Atoms of β-*d* by nmr are 0.2449 ± 0.1049. Total atoms of *D* by nmr and duplicate combustion are 1.830 ± 0.106 and 1.810 ± 0.003, respectively.

[h] Average of five determinations.

[i] ΔT = ± 0.2°.

atoms of β-D; see Appendix B). The standard deviation in the atoms of β-D, which clearly dominates sigma in the total atoms of D, reflects for our Varian XL-100 the difficulty in reproducing with high precision absorption bands of protons having chemical shifts less than ca. 1.7 δ. For any one experiment, σ in the methyl proton ratio was less than 0.105 but the number of these protons was found to be dependent upon the power used to lock-in on the tetramethylsilane absorption band. Thus, the average value obtained for each determination of the individual methyl proton ratio for III-2 and III-d_2-2 was used to arrive at the value 0.245 ± 0.105 without regard to the sigma for each methyl determination.

For III-d_2-1 an α-effect of 1.195 ± 0.006 is obtained upon correction of $< k_H/k_D >_{obs}$ to 2 atoms of α-D (eqs 7 and 8); also see experimental section. The $< k_H/k_D >_{obs}$ for III-d_2-2 was corrected to

$$V \pm \sigma_V = (X \pm \sigma_X)^{Y \pm \sigma_Y} \tag{7}$$

$$\sigma_V = V[(Y\sigma_X)^2/X^2 + (\sigma_Y \ell n X)^2]^{1/2} \tag{8}$$

2 atoms of α-D as follows. The contribution of α-deuterium to the experimental k_H/k_D for III-methyl-d_6[10] was calculated to be 1.0027 ± 0.013 by eq 7 where $X \pm \sigma_X$ equals 1.195 ± 0.006 and $Y \pm \sigma_Y$ equals 0.0150 ± 0.0075.[10] The k_H/k_D for 5.891 ± 0.005 atoms of β-D[10] is thus $(1.112 \pm 0.005)^{10}/(1.0027 \pm 0.0013)$ or 1.109 ± 0.005. Equation 7 then yields a β-effect of 1.018 ± 0.001 per atom of β-D. An identical value is obtained if the α-effect for III-d_2-1 is first extrapolated from 103.90° to 105.20°, the temperature at which k_H/k_D was determined for

III-methyl-d_6.[10] Equation 7 in which $Y \pm \sigma_Y = 0.2499 \pm 0.1049$ then gives a calculated value of 1.0043 ± 0.0019 for the contribution of β-deuterium to $< k_H/k_D >_{obs}$. For 1.585 ± 0.016 atoms of α-D, k_H/k_D is (1.1590 ± 0.0104)/(1.0043 ± 0.0019) or 1.1540 ± 0.0106 which when corrected to 2 atoms of α-D yields an α-effect of 1.198 ± 0.014 for III-d_2-2.

The α-effect for III-d_2-1 (1.195 ± 0.006) is in excellent agreement with the value for III-d_2-2 (1.198 ± 0.014). The standard deviation in the latter primarily reflects the magnitude of sigma in $< k_H/k_D >_{obs}$. In the III-2/III-d_2-2 measurements difficulty was encountered in achieving long-term temperature stability. However, these measurements were not repeated because of the excellent agreement in the α-effects.

It is important to note that the β-effect per D is 1.018[10] regardless of whether $(k_H/k_D)_\alpha$ of 1.27 or 1.195 is used to correct the experimental k_H/k_D for III-methyl-d_6 for α-deuterium.

Quantitative nitrogen evolution studies were undertaken because appreciably incomplete azo compound decomposition could yield erroneous isotope effects. Table VIII tabulates the results. The uncertainty in the percentage nitrogen evolved is ca. 1.5-2% from consideration of the standard deviation in the PV products and of solution preparation. The results obtained for both preparations of III and III-d_2 agree with the nitrogen yield obtained for III by Seltzer and Mylonakis;[8] the nitrogen yields obtained for meso-V and meso-V-d_2 agree with the value obtained for meso-V by Mylonakis, Scheppele and Seltzer.[42] Thus, in all instances the kinetic data and, hence, the isotope effects reflect 98-100 percent decomposition.

TABLE VIII

PERCENTAGE NITROGEN EVOLVED IN AZOALKANE PYROLYSIS IN ETHYLBENZENE

Compd.	T°, C	mmoles Compd x 10^2	mmoles N_2 x 10^2	% N_2 Evolved
III-1	155	9.986	10.08	100.9
III-2	155	10.15	10.16	100.1
III-d_2-1	158	9.819	9.763	99.4
III-d_2-2	160	9.861	9.958	101.0
III-ring-d_{10}	155	9.541	9.276	97.2
meso-V	155	10.17	9.962	98.0
meso-V-d_2	155	10.06	9.848	97.9
VI	155	9.849	9.614	97.6
VI-d_2	155	9.243	9.037	97.8
VII	158	10.22	10.20	99.8
VII-d_2	158	10.02	10.18	101.6

Discussion

The α-deuterium isotope effect for decomposition of **III** is a) 1.195 rather than 1.27[6a] and b) comparable in magnitude to those obtained for **V** through **VII**[13,14] and 3,12,15,24-tetraphenyl-1,2,13,14-tetra-1,13-cyclotetracosadiene (**XXII**).[21] To consider the implications of this result, α-effects for decomposition of **III** through **VII** and **XXII** are shown in Table IX. For purposes of comparison, the α-effects have been extrapolated to 105.28° on the assumption that $A_H/A_D = 1$.[43] Various experimental[44] and theoretical studies[1,45] have shown that the difference in loss of zero-point energy between protio and deuterio compounds in the ground states and transition states is principally responsible for the α-effect.[46] However, an A_H/A_D somewhat less than unity is indicated for α-effects in unimolecular decompositions. For the unimolecular decomposition of the *t*-cumyloxy-β-d_3 radical a least-squares fit of log k_H/k_D versus 1/T for ΔT of 84° yields an A_H/A_D of 0.93 ± 0.02[44b] or 0.976 per **D**. Seltzer and Hamilton[10] performed "exact" calculations for decomposition of **III**-d_2 and **III**-*methyl*-d_6. An A_H/A_D of 0.960 per α-**D** is calculated from the α-effect computed for transition-state model-I (the reason for choosing model-I is given below) at 273 and 373°K. For the model system $CD_3X \rightarrow CD_3 \cdots X^{\ddagger}$ "exact" calculations for the temperature range 300-325°K lead to an A_H/A_D of 0.94, 0.97, or 0.93 depending upon the magnitude of the decrease in the HCX bending force constant, f_{HCX}, in passing from the reactant to the transition state; these values give an average A_H/A_D of 0.982 per α-**D**. The possible consequence of such results on the extrapolation of the

TABLE IX

α-SECONDARY DEUTERIUM ISOTOPE EFFECTS FOR THERMOLYSIS OF AZOALKANES

Compd	$(k_H/k_D)_{exp}$[a]	T°, C	Position of D	$(k_H/k_D)_{105.28°}$[b]	$(k_H/k_D)_{105.28°}$[c] per α-D
III	1.195 ± 0.006	103.90	Benzyl	1.194	1.093
II	1.148 ± 0.012[d]	143.20	Benzyl	1.164	1.164
	1.036 ± 0.007[d]	143.20	Propyl	1.040	1.040
IV	1.13 ± 0.01[e]	161.00	Benzyl	1.151	1.151
	0.97 ± 0.01[e]	161.00	Methyl	0.966	0.989
meso-**V**	1.224 ± 0.006[f]	106.47	Benzyl	1.225	1.107
dℓ-**V**	1.202 ± 0.006[f]	106.47	Benzyl	1.203	1.097
VI	1.194 ± 0.008[g]	106.68	Benzyl	1.201[i]	1.096
	1.206 ± 0.014[g]	107.35			
VII	1.188 ± 0.004[g]	118.09	Benzyl	1.195	1.093
XXII	1.20 ± 0.02[h]	112.95	Benzyl	1.204	1.097[j] (1.048)[k]

[a] Corrected to maximum atoms of D at the indicated position.

[b] For maximum atoms of D at the indicated position.

[c] Calculated by taking the n^{-1} root of the value in column 5 where n is the number of atoms of D at a specified position.

[d] See reference 6b.

[e] See reference 7.

[f] See reference 13.

[g] See reference 14.

[h] See reference 21.

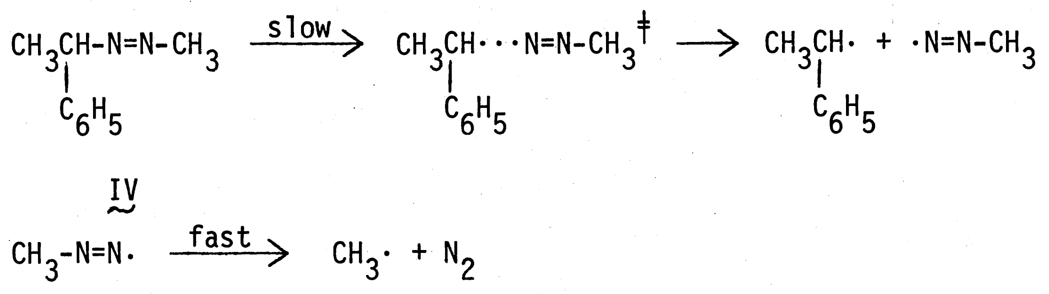
[i] Average of two extrapolated values, 1.195 and 1.208.

[j] k_H/k_D per 2-α-D.

[k] k_H/k_D per α-D.

experimental α-effects in Table IX were investigated by extrapolating the α-effects for **II** and **IV** at the benzylic position and for **VII** assuming $\mathbf{A}_{\mathbf{H}}/\mathbf{A}_{\mathbf{D}}$ values of 0.973 (average of above values) and 0.960 per **D**. These $\mathbf{A}_{\mathbf{H}}/\mathbf{A}_{\mathbf{D}}$ values increase the α-effects at 105.28° by 0.01 or less per atom of deuterium.

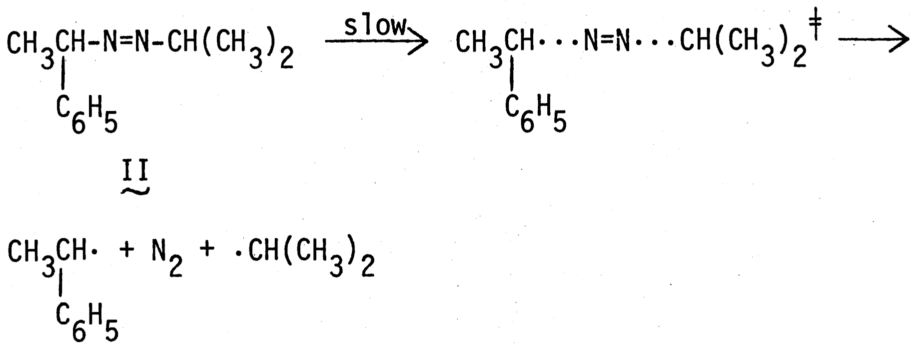
The previous conclusion[6,7,8] that the decomposition mechanism changes from symmetrical to unsymmetrical one-step cleavage to two-step cleavage in the series **III**, **II**, and **IV** is entirely consistent with an α-effect of 1.195 ± 0.006 for **III**. Consideration of the data for **IV**, **II**, and **III** in terms of the mechanisms presented in eq 9, 10, and 11 establishes the validity of this conclusion.



$$CH_3\underset{\underset{C_6H_5}{|}}{C}H\text{-}N{=}N\text{-}CH_3 \xrightarrow{\text{slow}} CH_3\underset{\underset{C_6H_5}{|}}{C}H\cdots N{=}N\text{-}CH_3{}^{\ddagger} \longrightarrow CH_3\underset{\underset{C_6H_5}{|}}{C}H\cdot + \cdot N{=}N\text{-}CH_3$$

IV

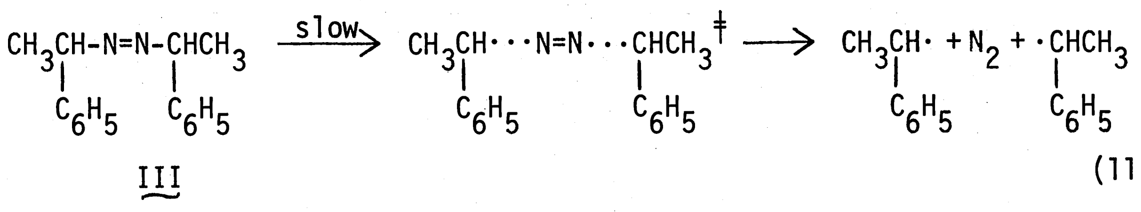
$$CH_3\text{-}N{=}N\cdot \xrightarrow{\text{fast}} CH_3\cdot + N_2 \qquad (9)$$



$$CH_3\underset{\underset{C_6H_5}{|}}{C}H\text{-}N{=}N\text{-}CH(CH_3)_2 \xrightarrow{\text{slow}} CH_3\underset{\underset{C_6H_5}{|}}{C}H\cdots N{=}N\cdots CH(CH_3)_2{}^{\ddagger} \longrightarrow$$

II

$$CH_3\underset{\underset{C_6H_5}{|}}{C}H\cdot + N_2 + \cdot CH(CH_3)_2 \qquad (10)$$



$$CH_3\underset{\underset{C_6H_5}{|}}{C}H\text{-}N{=}N\text{-}\underset{\underset{C_6H_5}{|}}{C}HCH_3 \xrightarrow{\text{slow}} CH_3\underset{\underset{C_6H_5}{|}}{C}H\cdots N{=}N\cdots \underset{\underset{C_6H_5}{|}}{C}HCH_3{}^{\ddagger} \longrightarrow CH_3\underset{\underset{C_6H_5}{|}}{C}H\cdot + N_2 + \cdot\underset{\underset{C_6H_5}{|}}{C}HCH_3$$

III

(11)

(1-Phenylethyl)azomethane (IV)

"Exact" calculations in model chemical systems have shown that the magnitude of the α-effect is dependent upon the change in the hydrogen-carbon leaving group bending force constant (HCX), i.e., $\Delta f_{HCX} = f_{HCX} - f^{\ddagger}_{HCX}$, in passing from the reactant state to the transition state.[1] Thus, the α-effect reflects the extent of bond rupture between the α-carbon and the leaving group at the saddle point. Consequently, the α-effect for IV at the benzylic position (k_H/k_D = 1.13 at 161°, see Table IX) demonstrates homolysis of the 1-phenylethyl carbon-to-nitrogen bond.[7] On the other hand, the α-effect of 0.97 at the methyl position suggests a slightly stronger CH_3-N bond in the transition state than in the reactant state.[7] The 13-carbon effect at the methyl group (k_{12}/k_{13} = 1.0068 at 161°) is also consistent with the latter conslusion, i.e., the experimental effect is less than $\nu_{1\ell}/\nu_{2\ell}$[7,8] (the classical mechanical contribution to the isotope effect). For a reaction mechanism (potential-energy reaction hypersurface) to be valid absolute-reaction-rate theory requires that it quantitatively reproduce (predict) the kinetic isotope effect for any molecular position. Thus, the fact that the "exact analysis of the isotope effects for IV yields a transition-state model for which the force constants are numerically consistent with the qualitative interpretation of the experimental data constitutes a significant interpretative result.[2] The observation[47] that optically active IV racemizes faster than it extrudes nitrogen is also consistent with the two-step mechanism shown in eq 9.

1-Methyl-1'-phenylazoethane (**II**)

For decomposition of **II** at 143.20° the α-effects of a) 1.15 at the 1-phenylethyl position and b) 1.036 at the 1-methylethyl position show that homolysis of both C-N bonds is occurring in the rate-controlling step.[6b] The conclusion concerning rupture of the $(CH_3)_2CH$-N bond follows from the fact that k_H/k_D exceeds the value of $\nu_{1\ell}/\nu_{2\ell} = 1.004$ calculated for a two-step mechanism (analogous to eq 9) by the mass fragment approximation.[48] Also "exact" analysis of both α-secondary deuterium and of the primary nitrogen isotope effects leads to a set of transition-state force constants consistent with eq 10. The diminuation in the energy and entropy of activation in going from **IV** (E_a = 38.6 kcal/mole, $\Delta S^{\ddagger}$ = 14.0 e.u.)[7] to **II** (E_a = 36.5 kcal/mole, $\Delta S^{\ddagger}$ = 9.3 e.u.)[5] is consistent with some rupture of and restricted rotation about the $(CH_3)_2CH$-N bond in the activated complex.[7,49] The results are mutually consistent with an unsymmetrical one-step mechanism for pyrolysis of **II**; the difference in degree of rupture of the two C-N bonds parallels the difference in stabilities of the 1-phenylethyl and 1-methylethyl radicals.

1,1'-Diphenylazoethane (**III**)

First, the results for **II** and **IV** render a two-step pyrolysis mechanism for **III** implausible. However, *a priori* estimation of k_H/k_D for two-step and concerted thermolysis of **III**/**III**-d_2 is difficult because the activation energy for **III** (E_a = 32.6 kcal/mole)[5] suggests a more reactant-like transition state and, hence, a smaller Δf_{HCX} per C-N bond rupture for III than for either II or IV. However, for decomposition of III via a two-step mechanism the α-effect for IV at the benzylic position predicts a $k_H/k_D \le$ 1.15-1.16 for thermolysis of III/III-d_2 at 105.28°. Alternatively for thermolysis via a concerted mechanism, since Δf_{HCX} is determined by the decrease in two f_{HCN}, the k_H/k_D for III/III-d_2 at 105.28° would necessarily be predicted to be larger than the extrapolated benzylic α-effects for II and IV. The experimental result (k_H/k_D = 1.195) is greater than the values obtained upon extrapolating (giving reasonable consideration to the possibility that A_H/A_D may be less than unity, vide supra) the observed benzylic α-effects for II and IV to 105.28° and, hence, is qualitatively most consistent with a concerted mechanism. From a quantative viewpoint it is significant that "exact" analysis of both the α-deuterium and primary nitrogen isotope effects results in a model for the activated complex in which the reaction coordinate is the symmetric stretch of both carbon-nitrogen bonds[8] (as discussed below, a k_H/k_D = 1.195 is not inconsistent with the "exact" analysis).[8] Other kinetic evidence which favors a concerted mechanism is as follows. The entropy of activation for decomposition of III is 7.0 e.u.[5] Thus both Ea and $\Delta S^{\ddagger}$ for III are in harmony with an activated complex involving delocalization of two incipient p-electrons over two aromatic π-systems attendant with restricted rotation of the phenyl groups. The absence of a viscosity dependence on the rate of thermolysis of the structurally related azoalkane 1,1'-dimethyl-1,1'-diphenylazoethane also constitutes indirect supporting evidence.[50] Considered together these results provide in the absence of any other data compelling evidence for a concerted one-step mechanism for III. Similarly the α-effects for V through **VII** and **XXII** and the activation parameters for both diastereomers of **V**,[13] **VI**[14] and **VII**[14] are entirely consistent with a concerted mechanism for thermolysis of these compounds.[2,13,14]

For decomposition of **III** the magnitude of the decrease in f_{HCN} upon passing from the reactant state to the transition state must be less than the decrease required to produce $k_H/k_D = 1.27$. Seltzer and Mylonakis[8] describe two transition-state models (IVa and IVb) which produce an α-effect of 1.27; in both models $f^{\ddagger}_{HCN}$, $f^{\ddagger}_{CH_3CN}$, $f^{\ddagger}_{C_6H_5CN}$, and $f^{\ddagger}_{CNN}$ are 40 percent of the corresponding reactant-state values. Model-IVb, which gives the better fit to k_{14}/k_{15}, differs from model-IVa in the magnitude of $f^{\ddagger}_{CN}$ and the interaction force constant $f^{\ddagger}_{ij}$. Transition-state model-I, described by Seltzer and Hamilton,[10] appears to be identical to model-IVa except that the bending force constants are *ca.* 55 rather than 40% of the reactant-state values. It is important to note that model-I predicts an α-effect of 1.193 at 373°K. Thus, it appears reasonable to conclude that model-IVb, in which $f^{\ddagger}_{HCN}$, $f^{\ddagger}_{CH_3CN}$, $f^{\ddagger}_{C_6H_5CN}$, and $f^{\ddagger}_{CCN}$ are *ca.* 55% rather than 40% of the reactant-state values, still constitutes a reasonable description of the bonding in the transition state for decomposition of 1,1'-diphenylazoethane.

The magnitude of k_H/k_D reflects the reduction in f_{HCN} upon passing from the reactant state to the transition state.[1a,6] Thus, if the force constants associated with the α-CH bond in the reactant states are transferable[51] within a few percent,[14] the α-effects for *dℓ*-**V**, **VI** and **VII** compared to **III** suggest that substitution of phenyl, ethyl, and methoxy for β-hydrogen in **III** does not seriously perturb that part of the potential-energy hypersurface involving motion of the α-hydrogen. If such perturbations do occur they must be compensated by factors such as coupling of vibronic motions and/or curvature in the barrier. As a first approximation the α-effects then indicate only a small substituent effect on the reactant-like:product-like character of the transition state. For *meso*-**V** k_H/k_D and k_{14}/k_{15} (1.0158 at 106.42°)[42] are larger and smaller than the respective values for **III** (k_{14}/k_{15} = 1.0229 at 105.02°);[8] see also Table IX. Previously the α-deuterium and primary nitrogen isotope effects were interpreted as favoring a more reactant-like transition state for *meso*-**V** than for **III**.[2,13,14] However, a problem arises in interpreting the nitrogen effect because the reduction in the C-N force constant is compensated in part by the increase in the N-N stretching constant.[8] Nevertheless, if in passing from the reactant state to the transition state changes in bending force constants are correlated with changes in stretching force constants,[8] and if the consequences[8] of this correlation on k_H/k_D and k_{14}/k_{15} are considered, the isotope effects for *meso*-**V** compared to **III** are consistent with smaller values of $f^{\ddagger}_{HCN}$ and $f^{\ddagger}_{CN}$ and an increased value for $f^{\ddagger}_{NN}$ for the former. Thus both the deuterium and the nitrogen isotope effects are qualitatively reconcilable with a more radical-like transition state for *meso*-**V** than for **III**.

Experimental Section

Azo Compounds

1,1'-Diphenylazoethane and 1,1'-diphenylazoethane-*1*,*1*'-d_2 were prepared by two methods. Samples prepared by $LiAlH_4$ and $LiAlD_4$ reduction of 1,1'-dichloro-1,1'-diphenylazoethane[41] are designated **III**-1 and **III**-d_2-*1*, respectively. Samples prepared by catalytic hydrogenation and deuteration of acetophenone azine[6a] are designated III-2 and III-d_2-2, respectively. Palladium on charcoal (5%), 3 g, suspended in 150 ml of purified benzene[14] was equilibrated with deuterium gas, and 11.0 g (0.047 mol) of azine was then reduced at atmospheric pressure; 4 hr were required for uptake of 0.094 mole of D_2. After filtration, the crude hydrazine was oxidized at room temperature with yellow mercuric oxide[13] (40 g). Crude III-d_2-2 was repeatedly recrystallized from methanol; mp 71.5-72.5°.

Previously prepared samples of III-2,[11] III-*ring*-d_{10},[11] *meso*-V,[13] *meso*-V-d_2,[13] VI,[14] VI-d_2,[14] VII,[14] and VII-d_2[14] were recrystallized as described.

Kinetics[52]

A weighed amount of azo compound (*ca*. 0.016 g) was dissolved in 3 ml of purified ethylbenzene[13] and the solution transferred to a quartz u.v. cell fitted with a quartz cell bearing a 10/30 inner joint. The solution was degassed at dry-ice temperature under high vacuum ($< 1\mu$) using a freeze-thaw procedure; the procedure was repeated until the pressure was that of ethylbenzene. The cell was then sealed under vacuum by allowing the tube heated below the 10/30 joint to collapse.

The sealed u.v. cells were placed in a Beckman D.U. spectrophotometer in which the cell compartment was enclosed by a temperature bath. The rates of protio and deuterio compounds were measured simultaneously by following the decrease in the $n \rightarrow \pi^*$ transition for the azo compound at 359 nm. An average of 100 points were recording at time intervals corresponding to *ca*. 0.01 change in optical density. Rate constants were obtained from a fit of the data points to the function $Y = A + Be^{-kt}$

where Y = optical density at time = t, B = optical density at time = 0 minus the optical density at infinite time (ten half-lifes), A = optical density at infinite time, and k = rate constant.

The temperature of the cell compartment was monitored before and after the kinetic run using a copper-constantan thermocouple and a Honeywell 2745 potentiometer. The thermocouple was calibrated against an NBS-calibrated thermocouple using a modified Cottrell pump.[53] The calibration was obtained from a linear least squares fit of the EMF of the NBS-thermocouple (y) vs. EMF of the measuring thermocouple (x). The solvents, EMF readings, and least squares analysis are presented in Table X.

Quantitative Nitrogen Evolution

Ampoules were constructed as follows. A 90 x 22 mm section of glass tubing was closed at one end. A 90 x 4 mm section of thick-walled glass tubing bearing a 10/30 inner joint and a 90 x 10 mm section of glass tubing containing a break seal and bearing a 12/30 outer joint were fused to the other end. A weighed amount of azo compound (ca. 0.1 mmol) was dissolved in 5 ml of purified ethylbenzene[13] and the resulting solution quantitatively transferred to an ampoule. The solution was degassed at dry-ice temperature under high vacuum ($< 1\mu$) using a freeze-thaw procedure; the procedure was repeated until the pressure was that of ethylbenzene. The ampoule was then sealed under vacuum by allowing the tube heated below the 10/30 joint to collapse. After the sample had been decomposed for a minimum of ten half-lives in a constant temperature bath, the ampoule was cooled in a dry ice-chloroform-carbon tetrachloride slurry and connected by two

TABLE X

THERMOCOUPLE CALIBRATION

Solvent	EMF(mv) NBS Thermocouple (Y)	EMF(mv) Measuring Thermocouple (X)	Least Squares Analysis	
			slope	intercept
Benzene	3.304	3.328		
Trichloroethylene	3.598	3.624		
2,2,4-Trimethylpentane	4.170	4.200		
Toluene	4.700	4.733		
n-Octane	5.413	5.453	0.9928 ± 0.0004	0.0001146 ± 0.0001617

liquid-nitrogen-cooled radiator traps to a quantitative gas analysis system. Before the ampoule was opened the volume above the break seal was evacuated. The noncondensable gases were Toepler-pumped to the calibrated gas buret. To ensure complete recovery of nitrogen, the contents of the ampoule were subjected to at least five warming-cooling-pumping cycles. Pressures were then recorded for three different gas volumes; the moles of nitrogen were calculated for each set of PV data and then averaged.

For a number of samples the gas was then transferred to a glass loop. Subsequent gas chromatographic analysis verified that the noncondensable gas was nitrogen.

Deuterium Content and Correction of Isotope Effects

The deuterium content of **III**-*d*$_2$-*1* and **III**-*d*$_2$-*2* was determined respectively by combustion[54] and by combustion and nmr. The nmr measurements involved a minimum of three independent determinations of the proton ratios for labeled and unlabeled compounds by integration following repetitive scanning with a Varian C-1024. Spectra of all samples were taken in chloroform-*d* (100 atoms % **D**). Assuming no excess deuterium in the phenyls, the atom fraction of deuterium was calculated by comparison of the proton ratios in the deuterated compounds to the corresponding ratios in the protium sample.

Equation 7 was used either to correct an isotope effect to maximum number of atoms of **D** or to compute an isotope effect given a specific number of atoms of **D**. In the former computations, V is the corrected effect, X is the effect to be corrected, and

$Y \pm \sigma_Y = Z/(W \pm \sigma_W)$ where Z and W are the maximum and experimental number of atoms of $\underset{\sim}{D}$, respectively, for the position of interest. In the latter computations, V is the isotope effect calculated for Y experimental atoms of $\underset{\sim}{D}$ at a position given the isotope effect X per $\underset{\sim}{D}$ for that position. In both cases $\sigma_{\underline{i}}$ represents the associated standard deviations. For calculations involving data for $\underset{\smile}{\mathrm{III}}$-$\underline{d}_2$-$\underline{1}$, the standard deviation in the experimental number of atoms of $\underset{\sim}{D}$ (W) was replaced by the average deviation. The standard deviation in V was calculated by eq 8, which was derived from the expression $\sigma_V = \pm\, [(\partial V/\partial X)^2 \sigma_X^2 + (\partial V/\partial Y)^2 \sigma_Y^2]^{1/2}$.[55]

CHAPTER IV

SECONDARY α-DEUTERIUM ISOTOPE EFFECTS IN THERMOLYSIS OF 2,2,2',2'-TETRAMETHYL-1,1'-DIPHENYLAZOPROPANE AND (2,2-DIMETHYL-1-PHENYLPROPYL)AZOMETHANE

Results

Excellent first-order kinetics were observed for decomposition (a) of 2,2,2',2'-tetramethyl-1,1'-diphenylazopropane (**VIII**) and 2,2,2',2'-tetramethyl-1,1'-diphenylazopropane-1,1'-d_2 (**VIII**-d_2) in ethylbenzene and (b) (2,2-dimethyl-1-phenylpropyl)azomethane (**IX**) and (2,2-dimethyl-1-phenylpropyl-1-d)azomethane (**IX**-d) in diphenylether-benzoquinone; see Appendix A. Experimental rate constants and associated percent deviations for **VIII**, **VIII**-d_2, and **IX** are presented in Table XI. The magnitude of the uncertainties in the rate constants are consistent with the fluctuations in bath temperature with time. The calculated rate constants, k_{calcd}, were obtained from a least-squares fit of log k_{obsd} vs. 1/T°K. Comparison of the observed and calculated rate constants indicate that the plot is essentially linear.

The observed and corrected isotope effects and the deuterium content determined by combustion for **VIII**-d_2 and **IX**-d are presented in Table XII. The isotope effect in the decomposition of **VIII**-d_2 in ethylbenzene was determined by simultaneously measuring the rates of

TABLE XI

COMPARISON OF OBSERVED AND CALCULATED RATE CONSTANTS FOR DECOMPOSITION OF **VIII**, **VIII**-d_2, AND **IX**

Compd	Temp,°C	k_{obsd} x 10^3, min^{-1}[a]	% dev, k_{obsd}	k_{calcd} x 10^3, min^{-1}	% dev, k_{calcd}
VIII	143.54 ± 0.24[b]	3.652 ± 0.027[c]	± 0.74	3.613	1.07
	153.84 ± 0.21[b]	10.894 ± 0.209[c]	1.92	11.141	-2.27
	163.81 ± 0.24[b]	31.871 ± 0.133[c]	0.42	31.501	1.16
VIII-d_2	143.54 ± 0.24[b]	3.158 ± 0.043[c]	1.36	3.124	1.08
	153.84 ± 0.21[b]	9.453 ± 0.166[c]	1.76	9.671	-2.30
	163.81 ± 0.24[b]	27.772 ± 0.130[c]	0.47	27.445	1.17
IX	170.42 ± 0.22	1.576 ± 0.028[d]	1.78	1.560	1.01
	179.88 ± 0.22	4.287 ± 0.045[e]	1.05	4.369	-1.93
	191.13 ± 0.21	14.205 ± 0.273[c]	1.92	14.078	0.89

[a] Not rounded for computational puproses. Deviations are standard deviations unless noted.

[b] Imprecision in thermocouple calibration contributes *ca.* ± 0.06° to uncertainties in temperature.

[c] Average of rate constants from isotope effect studies.

[d] Average of two determinations. Deviation is average deviation.

[e] Average of three determinations.

TABLE XII

ISOTOPE EFFECTS IN THE DECOMPOSITION OF 2,2,2',2'-TETRAMETHYL-1,1'-DIPHENYLAZOPROPANE-1,1'-d_2 AND (2,2-DIMETHYL-1-PHENYLPROPYL-1-d)AZOMETHANE[a,b]

Compd	Temp,°C	Atoms of α-d	$(k_H/k_D)_{obsd}$	$(k_H/k_D)_{cor}$[c]
VIII-d_2[d]	143.54 ± 0.24	1.998 ± 0.003[e]	1.1566 ± 0.0085[f]	1.157 ± 0.009
	153.84 ± 0.21	1.998 ± 0.003[e]	1.1524 ± 0.0074[g]	1.153 ± 0.007
	163.81 ± 0.24	1.998 ± 0.003[e]	1.1476 ± 0.0081[f]	1.148 ± 0.008
IX-d[h]	191.15 ± 0.22	0.980[i]	1.2023 ± 0.0310[j]	1.207 ± 0.031

[a] Column four is not rounded for computational purposes.

[b] Deviations are standard deviations unless noted.

[c] k_H/k_D observed corrected to maximum atoms of α-D.

[d] Decomposed in ethylbenzene.

[e] Calculated from average % D obtained from duplicate combustion analysis. Deviation is average deviation.

[f] Average of three determinations.

[g] Average of five determinations.

[h] Decomposed in diphenylether containing benzoquinone and sample in 20:1 mole ratio.

[i] As estimated from atom % D in III-d_2-1; see Table VIII.

[j] $(k_H/k_D)_{obsd} = (k_H)_{av}/(k_D)_{av}$. $(k_H)_{av}$ and $(k_D)_{av}$ are averages of six determinations.

decomposition of protio and deuterio compounds. For **IX**-*d* the observed isotope effect is the ratio of the average of the rate constants for decomposition of protio ($(\underset{\sim}{k}_{\underline{H}})_{av}$ = 1.42 x 10^{-2} min^{-1}) and deuterio ($(\underset{\sim}{k}_{\underline{D}})_{av}$ = 1.18 x 10^{-2} min^{-1}) compounds in diphenylether-benzoquinone. In order to minimize temperature effects the rates of thermolysis were measured alternately. The larger standard deviation in $(k_{\underline{H}}/k_{\underline{D}})_{obsd}$ for **IX** than for **VIII** reflects a) the effect of fluctuation in bath temperature which is essentially compensated for when the rates of decomposition of both labelled and unlabelled compounds are measured simultaneously, b) for our apparatus lower precision in the pressure data than in optical density measurements, and c) the larger fluctuations in bath temperature over extended periods of time at higher temperatures.

For **VIII**-$\underline{d}_2$ the atoms of **D** as determined by duplicate combustion[54] are 1.998 ± 0.003 which is essentially the maximum atoms of α-**D** for the molecule. However, duplicate combustion analysis for **IX**-*d* yielded a value of 1.072 ± 0.003 atoms of **D**; this value is in excess of the maximum value of one for the benzylic position. A value of 0.980 atoms of **D** in the benzylic position of **IX**-*d* was expected from the following considerations. The deuterium content of the $LiAlD_4$ (*ca*. 98%) used in the preparation of **IX**-*d* predicts *ca*. 0.980 atoms of α-deuterium. Furthermore, the atom % **D** in 1,1'-diphenylazoethane-1,1'-$\underline{d}_2$ (**III**-$\underline{d}_2$-*1*) which was prepared from the same $LiAlD_4$ is 98%;[56] this value is in excellent agreement with the isotopic purity of the $LiAlD_4$. To verify the presence of and to determine the location of *ca*. 0.092 (1.072-1.960/2) atoms of excess deuterium in **IX**-*d*, the proton ratios of **IX** and **IX**-*d* were obtained from integration of the nmr signals directly and following repetitive scanning with a Varian C-1024. Within the limits of data precision, the ratios of methyl and t-butyl protons to phenyl protons for **IX** were identical to the corresponding ratios for **IX**-*d*. The values for **IX** and **IX**-*d* are 3.191 ± 0.050 and 3.189 ± 0.126 and 9.023 ± 0.072 and 8.879 ± 0.256. Due to the magnitude of the errors associated with the experimental proton ratios, this result is not in disagreement with the presence of *ca*. 0.092 atoms of deuterium at positions other than the benzylic one. However, the contribution of 0.092 atoms of **D** either located at or randomly distributed over the phenyl, methyl, or t-butyl positions to the observed k_H/k_D is negligible. First, the isotope effect for ring deuterium would be classical mechanical in origin.[11] Thus, the contribution of excess aromatic deuterium is negligible;[11] i.e., $(k_H/k_D)_{ring-D} = (1.030)^{0.092/10.0}$ or 1.0003. The magnitudes of γ-deuterium isotope effects in solvolysis reactions not involving intramolecular migration are typically 0.970 to 1.015 per **D**.[57] Although one might expect γ-effects in free radical reactions to be less than those in solvolysis reactions, the presence of 0.092 atoms of excess deuterium in the t-butyl group has a negligible contribution to k_H/k_D for **IX** even when the γ-effect of 1.015 per **D**[57b] is assumed; i.e., $(1.015)^{0.092} = 1.001$. Finally, for the structurally related compound, (1-phenylethyl)azomethane (**IV**), the α-effect at the methyl position is $(0.97)^{1/3}$ or 0.990 per atom of **D**.[7] Assuming this result to be applicable to **IX**, the contribution of 0.092 atoms of deuterium in the methyl group of **IX** is $(0.97)^{0.092/3}$ or 0.999.

For **VIII**-d_2 the α-effect as a function of temperature is presented in Table XII. An A_H/A_D value of 0.98 ± 0.01 is obtained from a least-squares fit of $\ell n\ k_H/k_D$ versus 1/T°K. This ratio of pre-exponential factors per **D** (0.99) is in good agreement to those obtained per **D** from the unimolecular decomposition of the *t*-cumyloxy-β-d_3 radical[44b] (0.98) and from "exactly" calculated isotope effect for decomposition of 1,1'-diphenylazoethane-1,1'-d_2 (**III**-d_2) by Seltzer and Hamilton[10] (0.96 for transition-state model-I).

Since incomplete azo compound decomposition could yield erroneous isotope effects, quantitative nitrogen evolution experiments were performed to assess the extent of decomposition for each compound. These results are presented in Table XIII. For those gas samples containing both nitrogen and methane, the quantities of each were determined by gas chromatographic analysis. For **VIII** and **VIII**-d_2 and **IX** and **IX**-*d* the uncertainties in the percentages of nitrogen evolved are *ca*. 1.5-2 and 3-4%, respectively. These values are derived from consideration of the standard deviations in the PV products, solution preparation, and also in the case of **IX** and **IX**-*d* gas chromatographic analysis. Within experimental error the percentage decomposition of each compound is essentially 100%.

It is of interest to note that for the thermolysis of **IX** and **IX**-*d* in ethylbenzene, the primary fate (*ca*. 90%) of the methyl radical is the abstraction of hydrogen atom from the ethylbenzene. Since no ethane was found in the gaseous products, the remaining 10% of the methyl radicals couple with either or both the 1-phenylethyl or 2,2-dimethyl-1-phenylpropyl radicals. The quantitative recovery of nitrogen from the thermolysis and the following results provide good evidence that significant abstraction of hydrogen atom from the azo compound does not occur. Only *ca*. 5% of the theoretical quantity of

TABLE XIII

PERCENT NITROGEN EVOLVED IN AZOALKANE PYROLYSIS

Compd	mmole Compd x 10^2	mmole Gas x 10^2	% N_2 Evolved	% CH_4 Evolved
VIII[a]	9.861	9.750	98.87	
VIII[a]	10.140	10.071	99.32	
VIII-d_2[a]	10.015	9.967	99.52	
VIII-d_2[a]	10.076	10.138	100.62	
IX[a]	15.082	28.011	97.71[b]	88.01[b]
IX-d[a]	13.800	26.019	99.11[b]	89.42[b]
IX[c]	15.082	15.255	95.72[b]	5.42[b]
IX-d[c]	13.800	13.731	93.97[b]	5.53[b]
IX[d]	11.088	11.004	99.24	
IX-d[d]	11.605	12.103	104.29	

[a] Decomposed in ethylbenzene.

[b] Determined by gas chromatography.

[c] Decomposed in ethylbenzene containing 20:1 mole ratio of benzoquinone to compound.

[d] Decomposed in diphenylether containing 20:1 mole ratio of benzoquinone to compound.

methane was produced when IX or IX-*d* were decomposed in ethylbenzene which contained a 20:1 mole ratio of benzoquinone to azo compound. However, in diphenylether-benzoquinone, thermolysis of IX and IX-*d* yielded only nitrogen gas. The methyl radicals must be adding either to the benzoquinone or to the aromatic solvent, entirely.

It is important to note that thermolysis of IX or IX-*d* in ethylbenzene-benzoquinone produces approximately 5% of the theoretical quantity of methane. Hence, a value of *ca*. 5% constitutes an upper limit to the extent of methane formation from solvent-caged methyl radicals.

Table XIV presents the rate constants obtained from the decomposition of VIII as a function of solvent viscosity; i.e., ethylbenzene, tridecane, and octadecane. For thermolysis of VIII, the rate constants are seen to decrease with increasing solvent viscosity. However, the rate constant for thermolysis of IX was found to be independent of solvent viscosity. The rate constants for decomposition of IX in tridecane and in octadecane containing benzoquinone are $(8.71 \pm 0.19) \times 10^{-3}$ min^{-1} and $(8.80 \pm 0.14) \times 10^{-3}$ min^{-1}, respectively, at 188.64°C.

Discussion

For purposes of comparison, isotope effects and relative rate constants at 103.90° for and the activation parameters in the thermolysis of III, IV, VIII, and IX are presented in Table XV. For VIII the α-effect was calculated at 103.90° using the temperature dependence of the experimental effect; see Table XII. The α-effects for IX and IV were extrapolated to 103.90° assuming A_H/A_D to be unity.[43] Although the ratio of preexponential factors for

TABLE XIV

EFFECT OF SOLVENT ON DECOMPOSITION OF 2,2,2',2'-TETRAMETHYL-1,1'-DIPHENYLAZOPROPANE[a]

Solvent	T,°C	k x 10^2, min^{-1}	Relative Rate
Ethylbenzene	154.13	1.150[b]	1.00
Tridecane	154.13 ± 0.12	1.079 ± 0.018[c]	0.94
Octadecane	154.13 ± 0.10	1.039 ± 0.008[c]	0.90

[a] All deviations are standard deviations.

[b] Interpolated from data at other temperatures.

[c] Average of three determinations.

TABLE XV

ISOTOPE EFFECTS, RATE CONSTANTS, AND ACTIVATION PARAMETERS FOR THERMOLYSIS OF AZOALKANES

Compd	T,°C	$k_H \times 10^{-3}$, min^{-1}	$(k_H/k_D)_{exp}$[a]	(k_H relative) 103.90°	(k_H/k_D)[b] 103.90°	E_a kcal/mol	$\Delta S^{\ddagger}$, e.u.
VIII	153.84	10.89	1.153 ± 0.009	103[c]	1.177[d]	38.7 ± 0.7	12.2 ± 1.6
IX	191.15	14.21	1.207 ± 0.031	1[c]	1.261[e]	43.5 ± 0.7	15.7 ± 1.4
III	103.90	4.50[f]	1.195 ± 0.006[f]	17310	1.195[f]	32.6[g]	7.0[g]
IV	161.00	6.97[h]	1.13 ± 0.01[h]	31[c]	1.151[e]	38.6[h]	14.0[h]

[a] Corrected to maximum atoms of D at the benzyl position.

[b] For maximum atoms of D at the benzyl position.

[c] Extrapolated from data at other temperatures.

[d] Extrapolated from data at other temperatures using $(A_H/A_D)_{exp} = 0.98 \pm 0.01$.

[e] Extrapolated from data at other temperatures assuming $A_H/A_D = 1$; see reference 43.

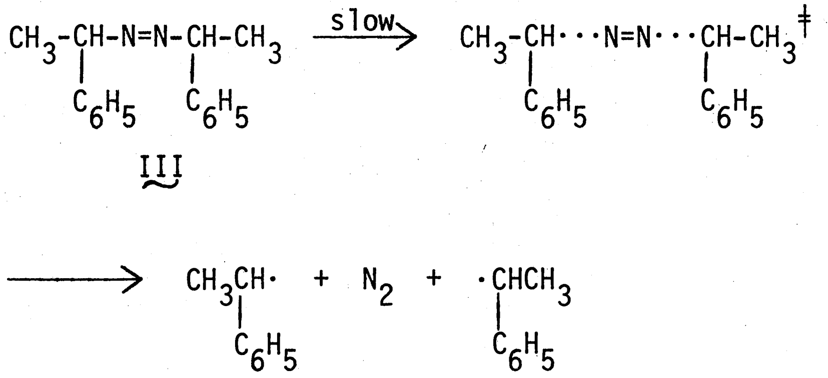
[f] See reference 56.

[g] See reference 5.

[h] See reference 7.

unimolecular decompositions is expected to be somewhat less than unity, extrapolation of α-effects assuming $A_H/A_D = 1$ produces a negligible change in the magnitude of the extrapolated isotope effects.[56]

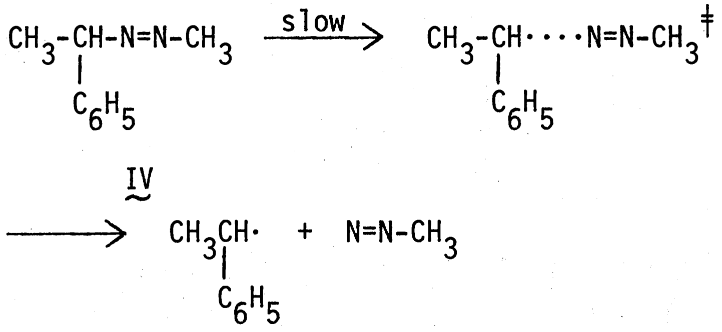
Various experimental studies indicate that thermolysis of III and IV proceed via a one- (eq 12) and two-step (eq 13) mechanism, respectively.[6a,7,8] For simplicity of discussion, the data for pyrolysis of VIII (Table XV) will be considered in terms of these two mechanisms.



$$CH_3\text{-}\underset{C_6H_5}{\underset{|}{CH}}\text{-}N{=}N\text{-}\underset{C_6H_5}{\underset{|}{CH}}\text{-}CH_3 \xrightarrow{\text{slow}} \left[CH_3\text{-}\underset{C_6H_5}{\underset{|}{CH}}\cdots N{=}N\cdots\underset{C_6H_5}{\underset{|}{CH}}\text{-}CH_3\right]^{\ddagger}$$

III

$$\longrightarrow CH_3\underset{C_6H_5}{\underset{|}{CH}}\cdot + N_2 + \cdot\underset{C_6H_5}{\underset{|}{CH}}CH_3 \qquad (12)$$



$$CH_3\text{-}\underset{C_6H_5}{\underset{|}{CH}}\text{-}N{=}N\text{-}CH_3 \xrightarrow{\text{slow}} \left[CH_3\text{-}\underset{C_6H_5}{\underset{|}{CH}}\cdots N{=}N\text{-}CH_3\right]^{\ddagger}$$

IV

$$\longrightarrow CH_3\underset{C_6H_5}{\underset{|}{CH}}\cdot + N{=}N\text{-}CH_3 \qquad (13)$$

$$\cdot N{=}N\text{-}CH_3 \xrightarrow{\text{fast}} N_2 + \cdot CH_3$$

One-Step Thermolysis Mechanism

For **VIII**, the α-effect at 103.90° (1.177) is smaller than the one obtained from thermolysis of **III** (1.195). The magnitude of k_H/k_D principally reflects the decrease in the H-C-N bending force constant, f_{HCN}, upon passing from the reactant state to the transition state.[1] Hence, if the correlation between the decrease in f_{HCN} and f_{CN} along the reaction coordinate is comparable for both compounds and assuming other factors to be equal, the α-effect for **VIII** compared to the one for **III** suggests qualitatively a more reactant-like transition state for the former than for the latter. However, the activation energy for **VIII** (38.7 kcal/mole) is *ca.* 6 kcal/mole greater than E_a for **III** (32.6 kcal/mole).[5] Thus, the Hammond postulate[16] leads to the prediction of a more product-like transition-state for **VIII** as compared to the one for **III**. Several possible explanations may be presented to explain this apparent discrepancy in interpretation. First, a direct relationship between the magnitude of k_H/k_D and reactivity demands transferability of the bending force constants associated with the α-hydrogen in the ground state.[14] For a series of homologous compounds, nontransferability would produce variations in the α-effect even though the reactant-like:product-like character of the transition state might be invariant to alteration in reactant structure. Model calculations indicate that to change the α-effect by a given percentage requires, in general, a similar percentage alteration in the force field associated with the α C-H bond in the reactant state.[14] Models are consistent with steric interactions in

VIII compared to III. It is conceivable that these steric interactions reduce the magnitude of one or more of the force constants associated with the benzylic hydrogens in the former compared to the latter. This apparent inconsistency between the α-effects and the activation energies could be reconciled if for VIII the smaller reduction in the force constants associated with the benzylic hydrogens in passing from the reactant state to the transition state reflects a reduction in the reactant-state force constants which more than compensates for smaller values in the transition state. To resolve the question concerning reactant-state-force-constant transferability would require a detailed normal-mode analysis of the infrared spectra of III and VIII. Force constant transferability in a series of alkanes can be construed as evidence against this explanation.[51]

Furthermore, the magnitude of the α-effects for these two compounds could reflect substituent effects on the curvature of the barriers and/or the correlation of bending and stretching force constants associated with the C-H and C-N bonds along the reaction coordinate. At the present time the occurrence of such phenomena would be difficult to recognize.

Alternatively, the Hammond postulate may not qualitatively predict the reactant-like:product-like character of the transition state. In this regard it is important to note that in thermolysis of 1,1'-dimethylazoethane, II, and III α-effects and the activation energies similarly lead to opposition predictions concerning the degrees of C-N bond homolysis.[6b]

Thus, a concerted pyrolysis mechanism for VIII does not appear to be the simplest qualitative explanation of the observed α-effect and activation energy, the data are insufficient to exclude such a mechanism quantitatively. In this regard, similar interpretative problems are presented by the α-effect and the activation energy for the symmetrical azo compound 3,3'-azo-1-propene.[58] For this compound the data are qualitatively most consistent with a two-step rather than a one-step mechanism.

It is important to note that the rate of thermolysis of **III** at 103.90° proceeds *ca*. 170 times faster than **VIII**. This result might be construed as indicating the absence of significant intramolecular repulsive interactions in the reactant. However, molecular models suggests its presence. Furthermore, application of the Severn-Kosower postulate[15] predicts 2.2 kcal/mole of strain energy in **VIII** as compared to **III**. Thus as a first approximation, the former should have decomposed faster than the latter. The results for **III** and **VIII** indicate that even if the Severn-Kosower postulate leads to a reasonable estimate of the variation in reactant-state nonbonded interactions with structure, it does not completely describe the factors controlling the reaction energetics for thermolysis of **VIII**. Timberlake has also questioned the quantitative prediction of steric effects from absorbance maxima for a series of tertiary azopropanes.[59] Furthermore, although Ohno and Ohnishi have used the postulate to explain the differences in the rates and activation energies for azopropane derivatives containing heteroatoms,[27b,60] no theoretical basis has yet been advanced for its validity. However, if the Severn-Kosower postulate is valid then for thermolysis of **VIII**, the effect of reactant-state nonbonded interactions on the potential-energy surface must necessarily be compensated by other factors. One conceivable factor is steric inhibition of resonance in the transition state (orthogonality between the incipient p orbital on C-α and the π system of the aromatic ring resulting from steric hindrance). Steric inhibition of resonance in the transition state has been advanced to explain the decrease in the rates of solvolysis of C_6H_5CHRCl as R is varied from CH_3 to CH_3CH_2 to $(CH_3)_2CH$ to $(CH_3)_3C$.[60] Similarly, steric inhibition of resonance in the transition state has been advanced as an explanation for the reduced rate of thermolysis of 1,1',2,2'-tetramethyl-1,1'-diphenylazopropane and 1,1'-diisoproyl-2,2'-dimethyl-1,1'-diphenylazopropane compared to the value for 1,1'-dimethyl-1,1'-diphenylazoethane.[62]

Two-Step Thermolysis Mechanism

The reaction coordinate for the first step in the thermolysis of IV involves extension of the benzylic C-N bond and compression of both the N=N and methyl C-N bonds;[7] the reaction coordinate for III involves simultaneous stretching of both benzylic C-N bonds and contraction of the N=N bond.[6] For the activated complexes these differences are reflected in the magnitudes of the force constants governing motion perpendicular and parallel to the reaction coordinate and in their positions along the reaction coordinate. Thus, if a step-wise mechanism attains for VIII the results for IV are appropriate to the interpretation of the data for it. The $(k_H/k_D)_{exp}$ for VIII then represents the product of the α-effects at each benzylic carbon. Based upon the inverse α-effect at the methyl position in IV,[7] the α-effect for C-N bond homolysis in VIII is ≥ 1.153 at 153.84°. This quantity can be estimated as follows. Assuming the deuterium to be statistically distributed over the two α-positions in VIII the atoms of α-D at each position is 1.998/2 = 0.999. Assuming the α-effect at the methyl position per D is transferable to the "nonreacting" position in VIII, its contribution to $(k_H/k_D)_{exp}$ equals $(0.97)^{.999/3}$ or 0.9899. Thus, the α-effect at the reacting bond in VIII at 153.84° is $(1.1524/0.9899)^{1/0.999}$ = 1.164. Because of the atom % D in VIII and the magnitude of $(k_H/k_D)_{CH_3}$ for IV the correction of the experimental k_H/k_D for incomplete deuteration is mechanism independent. Hence the α-effect for VIII is consistent with a two-step mechanism in which the first activated complex involves more bond breaking for VIII than for IV assuming that (a) the force field associated with the benzylic C-H bond is essentially the same for VIII as for IV, (b) the correlation between the reduction in f_{HCN} and f_{CN} along the two reaction coordinates are similar, and (c) the curvatures at the barriers are similar. This conclusion is likewise supported by the larger E_a values for VIII (38.7) compared to III (32.6)[5] and the similarity in the E_a values for VIII and IV (38.6).[7] The similarity between the latter two values appears not to be in complete harmony with the observed α-effects. Since, the sensitivity of E_a to changes in bond breaking is unknown and considering the magnitude of the uncertainty in E_a this discrepancy may be more ostensible than real. The decrease in $\Delta S^\ddagger$ in passing from IV to III was interpreted in terms of increased restricted rotation in the transition state of the former resulting from homolysis of both C-N bonds.[7] Thus the similarity in $\Delta S^\ddagger$ between VIII and IV also supports a two-step mechanism. It is important to note, however, that $\Delta S^\ddagger$ for VIII is predicted to be somewhat less than that for IV since the rate of thermolysis of VIII is favored by a statistical factor of two.

In an attempt to provide additional evidence concerning the pyrolysis mechanisms for **VIII**, the unsymmetrical compound **IX** was studied. In a structural sense **IX** is related to **VIII** as **IV** is related to **III**. The α-effect for **IX** is seen to be significantly larger than the ones for **VIII** and **IV**. In fact this represents the largest α-effect per **D** observed in azo compound thermolysis. The detailed gas evolution experiments and the observation of good first order kinetics are not consistent with contributions to $(k_H/k_D)_{exp}$ from primary deuterium isotope effects resulting from some amount of azo compound isomerization and/or benzylic hydrogen atom abstraction. It is noted that the increase in k_H/k_D is parallel by an increase in E_a. In fact E_a is more similar to the ones observed for decomposition of secondary azoalkanes than secondary azo compounds containing one phenyl group per α-carbon. It is seen that $\Delta S^{\ddagger}$ is similar for **IV**, **VIII**, and **IX**; from a statistical viewpoint $\Delta S^{\ddagger}$ should be lower for **VIII** than for **IV** and **IX**. A consistent rationalization for the variation in the α-effects, activation energies, and rates for these three compounds can be qualitatively advanced in terms of variation in reactant-state strain and in resonance stabilization of the incipient odd electron in the transition state. As a first approximation, any reactant-state non-bonded interactions in **IV** should be amplified by replacement of the α-benzylic methyl group by a *t*-butyl group to arrive at **IX**. Similarly, substitution of both methyl groups in **III** by two *t*-butyl groups should likewise amplify any such reactant-state interactions which are present in **III**; unfortunately a direct comparison of the data for **IV**, **VIII** and **IX** with that for **III** is not possible due to the difference in mechanism. However, qualitatively it is reasonable to expect the degree of reactant-state strain to increase in the series **IV**, **IX**, and **VIII**. Hence, if nonbonded interactions in the reactant are effective in reducing the activation energies, $\mathbf{E}_a$ should decrease in passing from **IV** to **IX** to **VIII**. Clearly, the $\mathbf{E}_a$ values for **VIII**, **IX** and **IV** are not in harmony with this prediction. The similar magnitude of $\mathbf{E}_a$ for **VIII** and **IV** suggests that the effective reduction in $\mathbf{E}_a$ for the former which results from steric strain in the reactant state is completely compensated by an increase in $\mathbf{E}_a$ corresponding to the diminuation in delocalization of the incipient odd electron in the transition state for **VIII** as compared to **IV**. This decrease in resonance stabilization completely dominates the reaction energetics for thermolysis of **IX** compared to **IV**.

Substantiative evidence for a two-step thermolysis mechanism attaining for **VIII** and **IX** is obtained from consideration of the viscosity effect for their thermolysis; see Table XIV. Various kinetic studies have shown that cage return in solution via radical recombination is prevalent only for the decomposition of a molecule preceeding by the cleavage of one bond.[63] For such a decomposition, the observed rate constant will decrease as the viscosity of the solvent increases, since, more geminate pairs will recombine at higher viscosities. For molecules which decompose by the simultaneous rupture of more than one bond, cage return does not occur and, hence, the rate constant is independent of solvent viscosity.[63] For thermolysis of **VIII**, the decrease in the rate constant with increase in solvent viscosity is evidence for the rupture of only one C-N bond in the rate controlling step. For thermolysis of **IX** in tridecane and octadecane, no viscosity dependence was observed. This result, however is not inconsistent with a two-step reaction mechanism for thermolysis of **IX**. For thermolysis of optically active IV, the observation[47] that IV racemizes faster than it extrudes nitrogen is consistent with a two-step pyrolysis mechanism. However, the rate constant for thermolysis of IV is independent of solvent viscosity. Evidently, before recombination can occur, cleavage of the diazenyl radical proceeds. Thus for thermolysis of IX, dissociation of the CH_3N_2 radical precludes recombination of the geminate radicals. This observation constitutes a viable explanation for the absence of a viscosity effect on the thermolysis rate for IX.

Experimental Section

Azo Compounds

2,2,2',2'-Tetramethyl-1,1'-diphenylazopropane (VIII) and 2,2,2',2'-tetramethyl-1,1'-diphenylazopropane-1,1'-d_2 (VIII-d_2) and (2,2-dimethyl-1-phenylpropyl)azomethane (IX) and (2,2-dimethyl-1-phenylpropyl-1-d)-azomethane (IX-d) were prepared by $LiAlH_4$ and $LiAlD_4$ reduction of 1,1'-dichloro-2,2,2',2'-tetramethyl-1,1'-diphenylazopropane and (1-chloro-2,2-dimethyl-1-phenylpropyl)azomethane, respectively.[41] For VIII, VIII-d_2, IX and IX-d, λ_{max} and molar extinction coefficients are: 369 nm, 23.5; 269 nm, 23.3; 359 nm, 22.6; and 359, 22.5, respectively.

Kinetics

For VIII-d_2 isotope effects were determined by simultaneously measuring the rates of decomposition of protio and deuterio compounds as described for thermolysis of III and III-d_2.[64] Temperatures were determined using a NBS-calibrated copper constantan thermocouple as previously described.[13] The solvents, EMF readings, and least squares analysis for the calibration are tabulated in Table XVI.

Rates of decomposition of **IX** and **IX**-d in diphenylether containing benzoquinone were followed by measuring the increase in pressure due to nitrogen evolution in a constant volume cell as a function of time. The kinetic system, flask and monometer, was essentially that described by Seltzer.[6b] To one end of the kinetic flask, a 100 ml cylinder (5.0 cm x 6.0 cm) creased to ensure efficient stirring, were attached two sections of capillary tubing and one section of 8 mm glass tubing at ca. 120° intervals. One of the capillary tubes bearing a 12/5 ball was attached to the manometer with Apiezon W wax; the other bearing a 2 mm vacuum stopcock was used for the introduction of dry and oxygen-free nitrogen to the flask. After a glass-encased stirring bar was added to the flask via the 8 mm tube, a teflon vacuum stopcock was fused to the tube. Above the stopcock a short section of 6 mm tubing was attached. To the 6 mm tube was fused a 40 ml addition funnel which was used as a reservoir for the sample. A 12/5 socket was fused to the base of the addition funnel and a glass rod bearing a 12/5 ball on one end and an encased metal bar on the other served as a magnetic valve for the introduction of sample from the funnel to the flask. Near the top of the funnel was fused a 2 mm vacuum stopcock for introduction of solvent or compound to the funnel; near the bottom was fused another stopcock for introduction of nitrogen into the reservoir.

Rate determinations were as follows. The cell was assembled and thermally equilibrated in a cylindrical thermostated bath; temperatures were determined using a NBS-calibrated thermocouple. To the kinetic

TABLE XVI

THERMOCOUPLE CALIBRATION

Solvent	EMF (mv) NBS Thermocouple (Y)	EMF (mv) Measuring Thermocouple (X)	Least Squares Analysis	
			Slope	Intercept
n-octane	5.411	5.446		
ethylbenzene	5.934	5.959		
n-pentylacetate	6.587	6.600		
bromobenzene	6.908	6.929		
o-dichlorobenzene	8.157	8.170	1.007 ± 0.003	-0.0695 ± 0.0196

flask was added 50 ml of distilled diphenylether containing ca. 1×10^{-2} mol of freshly sublimed benzoquinone. Nitrogen was vigorously passed through the solution which was stirred by a rotating magnet from above for 20 min. To the addition funnel was added 30 ml of diphenylether containing ca. 5×10^{-4} mole of azo compound and nitrogen was vigorously passed through the solution for 20 min. After reducing the pressure in the system to ca. 150 mm and allowing the mercury in the manometer to equilibrate, the sample was added to the kinetic flask and the teflon stopcock closed to minimize the volume of the system. The height of the mercury in the manometer was measured as a function of time using a cathetometer. Rate constants were obtained from a least-squares fit of ca. 60 data points to the function $Y = A + Be^{-kt}$ where Y = height of mercury at time = t, B = height at time = 0 minus height at infinite time (ten half-lifes), A = height at infinite time, k = rate constant, and t = time in minutes.

Quantitative Nitrogen Evolution

Samples of **VIII** and **VIII**-d_2 in ethylbenzene were decomposed for a minimum of ten half-lifes and the quantity of gas evolved was calculated from measurements of the pressure of the evolved gas in a calibrated gas buret as previously described.[56] Samples of **IX** and **IX**-d were similarly decomposed in ethylbenzene, ethylbenzene containing a 20:1 mole ratio of freshly sublimed benzoquinone to sample or diphenylether containing a 20:1 mole ratio of benzoquinone to sample. Subsequent gas chromatographic analysis of all gas samples using twelve foot Chromosorb 102 columns at -35°C verified that the noncondensible gases were nitrogen and methane. For those samples containing methane and nitrogen, the quantity of each gas was calculated from the relative peak areas using relative thermal responses.[65]

Effect of Solvent Viscosity on Decomposition of VIII and IX

The rate of decomposition of VIII was determined at 154.13° in distilled tridecane and octadecane. Due to the freezing points of the solvents, difficulties were encountered in degassing the quartz uv cells. Hence, the rates of decomposition were followed by measuring the nitrogen gas evolved as described for thermolysis of IX and IX-*d* in diphenylether-benzoquinone.

For IX, the rate of thermolysis was determined at 188.64° in tridecane and octadecane each containing a 20:1 mole ratio of benzoquinone to azo compound. Due to the low solubility and to the rate of sublimation of benzoquinone from these solvents, the rate of thermolysis of IX was followed by measuring the quantity of gas evolved with a calibrated gas buret[56] as a function of time. For each rate determination four ampoules containing *ca*. 0.1 mmol of IX in 5 ml of distilled solvent-benzoquinone were decomposed for *ca*. 0.25, 0.50, 0.75, and 1.00 fractions of reaction, respectively. Rate constants were obtained by a linear-least squares fit of $\ell n(n(N_2)_\infty - n(N_2)_t)$ vs. time.

Deuterium Content and Correction of Isotope Effects

The deuterium content of VIII-d_2 and IX-*d* was determined by combustion.[54] For IX-*d* the possible presence of deuterium at a position(s) other than benzylic was investigated by comparison of the proton ratios of labeled and unlabeled compounds as determined both by integration of the nmr signal directly and following repetitive scanning with a Varian C-1024. Within experimental error the proton ratios of **IX** and **IX**-*d* at all positions other than benzylic were unity.

The isotope effects in the thermolysis of **VIII**-d_2 and **IX**-*d* were corrected to two and one atoms of α-**D**, respectively.[56] The standard deviation in each of the corrected α-effects was calculated from σ in the experimental isotope effect and the average deviation in the atoms of α-deuterium as previously described.[56]

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APPENDIX A

TABULATION OF RATE DATA FOR THERMOLYSIS OF AZOALKANES

1,1'-Diphenylazoethane and 1,1'-diphenylazoethane-*1*,*1*'-d_2 were prepared by two methods. Samples prepared by $LiAlH_4$ and $LiAlD_4$ reduction of 1,1'-dichloro-1,1'-diphenylazoethane are designated **III**-1 and **III**-d_2-*1*, respectively. Samples prepared by catalytic hydrogenation and deuteration of acetophenone azine are designated **III**-*2* and **III**-d_2-*2*, respectively. Samples of 2,2,2',2'-tetramethyl-1,1'-diphenylazopropane and 2,2,2',2'-tetramethyl-1,1'-diphenylazopropane-*1*,*1*'-d_2 are designated as **VIII** and **VIII**-d_2. (2,2-dimethyl-1-phenylpropyl)-azomethane and (2,2-dimethyl-1-phenylpropyl-*1*-*d*)azomethane are designated **IX** and **IX**-*d*.

Compd.	Temp °C	Measured EMF, mv	Calculated EMF, mv	k x 10^3, min^{-1}	k_H/k_D
III-*1*	103.92	4.463 ± 0.002	4.431	4.529	1.190
III-d_2-*1*	103.92	4.463 ± 0.002	4.431	3.806	
III-*1*	103.88	4.461 ± 0.002	4.429	4.490	1.187
III-d_2-*1*	103.88	4.461 ± 0.002	4.429	3.783	
III-*1*	103.88	4.461 ± 0.002	4.429	4.474	1.203
III-d_2-*1*	103.88	4.461 ± 0.002	4.429	3.720	

Compd.	Temp °C	Measured EMF, mv	Calculated EMF, mv	$k \times 10^3$, min^{-1}	k_H/k_D
III-1	103.88	4.461 ± 0.002	4.429	4.465	1.189
III-d_2-1	103.88	4.461 ± 0.002	4.429	3.756	
III-1	103.90	4.462 ± 0.002	4.430	4.530	1.193
III-d_2-1	103.90	4.462 ± 0.002	4.430	3.798	
III-1	103.90	4.462 ± 0.002	4.430	4.505	1.186
III-d_2-1	103.90	4.462 ± 0.002	4.430	3.799	
III-2	104.01	4.467 ± 0.002	4.435	4.576	1.155
III-d_2-2	104.01	4.467 ± 0.002	4.435	3.961	
III-2	103.86	4.460 ± 0.002	4.428	4.517	1.171
III-d_2-2	103.86	4.460 ± 0.002	4.428	3.857	
III-2	103.86	4.460 ± 0.002	4.428	4.564	1.169
III-d_2-2	103.86	4.460 ± 0.002	4.428	3.904	
III-2	103.88	4.461 ± 0.002	4.429	4.573	1.151
III-d_2-2	103.88	4.461 ± 0.002	4.429	3.974	
III-2	103.92	4.463 ± 0.002	4.431	4.593	1.149
III-d_2-2	103.92	4.463 ± 0.002	4.431	3.998	
VIII	143.48	6.351 ± 0.005	6.328	3.644	1.165
VIII-d_2	143.48	6.351 ± 0.005	6.328	3.127	
VIII	143.66	6.360 ± 0.004	6.337	3.630	1.156
VIII-d_2	143.66	6.360 ± 0.004	6.337	3.140	
VIII	143.50	6.352 ± 0.004	6.329	3.683	1.148
VIII-d_2	143.50	6.352 ± 0.004	6.329	3.207	
VIII	153.88	6.864 ± 0.002	6.844	11.016	1.148
VIII-d_2	153.88	6.864 ± 0.002	6.844	9.594	

Compd.	Temp °C	Measured EMF, mv	Calculated EMF, mv	$k \times 10^3$, min^{-1}	k_H/k_D
VIII	153.94	6.867 ± 0.002	6.847	11.193	1.160
VIII-d_2	153.94	6.867 ± 0.002	6.847	9.652	
VIII	153.80	6.860 ± 0.007	6.840	10.760	1.143
VIII-d_2	153.80	6.860 ± 0.007	6.840	9.418	
VIII	153.80	6.860 ± 0.002	6.840	10.830	1.160
VIII-d_2	153.80	6.860 ± 0.002	6.840	9.338	
VIII	153.72	6.856 ± 0.002	6.836	10.673	1.152
VIII-d_2	153.72	6.856 ± 0.002	6.836	9.263	
VIII	163.81	7.359 ± 0.005	7.343	31.994	1.150
VIII-d_2	163.81	7.359 ± 0.005	7.343	27.827	
VIII	163.81	7.359 ± 0.005	7.343	31.729	1.139
VIII-d_2	163.81	7.359 ± 0.005	7.343	27.865	
VIII	163.83	7.360 ± 0.005	7.344	31.888	1.154
VIII-d_2	163.83	7.360 ± 0.005	7.344	27.623	

Compd.	Temp °C	Measured EMF, mv	k x 10^3, min^{-1}	Average k x 10^3, min^{-1}
IX	190.92	8.737 ± 0.004	14.031	
IX	191.17	8.750 ± 0.004	14.437	
IX	191.17	8.750 ± 0.004	13.842	
IX	191.21	8.752 ± 0.004	14.240	
IX	191.21	8.752 ± 0.004	14.584	
IX	191.09	8.746 ± 0.004	14.099	14.21
IX-*d*	191.48	8.766 ± 0.004	11.992	
IX-*d*	190.98	8.740 ± 0.004	11.623	
IX-*d*	191.19	8.751 ± 0.004	11.698	
IX-*d*	191.08	8.745 ± 0.004	12.133	
IX-*d*	191.15	8.749 ± 0.004	11.667	
IX-*d*	191.19	8.751 ± 0.004	11.778	11.82
IX	179.88	8.164 ± 0.003	4.254	
IX	179.90	8.165 ± 0.003	4.338	
IX	179.86	8.163 ± 0.003	4.268	4.287
IX	170.40	7.678 ± 0.003	1.548	
IX	170.42	7.679 ± 0.003	1.605	1.576

APPENDIX B

DEUTERIUM CONTENT OF 1,1'-DIPHENYLAZOETHANE-1,1'-d_2 AS DETERMINED FROM NMR ANALYSIS

For 1,1'-diphenylazoethane-1,1'-d_2 (**III**-d_2-*2*) prepared by catalytic deuteration of acetophenone azine followed by oxidation with mercuric oxide, the deuterium content was obtained by comparison of the proton ratios of the deuterated compound to the corresponding ratios in the protium sample as determined by integration following repetitive scanning with a Varian C-1024 computer of average transients. Throughout the analysis the phenyl group was assumed to contain no excess deuterium and, hence, served as an internal standard for analysis of the methyl and benzylic positions.

All deviations are standard deviations. Each data set is the average of approximately 20 integral scans. For each data set the experimental scans were tested for acceptance or rejection using 95% confidence interval. The average of the data sets were averaged and data sets greater than 1.68 σ (98% confidence interval) from the mean were rejected. For the unlabeled sample two data sets were rejected; for the labeled sample no data sets were rejected.

	Proton Ratios		
Sample	Phenyl	Benzylic	Methyl
III-d_2-2	10.00	0.4316 ± 0.0200	5.6690 ± 0.1000
III-d_2-2	10.00	0.4334 ± 0.0200	5.6940 ± 0.0800
III-d_2-2	10.00	0.4298 ± 0.0100	5.6560 ± 0.0500
Average	10.00	0.4316 ± 0.0018	5.6730 ± 0.0193
III-2	10.00	1.9959 ± 0.0200	5.8693 ± 0.0200
III-2	10.00	1.9731 ± 0.0400	5.8764 ± 0.0500
III-2	10.00	2.0033 ± 0.0200	5.9716 ± 0.0300
III-2	10.00	2.1312 ± 0.0400	5.9964 ± 0.0800
III-2	10.00	2.1691 ± 0.0500	5.9551 ± 0.0800
III-2	10.00	2.1877 ± 0.0200	6.0607 ± 0.0200
III-2	10.00	2.1493 ± 0.0500	6.0467 ± 0.0800
III-2	10.00	2.0998 ± 0.0100	5.7916 ± 0.0200
III-2	10.00	2.0941 ± 0.0600	5.7915 ± 0.0500
III-2	10.00	1.9968 ± 0.0400	5.7850 ± 0.0400
Average	10.00	2.0800 ± 0.0809	5.9144 ± 0.1059

Using the average proton ratios at the benzylic position in both labeled and unlabeled sample the atoms of α-hydrogen are

$$\alpha\text{-H} = \left(\frac{0.4316 \pm 0.0018}{2.0800 \pm 0.0809}\right)\left(2\right) = 0.4150 \pm 0.0162$$

or the atoms of α-D are

$$\alpha\text{-D} = 2-(0.4150 \pm 0.0162) = 1.5850 \pm 0.0162 \quad .$$

Similarly the atoms of β-D were found to be

$$\beta\text{-D} = 6 - (6)\left(\frac{5.6730 \pm 0.0193}{5.9144 \pm 0.1059}\right) = 0.2449 \pm 0.1049$$

The total atoms of deuterium in III-$\underline{d}_2$-2 is the sum of α-$\utilde{D}$ and β-$\utilde{D}$ or 1.8299.

VITA

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Doctor of Philosophy

Thesis: SECONDARY α-DEUTERIUM ISOTOPE EFFECTS AS A PROBE TO THE RELATIONSHIP BETWEEN STRUCTURE AND MECHANISM OF PYROLYSIS OF SECONDARY AZOALKANES

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