ALUMINA CATALYZED SELF-CONDENSATION OF KETONES

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CHAPTER I

INTRODUCTION AND HISTORICAL

Historical Origin of the Aldol Reaction

The aldol condensation takes its name from 3-hydroxybutanal which was prepared by Wurtz from acetaldehyde in 1872[1]. This name has been generalized to a type of reaction in which base catalyzed self-condensation of acetaldehyde is the simplest example. Aldol condensations are often used to close five- and six-membered rings. Such ring closures generally take place with ease, even where a ketone condenses with a ketone. An important example is the Robinson annulation reaction[2] which has often been used in the synthesis of steroids and terpenes. The aldol condensation may be discussed[3] under different headings in which reaction takes place between two molecules of an aldehyde or different aldehydes or an aldehyde and a ketone. It can also take place between two molecules of the same ketone or different ketones. Concensation of furfural with acetaldehyde or acetone was discovered by Schmidt[4] in 1880 and later developed by Claisen[5], so it is often called the Claisen-Schmidt condensation. Schmidt was first to employ a basic catalyst for the aldol condensation. Of all reactions, the aldol condensation is the only one to which an entire volume of Organic Reactions has been devoted[6].

Condensation Between Two Molecules of an Aldehyde

The most effective catalysts are bases. Due to favorable equilibrium, the reaction is feasible. Many aldehydes have been converted to aldol products and their dehydration products. A commercially important condensation of this type employes basic ion-exchange resins as the most effective catalysts[7].

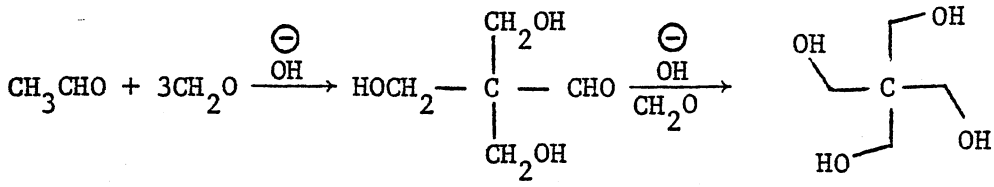
Condensation Between Two Molecules of a Ketone

This reaction is feasible only if the equilibrium can be shifted to favor product. This can be done by allowing the reaction to proceed in a Soxhlet extractor[8] or by adding di- or trivalent metal salts such as those from zinc, magnesium or aluminum. These polyvalent cations presumably form a chelate which minimizes steric interactions.[9,10]

Condensation Between Two Different Aldehydes

In the general case, this reaction produces a mixture of products and its usefulness in synthesis is limited. However, if one aldehyde does not have an α-hydrogen, only two aldols are possible and in many cases, the crossed product is the main product; for example, a commercially important condensation involves acetaldehyde and an excess of formaldehyde in the presence of calcium hydroxide. Condensation occurs to produce tris(hydroxy methylene acetaldehyde), which undergoes a Cannizzaro reaction[11,12] with more formaldehyde to give pentaerythritol

(1) as shown below.



1

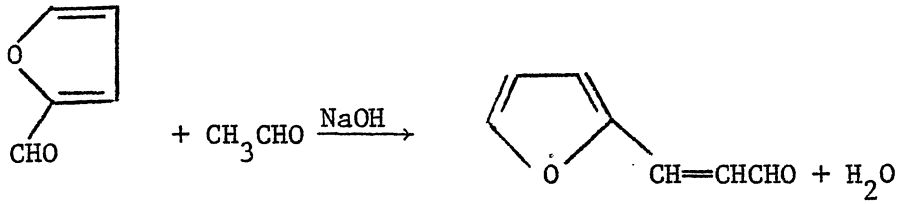
Pentaerythritol (1) is widely used in the preparation of surface coatings and in the formation of explosives.

Condensation Between Two Different Ketones

As a preparative reaction, this is seldom attempted since it produces a complex mixture of products.

Condensation Between an Aldehyde and a Ketone[13]

This is usually feasible, especially when the aldehyde has no α-hydrogen. Even when the aldehyde has an α-hydrogen, it is the α-carbon of the ketone which adds to the carbonyl of aldehyde and not the converse. Although in some cases, the conditions used for crossed aldol condensations can be worked out to favor one of several products. Such condensations are limited to situations in which a ketone with α-hydrogens is condensed with an aldehyde without α-hydrogen atoms. An important example of this type of crossed aldol condensation is the Claisen-Schmidt condensation[4,5]. It is most often taken to be the condensation of an aromatic aldehyde with an aliphatic aldehyde or ketone to yield an α,β-unsaturated aldehyde or ketone, usually in the presence of a basic catalyst.



2

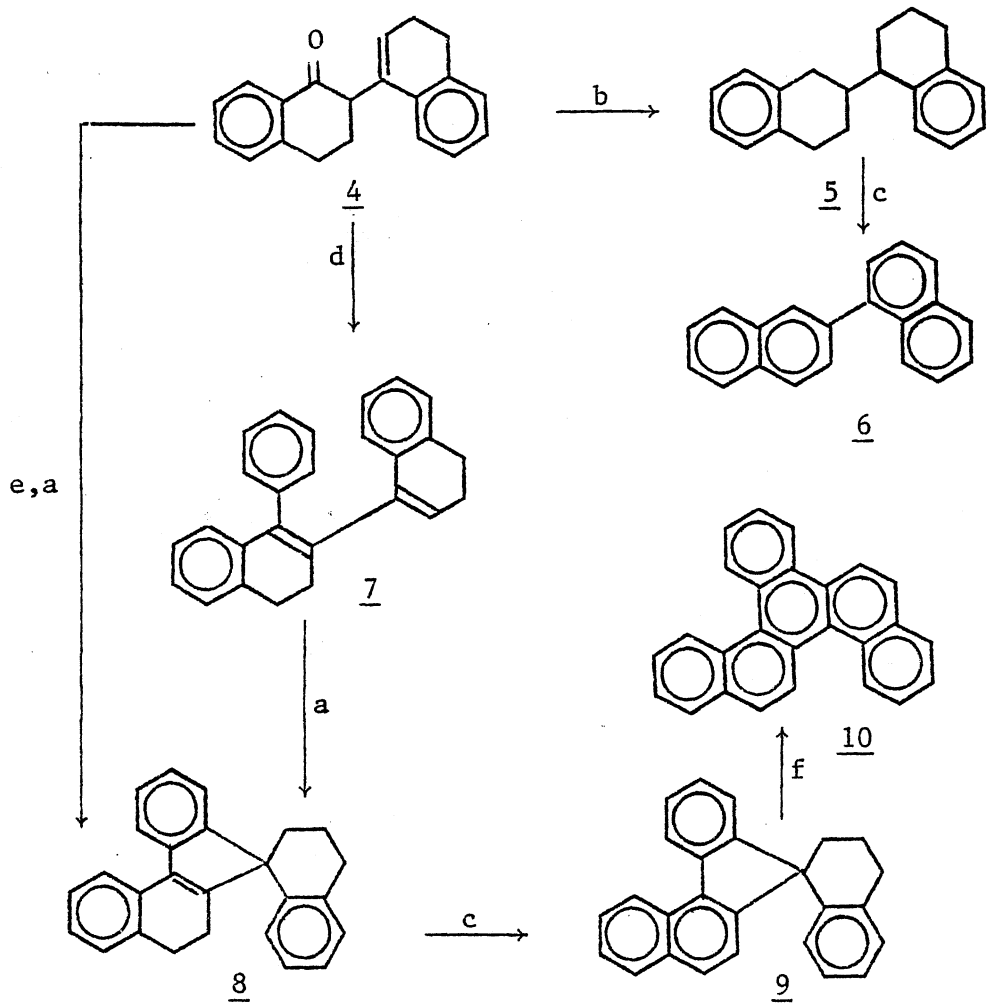
However, the term has been extended to include many types of aldehyde-ketone condensations (e.g., 3 formation[14]) employing either acidic or basic catalysts.

$$C_6H_5CHO + CH_3COC_6H_5 \xrightarrow{\overset{\oplus}{H} \text{ or } \overset{\ominus}{OH}} C_6H_5CH{=}CHCOC_6H_5 + H_2O$$

3

Aldol Dimer Ketones as Precursors in the Synthesis of Polycyclic Systems

Aldol condensation of ketones has been extensively reviewed in the past[15]. However, dimerization of ketones, in particular hydroaromatic cyclic ketones, has not received wide attention despite the attractiveness of these products as precursors in the synthesis of polycyclic systems[16]. An example is shown below[16], wherein the dimer ketone 4, derived from 1-tetralone, in a series of reactions involving addition of Grignard reagent, acid-catalyzed dehydration to the diene 7 and cyclization, gives 8. The latter is dehydrogenated with Pd/C to 1',2',3',4'-tetrahydrospiro[7H-benzo[c]fluorene-7,1'-naphthalene] 9 and then 9 is converted to dibenzo[c,p]chrysene 10 by heating in the presence of Pd/C and sulfur.



[a] Amberlyst-15, toluene, Δ.

[b] Pd/C, H_2, CH_3CO_2H.

[c] Pd/C, Δ.

[d] C_6H_5MgBr, H_3O^+, $-H_2O$.

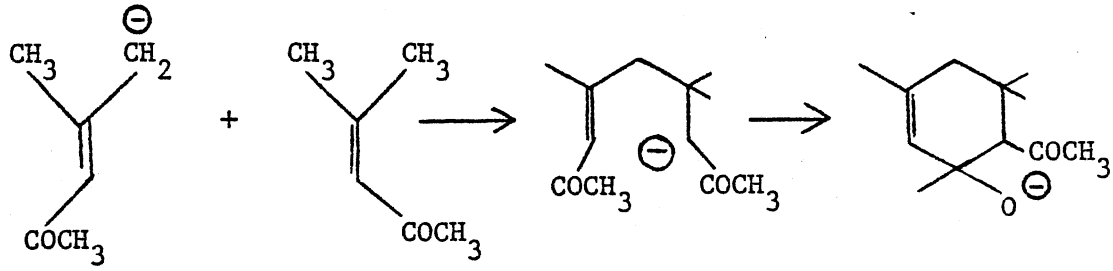
[e] C_6H_5Li.

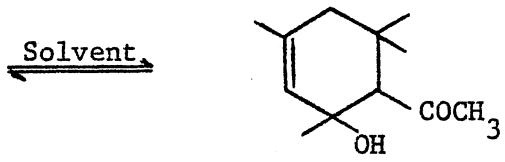
[f] Pd/C, S, Δ.

Side Reactions in the Aldol Dimerization

A possible explanation for the failure to exploit this interesting area of the aldol condensation may be found in low yields and side reactions. These side reactions result from the failure to stop the

self-condensation reaction of the ketone at the dimer stage[16]. Dimer products obtained "in situ" may undergo further transformation to more stable and in some instances, aromatic compounds. Such reactions may be catalyzed either by acids or bases. Michael additions to α,β-unsaturated ketones are the basis for many side reactions[15], for example,





11

In this study of alumina catalyzed self-condensation of ketones, we have attempted to minimize the side reactions and optimize the yield by employing ultrasonic and sieve-shaker agitation.

Survey of Reagents

A variety of reagents have been made to use in ketone dimerization[17]. In the past, many reagents ranging from acidic to basic have been used as the catalysts for the aldol self-condensation of ketones. Basic aluminum oxide has been used only in one case for converting acetophenone to dypnone[18]. Acidic reagents used for the self-condensation of ketones include mineral acids[19], resins[20],

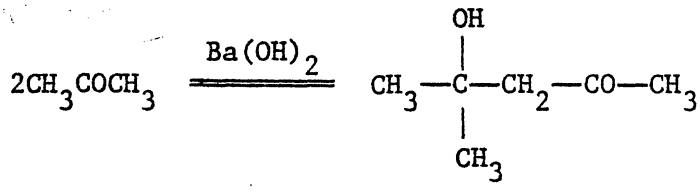
p-toluenesulfonic acid[21] and polyphosphate ester[22]. Polyphosphate ester is a solution of phosphorus pentoxide (P_4O_{10}) in ethyl ether and chloroform[23]. Basic reagents used for the self-condensation of ketones include strong alkali hydroxides[24], aluminum tertiary butoxide[25], barium hydroxide[7] and basic anion exchange resins[20]. Special reagents[26,27] have also been used for the self-condensation of ketones. These include oxides of metal[28], Grignard reagents[29], enamines[30] and calcium hydride[31].

In the aldol condensation the α-carbon of one aldehyde or ketone molecule adds to the carbonyl carbon of another. Various acids and bases have been used for this reaction[19,32]. The base most often used is OH^-, although stronger bases, e.g. aluminum tertiary butoxide, are sometimes employed. Alcohol dehydration in the acid catalyzed aldol condensation is spontaneous, since the new double bond will be in conjugation with the carbonyl bond. In a number of cases, the final result of the aldol condensation may be determined by the nature of the catalyst used. Thus a base-catalyzed condensation is much more likely to stop at the aldol stage than is an acid-catalyzed condensation. Significantly, the aldol condensation is one of the important methods of preparing α,β-unsaturated aldehydes and ketones as well as β-hydroxy aldehydes and ketones.

Sulfuric acid has been used only on rare occasions[19], as it also produces side products. When p-toluenesulfonic acid is used as a catalyst, to self-condense ketones, it is not very effective even at reflux temperature of the solvent. Cation exchange resins[33,34] including strongly acidic resins can be used directly or after treatment with 10% hydrochloric acid. The carbonyl compound and the ion-exchange

resin are agitated in a flask equipped with a condenser, nitrogen bubbler, magnetic stirrer and if necessary, a Dean-Stark trap.

Ketones undergo the aldol condensation less readily than do aldehydes. In the presence of catalytic amounts of bases, acetone is converted reversibly to diacetone alcohol[35].



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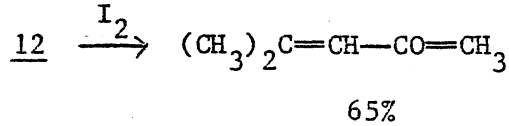
The equilibrium for this reaction lies so far to the left that practically no diacetone alcohol is obtained unless the equilibrium is altered in some way. This may conveniently be done by placing the catalyst in the thimble of a Soxhlet extractor and refluxing acetone over it. Conversion of acetone to diacetone alcohol occurs on contact with the catalyst; the higher-boiling diacetone alcohol accumulates in the pot, and is stable, out of contact with the catalyst. In this way, a yield of 71% of diacetone alcohol can be obtained, based on the total acetone employed in the process. Diacetone alcohol may be conveniently dehydrated to mesityl oxide by distillation in the presence of a catalytic amount of iodine[35].



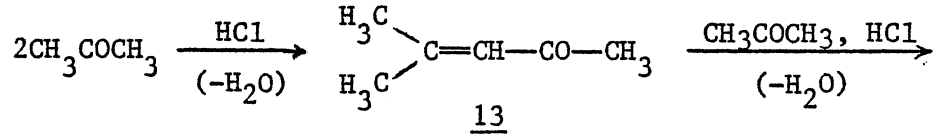
65%

13

Although mesityl oxide 13 can be prepared in small yield by the action

of acid condensing agents on acetone (as shown below), this preparation through diacetone alcohol is much superior.

As shown below, in the presence of the more powerful acidic and basic condensing agents, acetone gives trimeric condensation products in addition to mesityl oxide. When, for example, acetone is saturated with hydrogen chloride and allowed to stand for several days, mesityl oxide 13, and phorone, 14, are the products.[36,37]



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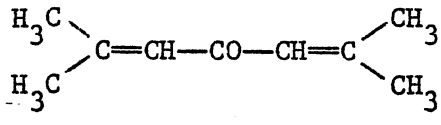

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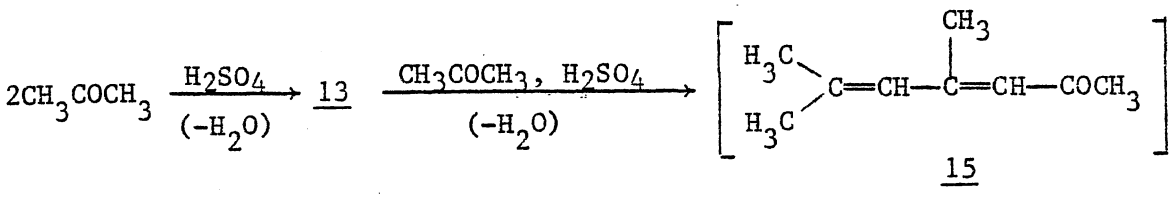
The action of concentrated sulfuric acid on acetone[38] leads to the formation of mesitylene 16 presumably by the following sequence of reactions.



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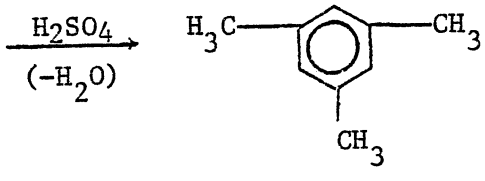
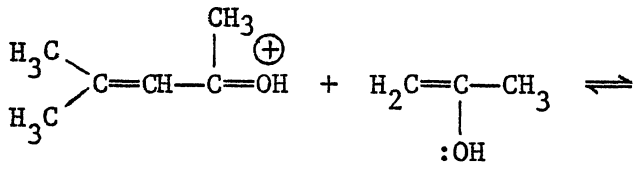
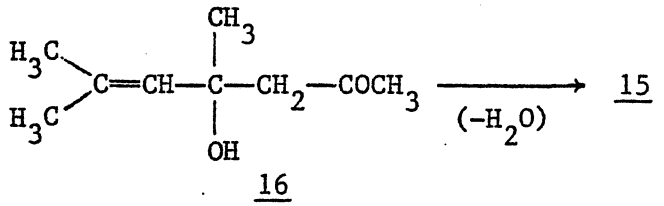


16

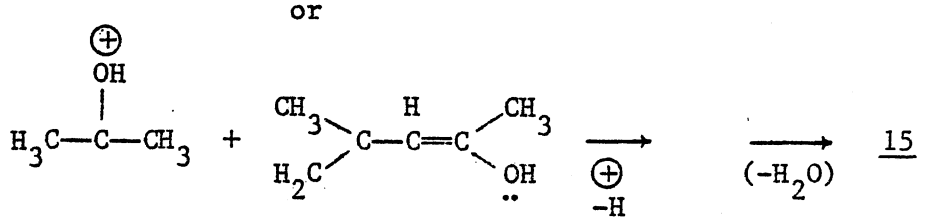
The intermediate involved here, 15, may conceivably be formed by either or both of two possible aldol condensations of mesityl oxide with acetone as follows.





16

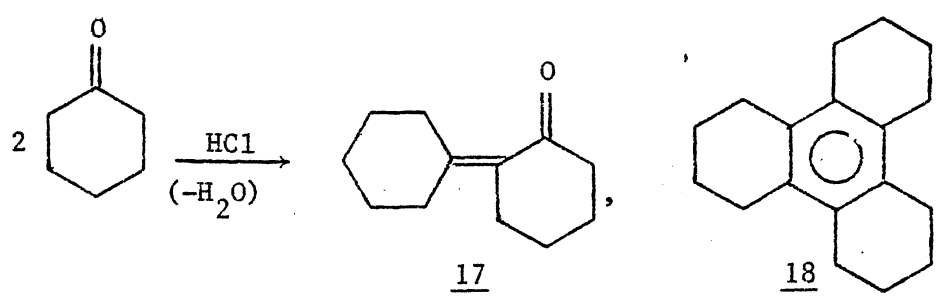
or



The yield of mesitylene from such processes is not high; it is accompanied by mesityl oxide, phorone, 1,2,3,5-tetramethyl benzene as the condensation products of acetone.

Aluminum tertiary butoxide brings about the aldol self-condensation[25] wherein it absorbs the water formed during the dehydration step of the aldol condensation. Since tertiary butyl alcohol is formed during the condensation, it must be distilled out of the reaction mixture.

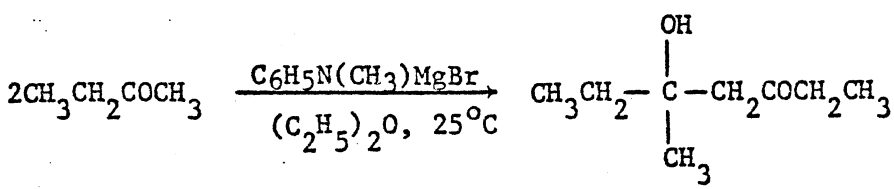
Cyclic ketones undergo the aldol condensation on treatment with acids or bases. Thus the action of hydrogen chloride on cyclohexanone[39,40] yields 2-cyclohexylidenecyclohexanone 17.



17 18

Heating cyclohexanone with alcoholic sulfuric acid leads to the formation of 18, a reaction analogous to the formation of mesitylene from acetone[38].

Special reagents used for the aldol dimerization reaction include enamines[30] and Grignard reagents[29]. The self-condensation of enamine derived from ketones and secondary amine gives dimer ketone. The halomagnesium salts of secondary amines, for example, $C_6H_5N(CH_3)MgBr$, have been suggested[42] as general reagents for the conversion of aliphatic ketones to β-hydroxy ketones. Yields of the order of 60-80% of ketols have been obtained. The bromomagnesium salt of N-methylaniline is prepared by interaction of ethylmagnesium bromide with N-methylaniline. The preparation of 19 is a typical example.



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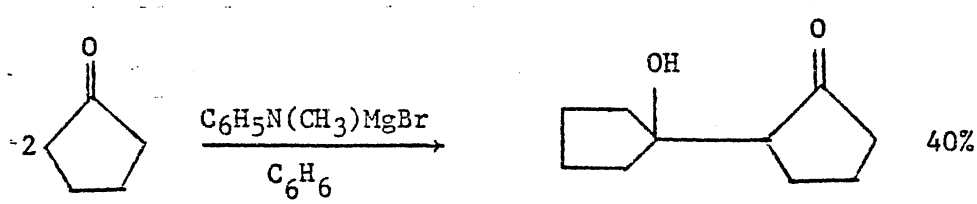
Cyclic ketones yield ketols on treatment with bromomagnesium methyl aniline in benzene, although the yields are smaller than in the case of aliphatic ketones; for example[42],



20

Less common are such reagents[15] as calcium hydride, aluminum chloride, diethyl zinc, a mixture of zinc chloride and acetyl chloride, phosphorus pentachloride, triphenyl aluminum and even benzoic acid

have been reported as catalysts for the aldol dimerization of ketones.[19]

Mechanism of the Base-Catalyzed Aldol Condensation[43]

As shown in Figure 1, addition of an enolate anion to a carbonyl group, followed by protonation involve a series of equilibria.

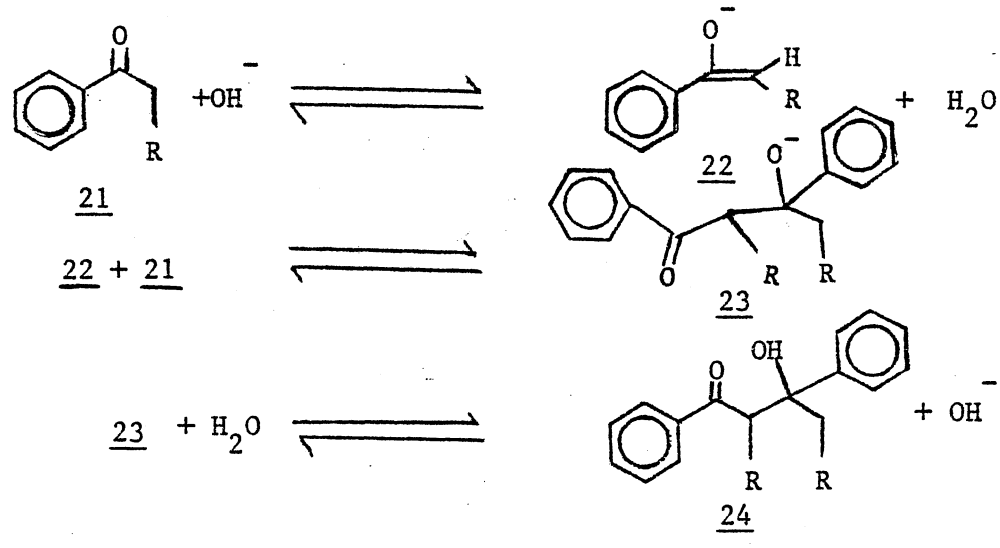


Figure 1. Mechanism of the Base-Catalyzed Aldol Condensation.

Kinetically either proton abstraction or carbon-carbon bond formation step may be rate limiting. The mechanism has been studied in some detail in a series of papers by Noyce and coworkers.[44,45] The proton abstraction step becomes rate limiting at the relatively

high reactant concentrations normally employed for the aldol dimerization reactions. The first equilibrium shown in Figure 1 is usually favorable. The reaction is feasible only if the second equilibrium shown in Figure 1 for the formation of 23 can be shifted. This can be done in different ways. One way is to employ Soxhlet extractor[8] or in certain cases[9,10], it can be done by adding di- or tri-valent metal salts which presumably form a more stable chelate cation in which steric interactions are minimized. Any technique of trapping the adduct of carbon-carbon bond formation and preventing reversal should work for this condensation reaction.

Mechanism of the Acid-Catalyzed Aldol Condensation

In acidic medium, the carbonyl group of 20 is protonated to form resonance stabilized hybrid 25, as shown in Figure 2.

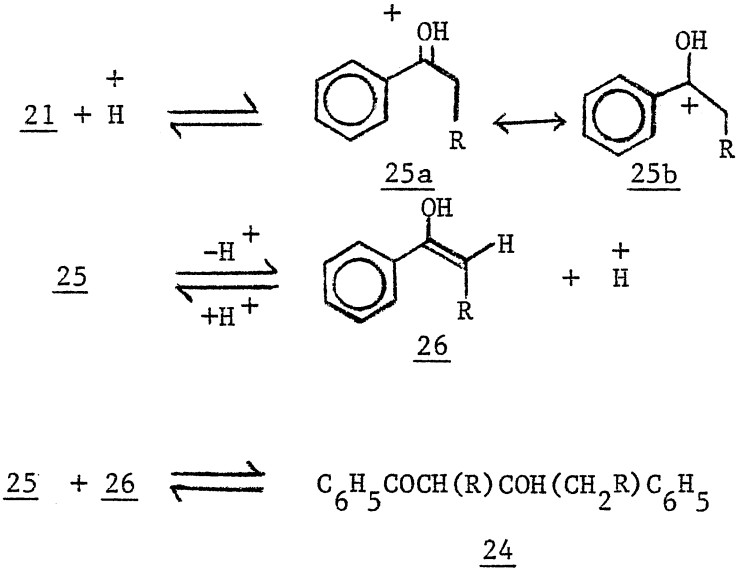


Figure 2. Mechanism of the Acid-Catalyzed Aldol Condensation.

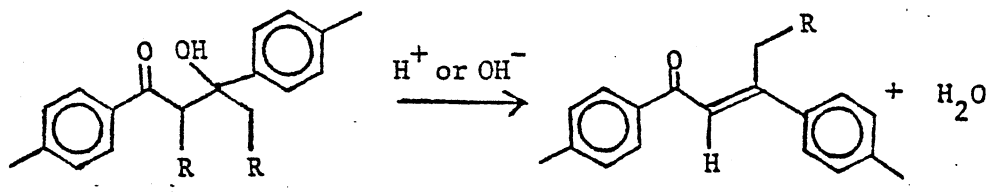
Loss of proton results in the formation of the intermediate enol 26. Enol 26 reacts in a rate limiting step with 25b to produce a ketol 24. However, in the acid catalyzed aldol condensation α,β- or β,γ-unsaturated carbonyl compounds (rather than ketol) are the most frequently encountered products because of rapid dehydration. In most cases, it is irreversible. The dehydration step can be different in both types of (acid and base catalyzed aldol) condensation. Acid catalyzed dehydration may occur by two different pathways.[46] Either a carbonium ion mechanism or a synchronous mechanism appears to be operative in the case of dehydration step during the aldol reaction. Normally, a simple 1,2-trans elimination is the preferred explanation for dehydration.

Stereochemistry

A stereoselective reaction is one in which a single reactant has the capacity of forming two or more stereoisomeric products in a particular reaction, but one is formed preferentially.[47] According to this definition, the aldol condensation is a stereoselective reaction. There is a strong preference for formation of compounds having trans C-C double bonds in the self-condensation of aromatic ketones. This stereoselectivity can be traced to the dehydration step. The transition states leading to cis and trans products involves attainment of coplanarity of the leaving groups. This occurs as the elimination proceeds.

The steric compression that develops between the phenyl groups during elimination of water from an aldol (27) raises the energy of the transition state that leads to cis product, and therefore the

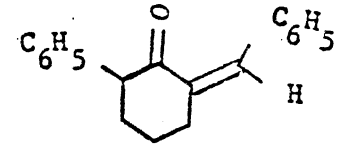
trans product is preferentially formed as shown below:



27 28

Another important stereochemical question concerns cis-trans isomerism of α,β-unsaturated carbonyl compounds derived from ketols and aldols. Hassner and Mead[48] observed during the preparation of benzal ketone that the most highly favored product was the trans isomer. Their conclusions are based on evidence from the infrared spectrum of cis-benzal ketone 29 where the intensity ratio is

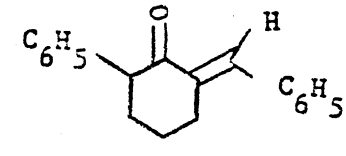
$$\frac{\nu_{C=C}}{\nu_{C=O}} = 0.2 \text{ to } 0.3$$



29

with respect to spectrum of the trans-isomer where intensity ratio is

$$\frac{\nu_{C=C}}{\nu_{C=O}} = 1$$



30

Cis-isomer 29 may sometimes be isomerized to trans-isomers with acid or base catalysts,[49] the reverse transformation is frequently achieved by irradiation with light.[50]

An acid catalyzed mechanism for the isomerization of cis-4-methoxy

chalcone 31 is illustrated in Figure 3, cis-4-methoxy chalcone 31 is protonated to 32 which is resonance stabilized as shown by its canonical structure. This enol 33 rotates about a carbon-carbon single bond to give 34, then loses proton to give trans-4-methoxy chalcone 35. Practical preparation of cis-dypnone and its derivatives by irradiation of the trans-dypnone have been developed.[50] This consists of irradiating a 5% solution of trans-dypnone in 95% ethanol with sunlight. This isomerization is complete in 24 h. Evaporation of the solvent and distillation of the residual oil under reduced pressure gives pure cis-dypnone in 78% yield.

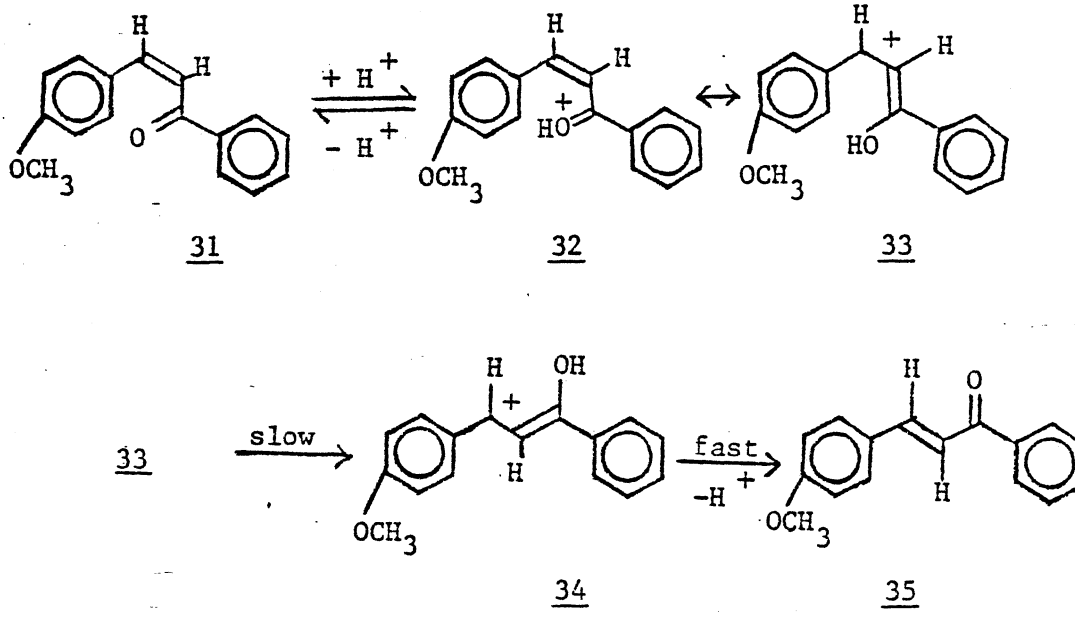
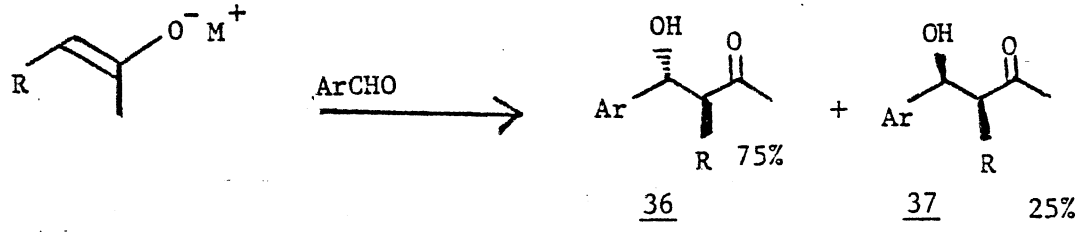
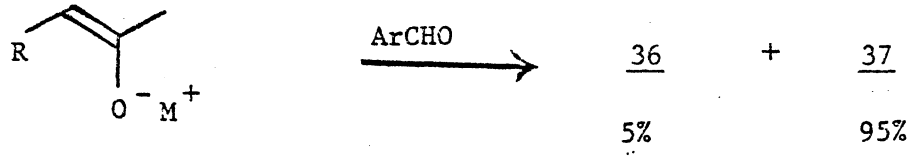


Figure 3. Isomerization of cis-4-Methoxychalcone.

Using systems such as potassium hydroxide in methanol, the French

chemist, J. E. Dubois, and his coworker, M. Dubois, carried out the first careful investigations of the aldol stereochemistry.[51] They established a potentially useful generalization: (E) enolates show threo stereoselectivity and (Z) enolates show erythro stereoselectivity. Masamune and coworkers[52] noticed that the cis enolate is more highly selective than trans as shown in the formation of 36 and 37. Jeffery, Meisters and Mole[53] examined the case of the aluminum enolate derived from methyl neopentyl ketone. Heng and Smith[54] examined the reactions of the corresponding zinc enolates. Izawa and Mukaiyama[55] studied the stereoselective reactions of the titanium enolate in the aldol condensation. Several reagents are now available which show good stereoselection. Better reagents are still needed, however, since some of the currently available ones require several additional steps to convert the initial aldol into the more desirable β-hydroxy keto compounds. Nevertheless, the venerable aldol condensation has undergone considerable maturation during the past decade.



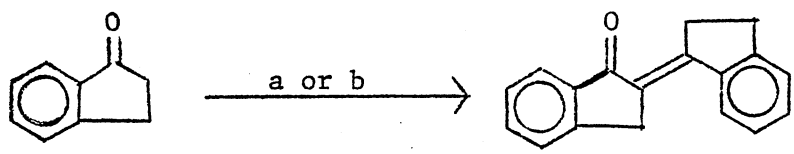


R = Alkyl
Ar = Aryl
M = Metal

CHAPTER II

RESULTS AND DISCUSSION

Dimer ketone is the term used in this study for the self-condensation product of a ketone as shown for 39 obtained from 38.



38 39

[a]Basic Al_2O_3, cyclohexane, 80 °C, 24 h
[b]$TiCl_4$, -10 °C. (38) in Et_3N

Figure 4. Routes for the Synthesis of Dimer Ketones.

As outlined in Figure 4, two synthetic reactions were studied in detail. One employed titanium tetrachloride[56] and the other used activated basic aluminum oxide.[57]

Titanium Tetrachloride Catalyzed Aldol Dimerization

The self-condensation of 1-tetralones leads to α,β-linked dimers.

This constitutes an excellent route to the 1,2-binaphthyl systems and their derivatives free of 1,1- and 2,2- isomers. Dimerization of 1-tetralone and its derivatives using the Massa and Guarna's procedure was first attempted by A. G. Holba.[58] As shown in Figure 5 using equimolar quantities of 40 and the preformed enolate 41 in the presence of anhydrous triethylamine gave 4 in 70% yield. The presence of 42 could not be detected. This result prompted the study of various ketones to gain information about the regioselectivity in the formation of the dimer ketones derived from acetophenone, α-tetralone and its derivatives as well as 1-indanone and its derivatives. The results are summarized on page 32 of this thesis.

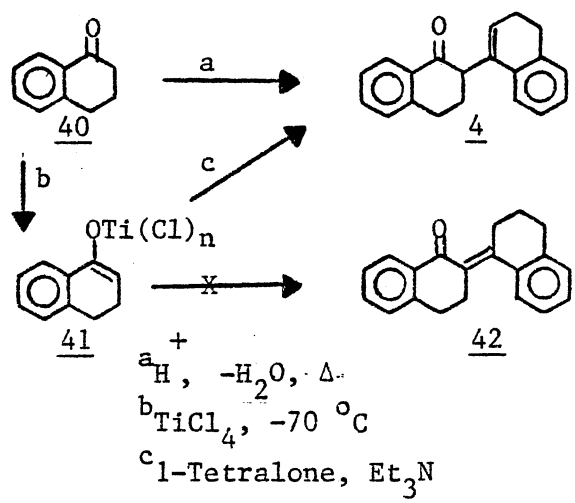
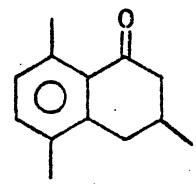


Figure 5. Aldol Dimerization of 1-Tetralone Using Titanium Tetrachloride.

Crossed condensation of preformed enolate of 1-tetralone with 1-indanone as well as preformed enolate of 1-indanone and 1-tetralone gave an intractable complex mixture in both cases. GC/MS studies

showed these to be similar mixtures of C_{18}, C_{19} and C_{20} dimers.[59] As expected, the titanium enolate method is sensitive to steric effects. Dimerization of 43 as a test case was attempted. GC/MS studies showed that a trace of the expected dimer of 43 may have formed.



43

Titanium tetrachloride is a valuable reagent promoting various synthetic reactions[60] including the aldol dimerization. Other variation[61] of this method include use of pyridine instead of triethylamine and use of either THF or dioxane instead of dichloromethane.

Use of Ultrasonic Agitation in Aldol Dimerization

Application of ultrasonic irradiation in organic synthesis, for a variety of purposes, is becoming popular. However, there does not appear to be a review and therefore some of the important work which is being carried out by organic chemists using ultrasonic irradiation is included.

Han and Boudjouk[62] have shown that using ultrasonic irradiation; simple and even deactivated aryl halides can be reduced with lithium aluminum hydride. They have also demonstrated the usefulness of ultra sound in coupling reactions.[63] In the presence of lithium wire, coupling of chlorosilanes as well as several organic halides has been

carried out. This includes the Reformatsky reaction[64] and the preparation of a diene[65] in good yield from the reaction of zinc with α,α'-dibromo-o-xylene.[66]

Repic's[67] group used ultra sonic agitation for large scale preparation of cyclopropane. Cyclopropanes are synthesized using olefins with zinc and diiodomethane. Japanese workers[68] have successfully demonstrated that heterogeneous organic reactions like oxidation of alcohols can be carried out using solid potassium permanganate. Synthesis of aromatic acyl cyanides is another example.[69] Reductive alkylation of coal[70] and alkylation of carbonyl compounds[71] with alkyl halide have been performed using ultrasonic irradiation.

Davidson and co-workers[72] were able to carry out N-alkylation of amines using phase transfer catalysis with ultrasound. A phase transfer reaction[73] was reported for the displacement of halide by thiocyanate ion.

Luche and co-workers[74] successfully prepared organocopper and organolithium reagents using ultrasound. Solvolysis ultrasound reactions were carried out using 2-chloro-2-methylpropane.[75] Thioamide[76] and dichlorocarbene[77] have been prepared using ultrasound. Cleavage reactions including cleavage of aromatic and heterocyclic rings and cleavage of halogens have been demonstrated.[78]

Hydrolysis of various esters has been shown to occur rapidly under the influence of ultra sound. The types of compounds which have been hydrolyzed[79] include ester of nitrophenols and carboxylic acids.

In our search for improved methods to prepare aldol dimers of ketones, we decided to try ultrasonic agitation[80] using basic alumina

as a condensing agent. Heterogeneous organic reactions using a high surface solid reagent like alumina are becoming useful[81] in laboratory scale synthesis. These reactions are often more selective and proceed under milder conditions than the corresponding homogeneous reactions.[82] Basic aluminum oxide, 60-250 mesh, is commercially available.[83] When this alumina is heated at 270 °C for 24 h prior to use, it is said to become activated. Activated alumina is a porous form of aluminum oxide of high surface area. Activated alumina absorbs liquids, vapors and gases without change of form or properties. It finds multiple uses in several important industrial processes involving dehydration, isomerization, petroleum cracking, polymerization, condensation and alkylation.[84]

Activated alumina has also been used in the removal of environmental wastes. These special uses of activated aluminum oxide include:

(a) Phenol removal from waste water;[85]

(b) Fluoride removal from drinking water;[86]

(c) Arsenic recovery from alkaline solutions;[87]

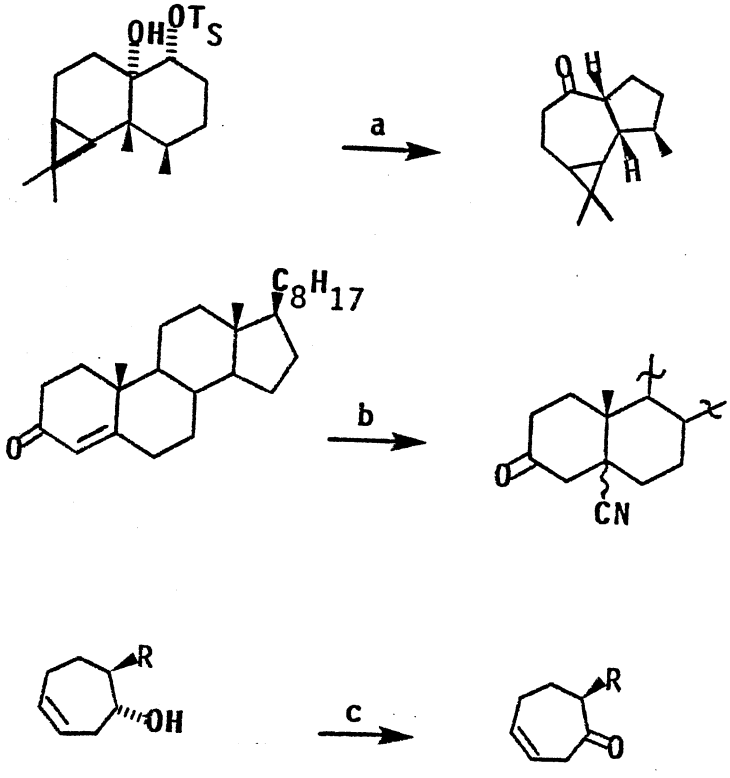
(d) Carbon dioxide removal from gas streams;[88]

(e) Cooling of petroleum pyrolysis gases;[89]

(f) In ion-exchanger for treatment of sewage.[90]

Specific reactions[91] using alumina are shown in Figure 6.

There are limitations to the use of alumina. Immediately before use, commercial alumina must be dried at high temperature under vacuum. There is also the problem of violent bumping when alumina is heated as a suspension in organic solvents. This is due to the high density[92] of alumina and also relatively large quantity used



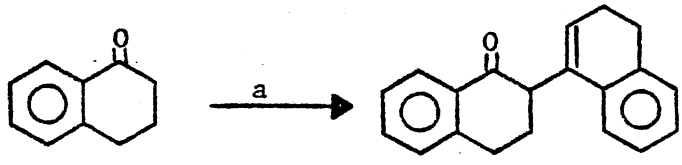
[a] Al_2O_3, 25 °C.

[b]  , Al_2O_3.

[c] CCl_3CHO, Al_2O_3, 55 °C, 24 h.

Figure 6. Typical Reactions Using Alumina.

in some heterogeneous organic reactions. Conventional means of stirring to prevent bumping in most cases are not reliably applicable. One of the ways to prevent bumping is the use of ultrasonic irradiation. The use of ultrasonic irradiation as a method of agitating heterogeneous reaction systems is effective. We have found this method will more than double the yield of aldol product as compared to acid-catalyzed dimerization of 1-tetralone.[93,94] This modification shortened the reaction time from the reported[95] five days to 24 h at 80 °C as shown in Figure 7 and provided a consistent yield increase. The yields and other information are collected in Table 1.



[a]Basic alumina, cyclohexane, argon atmosphere, sonic agitation at 80 °C for 24 h.

Figure 7. Typical Reaction Using Ultrasonic Agitation.

Due to internal dimensions of the sonic apparatus tank,[96] our work was limited to a 1-liter flask containing 0.25 mol. of ketone, 50 ml of cyclohexane and 125 g of activated basic alumina.

What is ultrasonic irradiation and how does it work? Sound with a frequency above 17,000 Hz which is the upper threshold of hearing for the human ear is called ultrasonic. Ultrasonic irradiation is

TABLE I

Dimer Ketones Obtained Using Ultrasonic Agitation

Product	°C	h	% Yield[a]	m. p. or b. p./ °C	
4	80	24	77	130 - 131	
39	80	24	90	240 - 242	
44, 45	25-30	144	83[b]	140/0.4 mm	9
	25-30	12	30		
	80	24	91		

[a]Yield calculation based on recovered starting material.

[b]We substantiated the ratio of E/Z (89:11) observed in the earlier work.[57]

effective due to cavitation which is described as a process in which strongly agitated water (used in the tank as a medium) raptured into tiny cavities, each containing gas at a high pressure. When the cavities burst, they produced an intense shock wave. The extent of cavitation produced in ultrasonic irradiation depends on the factors such as tank geometry, water height and continuous operation time.[97] As an example, a 32 x 200 mm pyrex tube containing 20 ml of a saturated solution of carbon tetrachloride in distilled water was clamped vertically in each of the nine positions shown in Figure 8. The liquid level inside was the same as in the tank. The amount of chlorine liberated by cavitation during ten seconds irradiation was measured by adding one ml of orthotolidine reagent.[97] As shown in Figure 8, a typical set of results was obtained. The numerical scale was based on a value of 200 for one ppm of free chlorine. It is apparent that the cavitation intensity is greatest at the geometric center of the horizontal plane, and is comparatively minor in the corners.

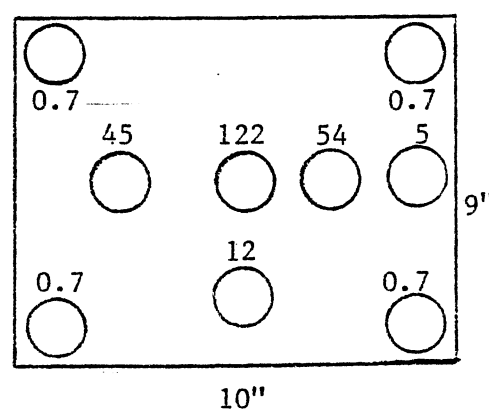


Figure 8. Relative Cavitation at Different Positions in the Tank.

A second variable, the height of water in the tank, was also studied. A periodic dependence of cavitation intensity on water height was found, as shown in Figure 9, where an ordinate of 1 indicates 0.5 ppm of chlorine.

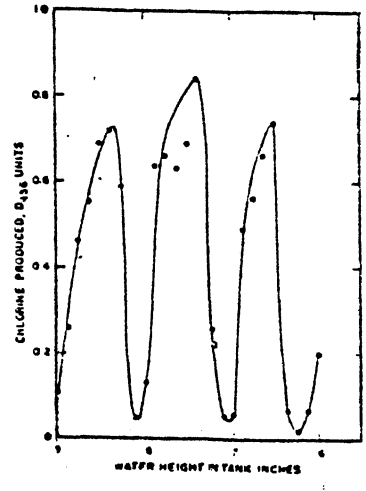


Figure 9. Cavitation Intensity as a Periodic Function of Water Height in the Tank.

The third factor studied was the effect of continuous operation on the cavitation intensity. Figure 10 shows that there was a declining trend in cavitation intensity with increasing time of continuous operation.[97]

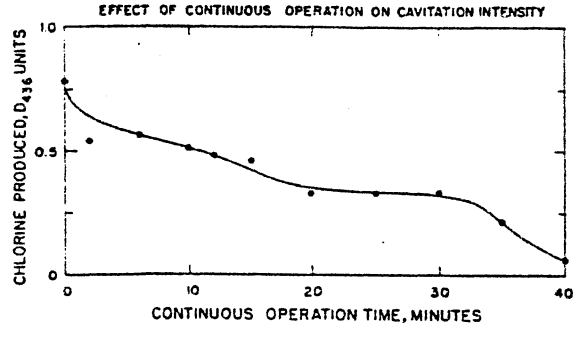


Figure 10. Effect of Continuous Operation on Cavitation Intensity.

Thus a basic knowledge of the mechanism of ultrasonic agitation helps to establish its use with maximum benefit. When the three variables are taken into consideration, basic alumina catalyzed aldol dimerization can be carried out with high efficiency. We anticipate that a larger apparatus and further modification[98] would permit a large scale aldol dimerization.

Sieve Shaker and Modification

In order to have a larger apparatus that would permit proportionate increase in reaction scale, we decided to modify a vibrator type sieve shaker. This sieve shaker, commercially available, is quite efficient as a shaking device. It has a clamp to take a stack of four standard 8" (203 mm) sieves with receiving pan and cover. The intensity of shaking is adjustable producing 3600 impulses per minute. A rheostat control, with reference setting dial on the front panel, permits adjustment of vibration amplitude. The maximum height of the sieve stack is 283 mm and maximum sample load can be 2.3 kg. The clamping head has a sponge rubber cushion on the vibrator base, which minimizes the noise even at maximum impulse rate. The only drawback in this commercially available sieve shaker is that there is no facility to carry out a reaction at any other temperature than room temperature. We decided to modify this device (Figure 11) as shown in Figure 12. We first redesigned the clamping devide (yoke). The yoke as shown was rebuilt to fit a new reactor head which has provisions for inserting a thermocouple probe to measure reaction temperature and gas inlet and outlet. The stainless steel vessel is ideal for reactions in

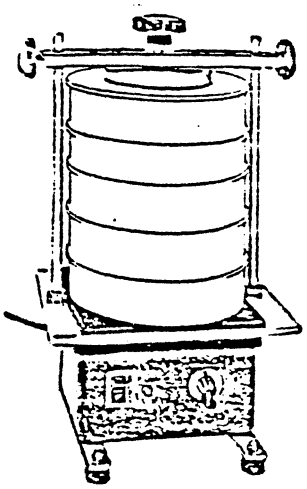


Figure 11. Thomas® Sieve Shaker Before Modification.

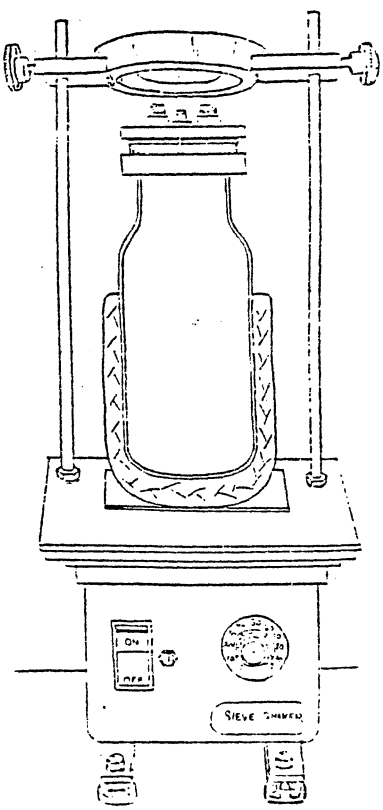


Figure 12. Modified Sieve Shaker.

which flask breakage presents a hazard. The flask can be heated using a heating mantle and the reaction can be carried out at any desired temperature under pressure to 55 psig. As shown in Figure 13, addition of a teflon bellows adaptor enables attachment of a condenser. Direct attachment of a condenser causes reduced vibration but also introduces the possibility of breaking the condenser if it is constructed of glass. The teflon bellows adaptor connects the stainless steel vessel to a condenser which makes it possible to carry out the heterogeneous reaction at reflux temperature of the solvent.

Use of the modified sieve shaker is operationally simple. The product isolation usually involves filtration and solvent removal. The reaction can be carried out at desired temperatures up to the boiling point of the solvent without any problem of bumping.

The stainless steel apparatus may be assembled from the commercially available components except for the adapter, stainless steel reactor head and the split-ring clamp. The o-ring ball joints used withstand unequal expansion and contraction because of the cushioning effect of the plastic o-ring.[99]

Discussion of the Stereochemistry and ^{13}C NMR Assignments of the Dimer Ketones of 1-Tetralones

The ^{13}C-chemical shift values for the dimer ketones of 1-tetralones are given in Table II. Carbons 1-8 are numbered on the tetralone ring starting from the carbonyl carbon as shown in spectrum 2. Numbers 1'-8' refer to the carbons of the remaining rings of the

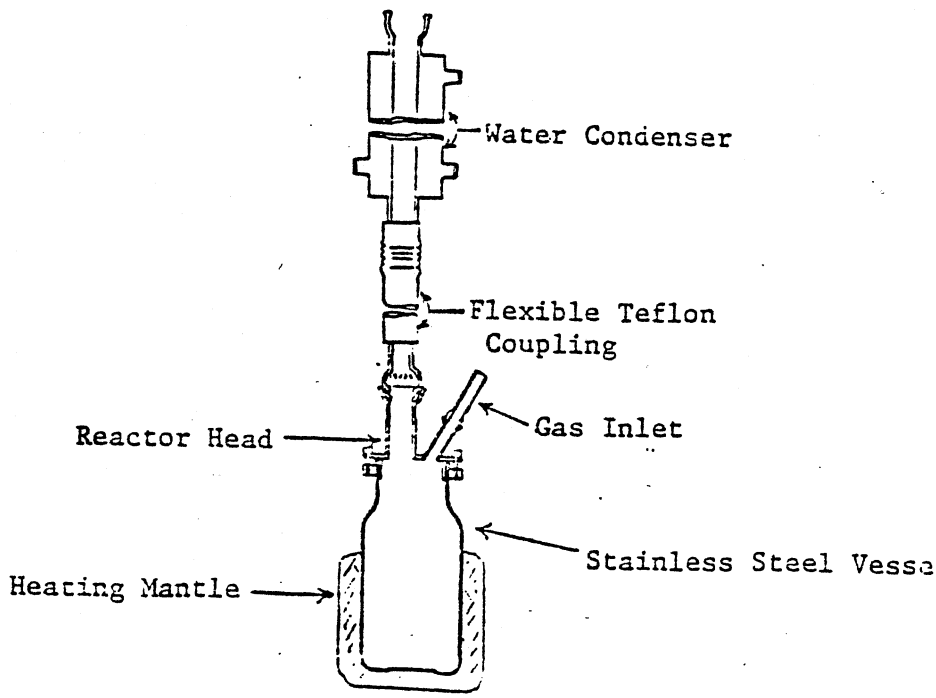


Figure 13. Stainless Steel Vessel and Attachments for Use with Modified Sieve Shaker.

TABLE II

^{13}C NMR Data of Dimer Ketones of 1-Tetralones

Dimers of 1-Tetralones	^{13}C NMR (ppm from TMS)		$\Delta\delta$[a]	
	Carbonyl[b]	Methine[c]	Carbonyl	Methine
4	199.1 (197.4)	50.7 (36.0)	17	14.7
46	198.6 (196.6)	50.4 (38.7)	2.0	11.7
47	197.9 (197.8)	50.5 (38.8)	0.1	11.7
48	198.3 (197.8)	50.1 (39.0)	1.5	11.1
49	198.7 (197.5)	49.6 (38.3)	1.2	11.3

[a]Shifted value in ppm from monomer to dimer ketone.

[b]Shift value of monomer ketone for carbonyl is noted in parentheses.

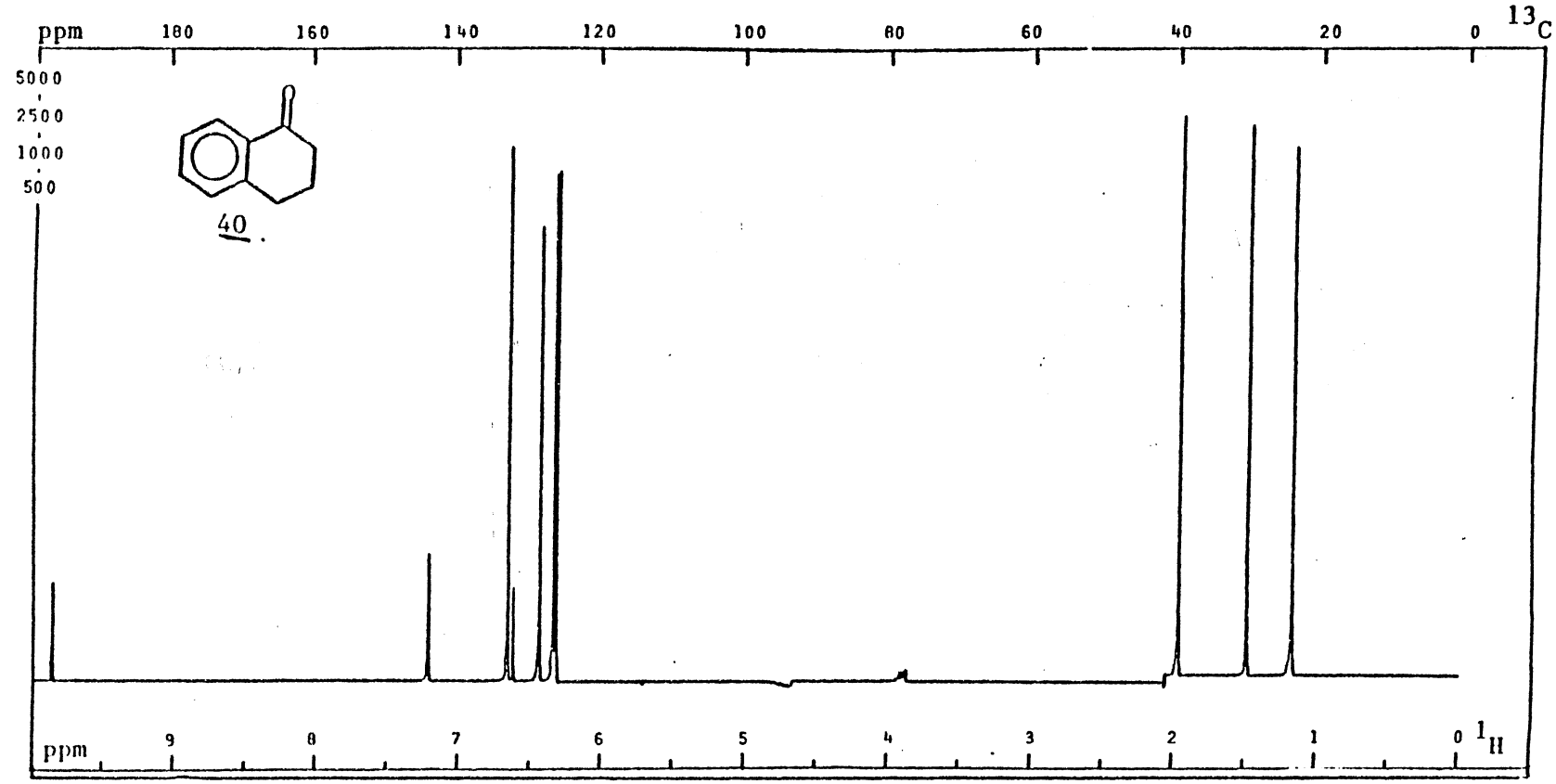
[c]α to carbonyl.

dimer ketone. With respect to monomer ketone, all dimer ketones show a 1-2 ppm deshielding at C-2 which is due to substitution at that carbon. Thus since this aliphatic carbon is not part of a double bond, the ^{13}C NMR clearly establishes the absence of double bond conjugation with the carbonyl group.

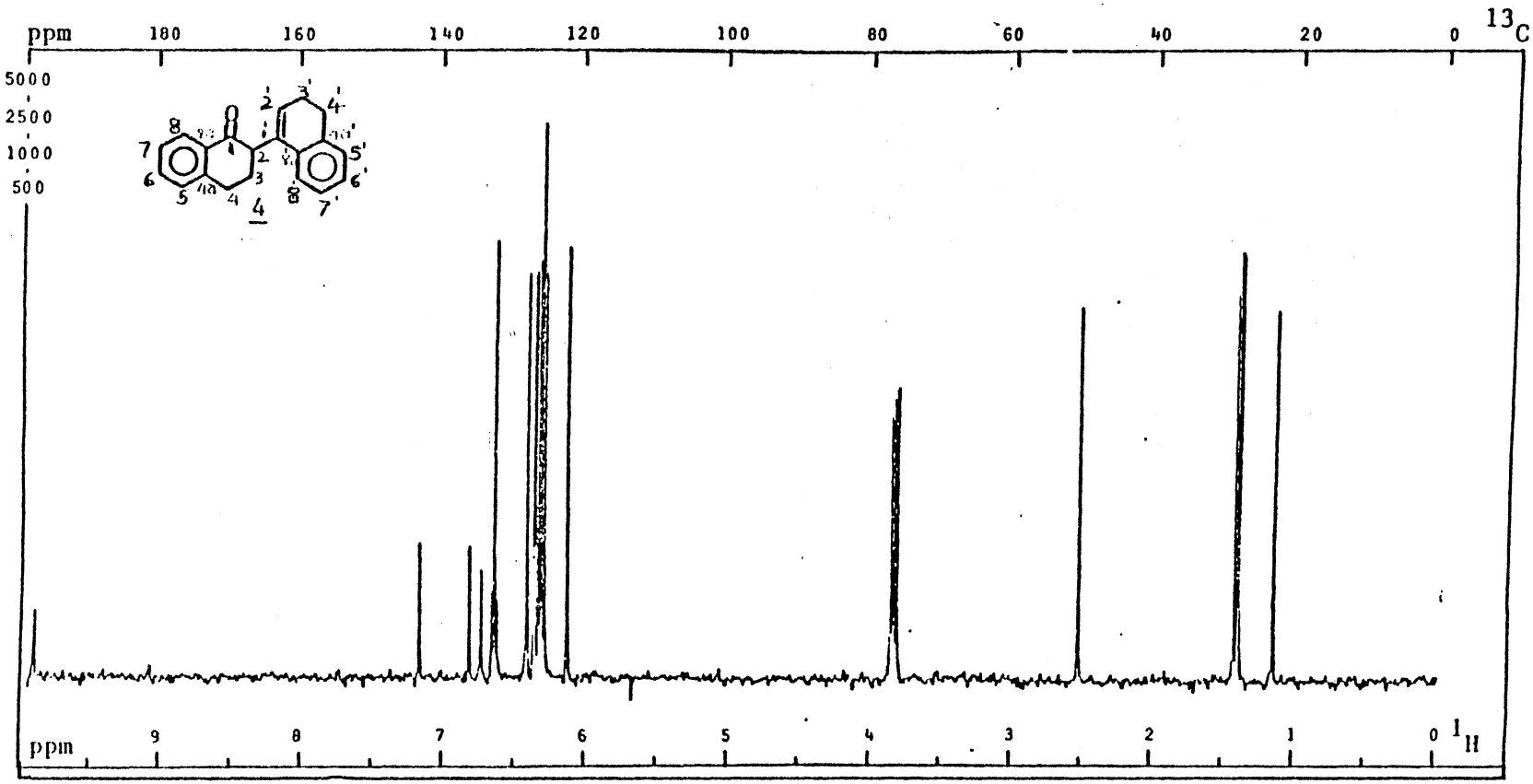
The chemical shifts of aromatic carbons of all the dimer ketones (listed in Table II) are in the range of 110-145 ppm. Generally, the carbons bearing the substituent can be recognized by their substantially lower intensity and off-resonance decoupled spectrum. The most interesting observation in such systems is the deshielding effect on carbonyl carbon when the monomer ketone is converted to dimer ketone. ^{13}C Nuclear shieldings of the carbonyl carbons are not nearly so sensitive to alkyl substitution as the saturated carbons in hydrocarbons. For the latter, it is established that the replacement of an α- or β- hydrogen at a given carbon by a methyl group deshields the carbon nucleus by as much as 9 ppm. This shielding effect is significant for conjugated carbonyl systems, in which either an olefinic bond or an aryl ring is in the α,β-position.

Spectra 1 and 2.

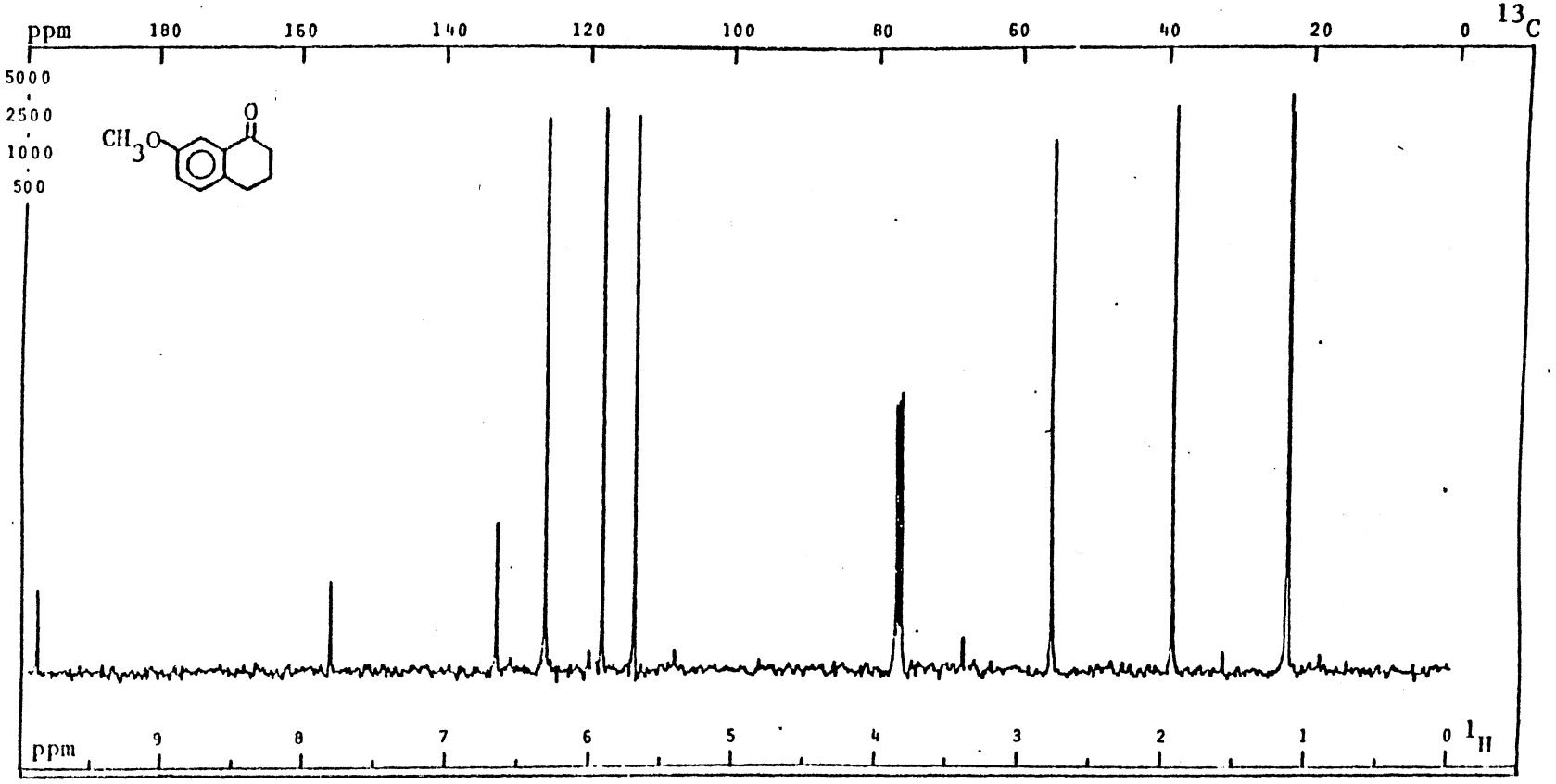
Spectrum 1 shows the ^{13}C-NMR spectrum of 1-tetralone. The chemical shift of the carbonyl resonance of this ketone is at 197.4 ppm. When 1-tetralone is converted to its corresponding dimer ketone (4), the chemical shift of the resulting carbonyl carbon is changed as shown in spectrum 2. The difference ($\Delta\delta$) is 1.7 ppm. However, this deshielding is small. But a significant change in chemical shift occurs at carbon-2. In spectrum 1 (1-tetralone)



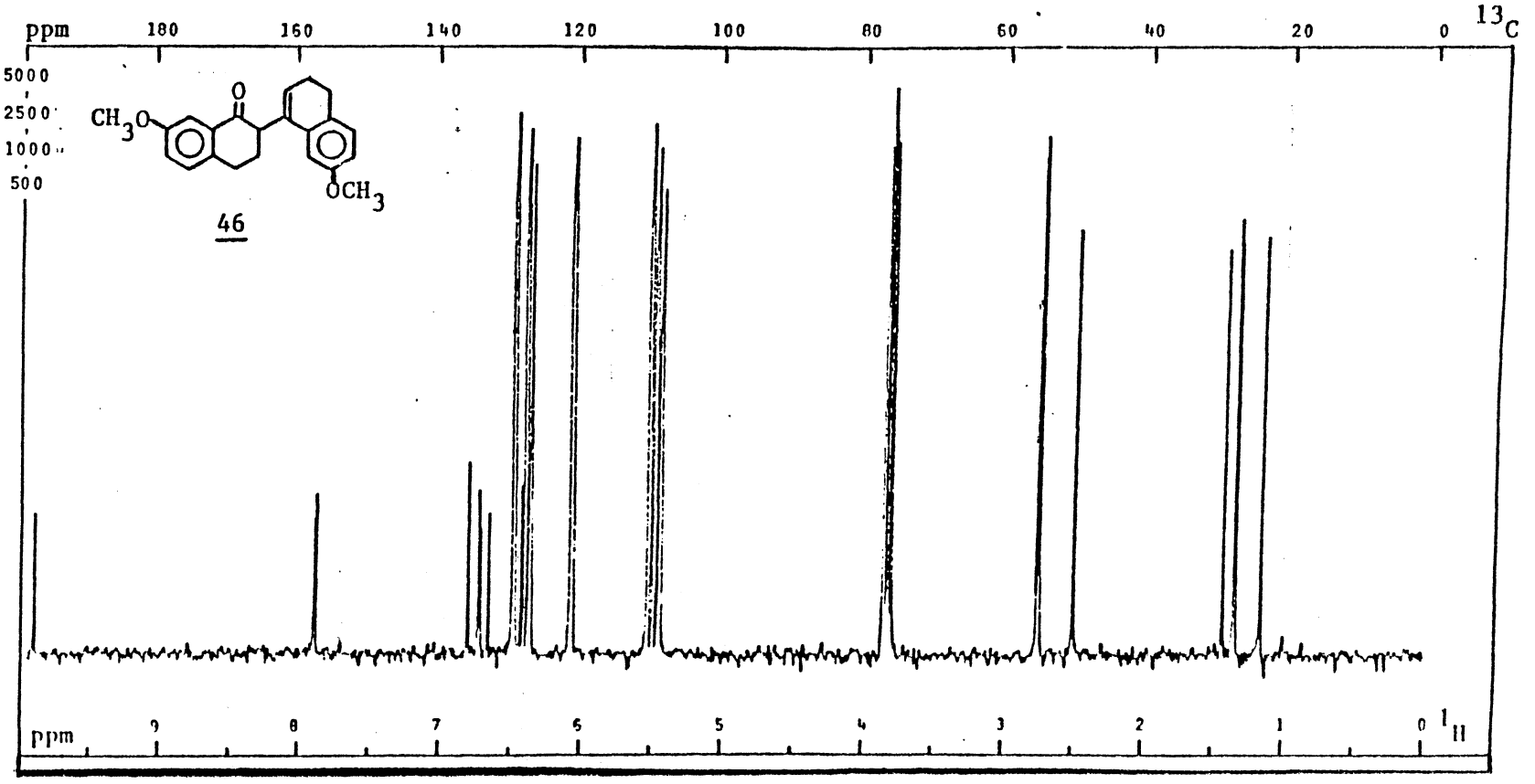
Spectrum 1. ^{13}C NMR of 1-Tetralone (40).



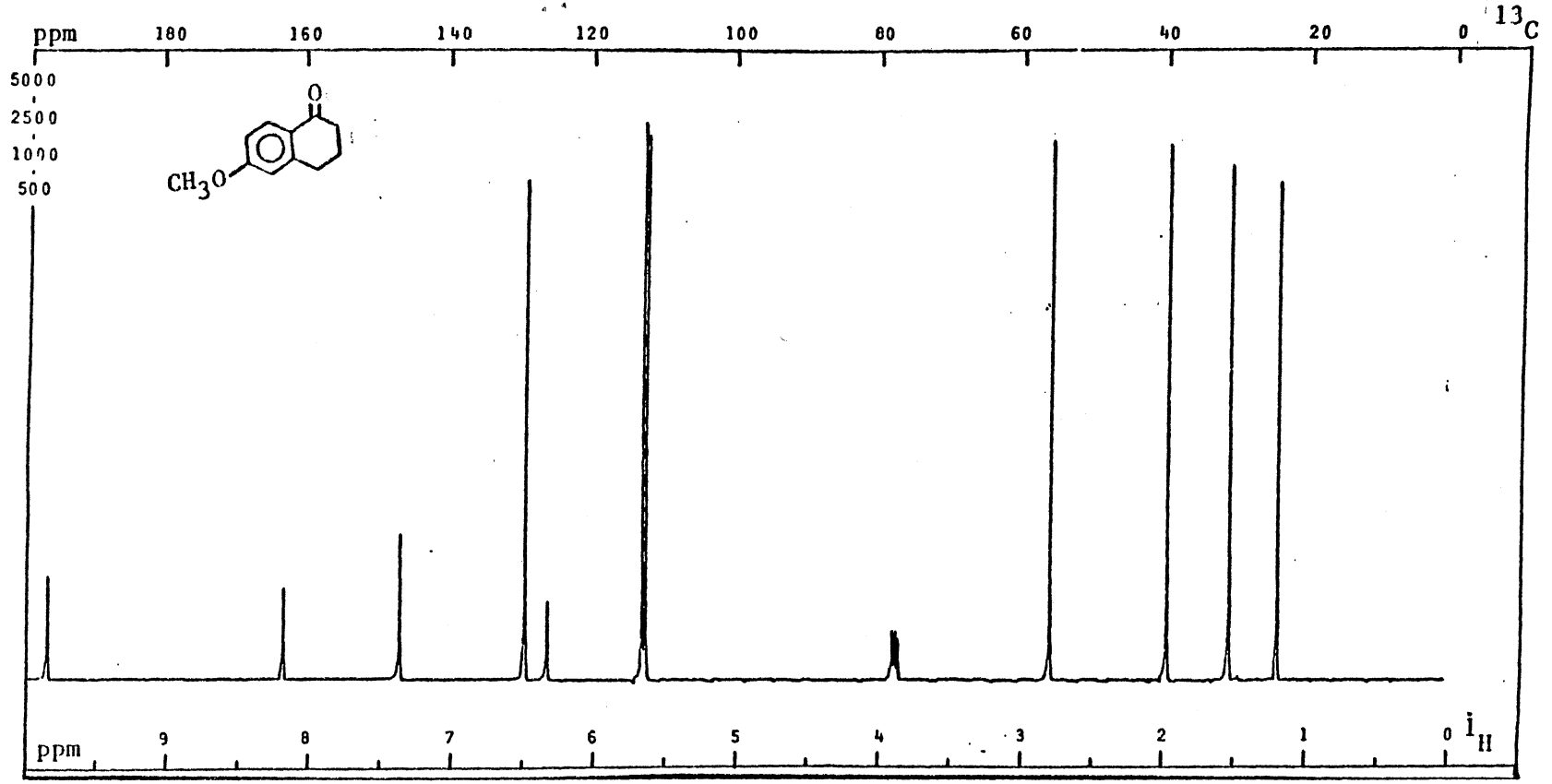
Spectrum 2. ^{13}C NMR of 3,3',4,4'-Tetrahydro 1',2-binaphthalen-1(2H)-one (4).



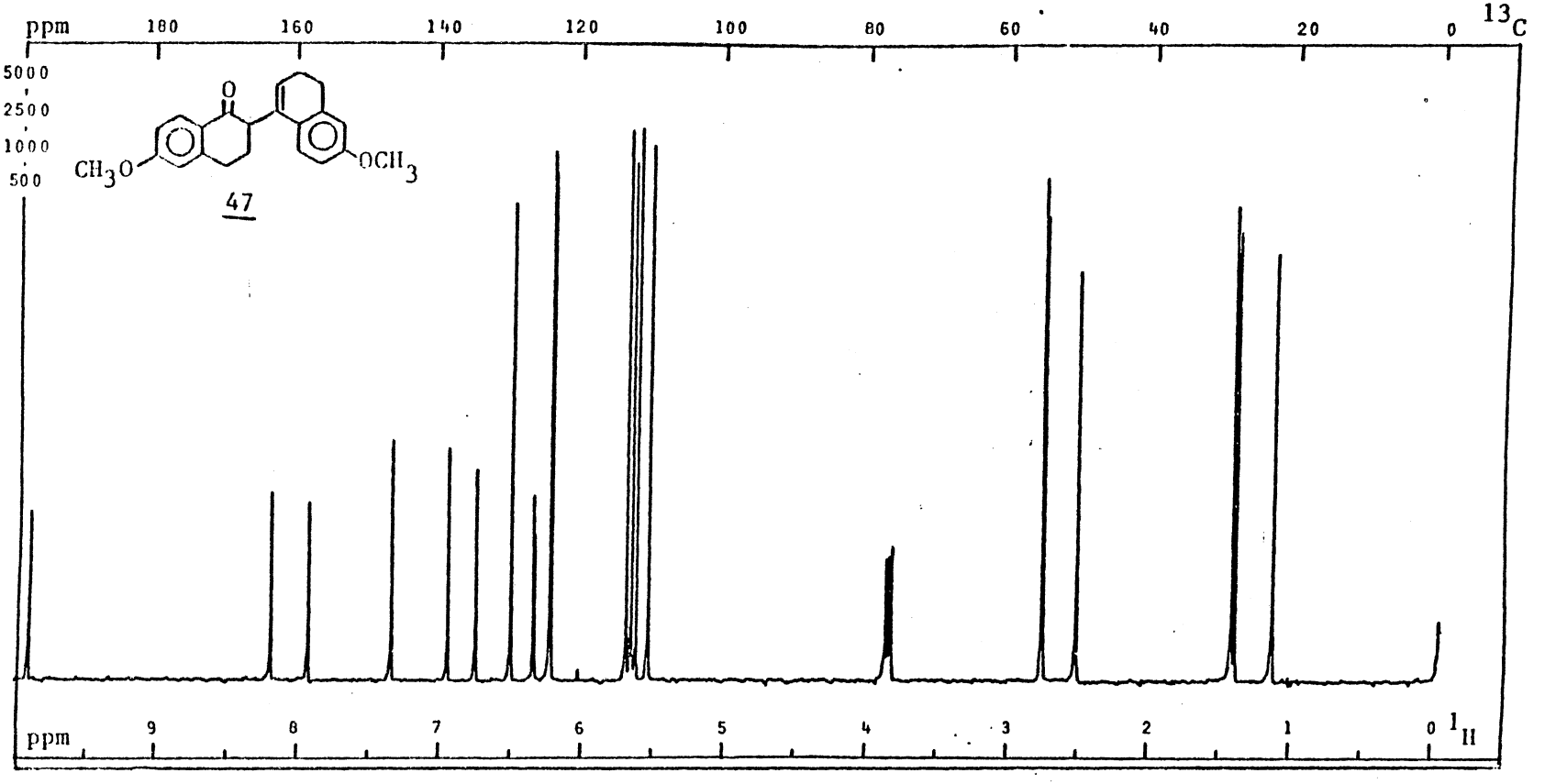
Spectrum 3. ^{13}C NMR of 7-Methoxy-1-tetralone.



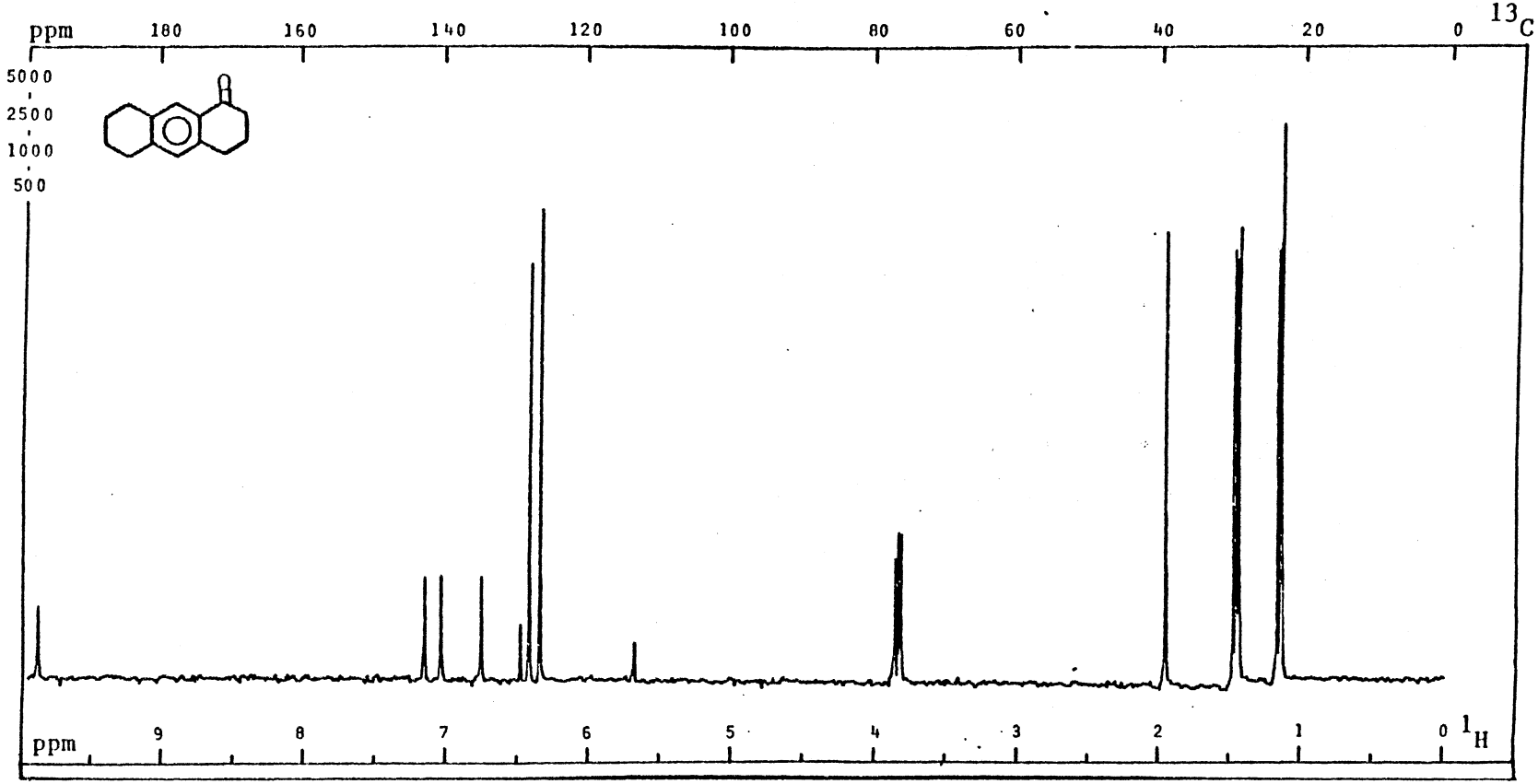
Spectrum 4. ^{13}C NMR of 7,7'-Dimethoxy-3,3',4,4'-tetrahydro-1',2-binaphthalen-1(2H)-one (46).



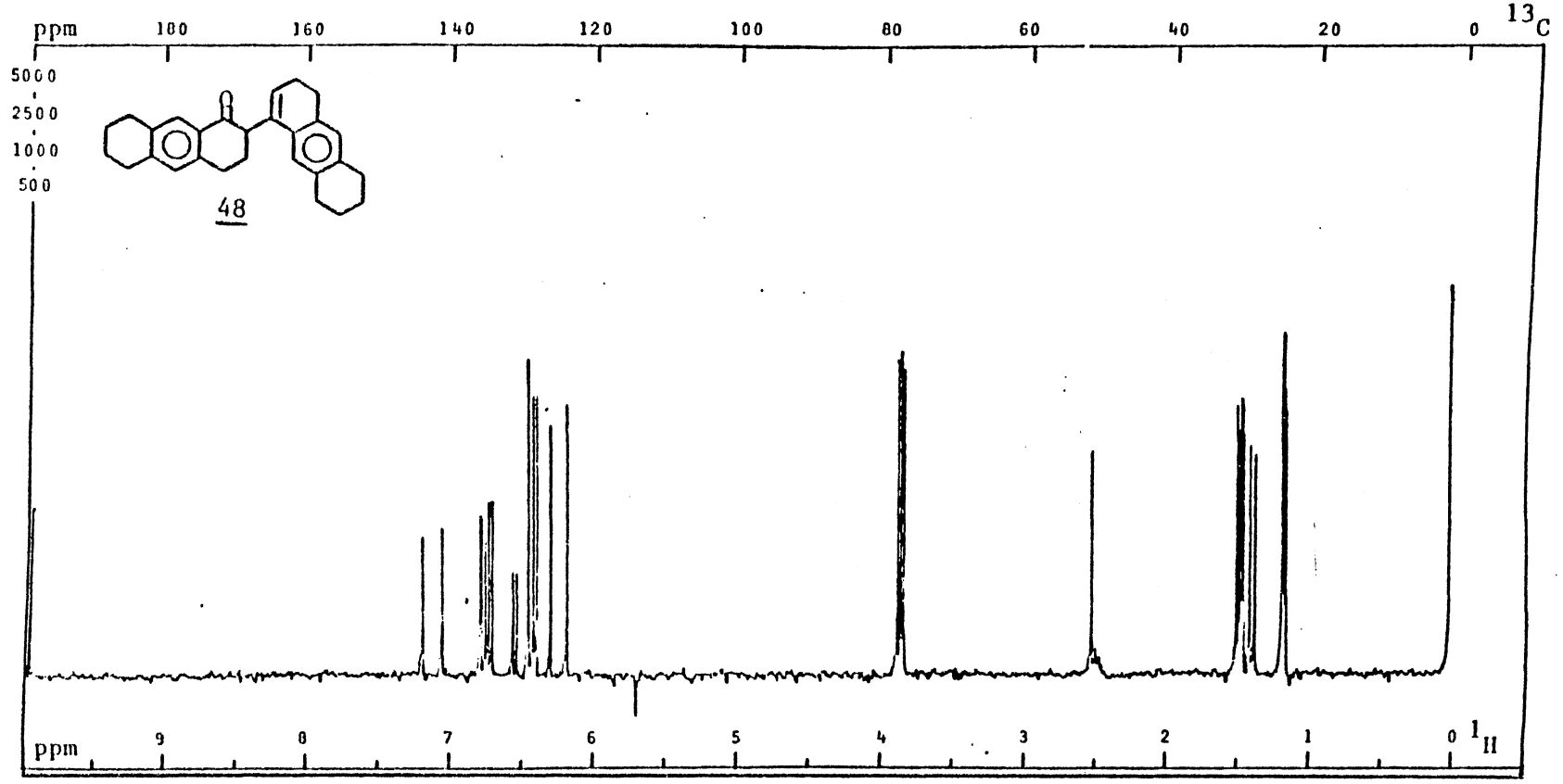
Spectrum 5. ^{13}C NMR of 6-Methoxy-1-tetralone.



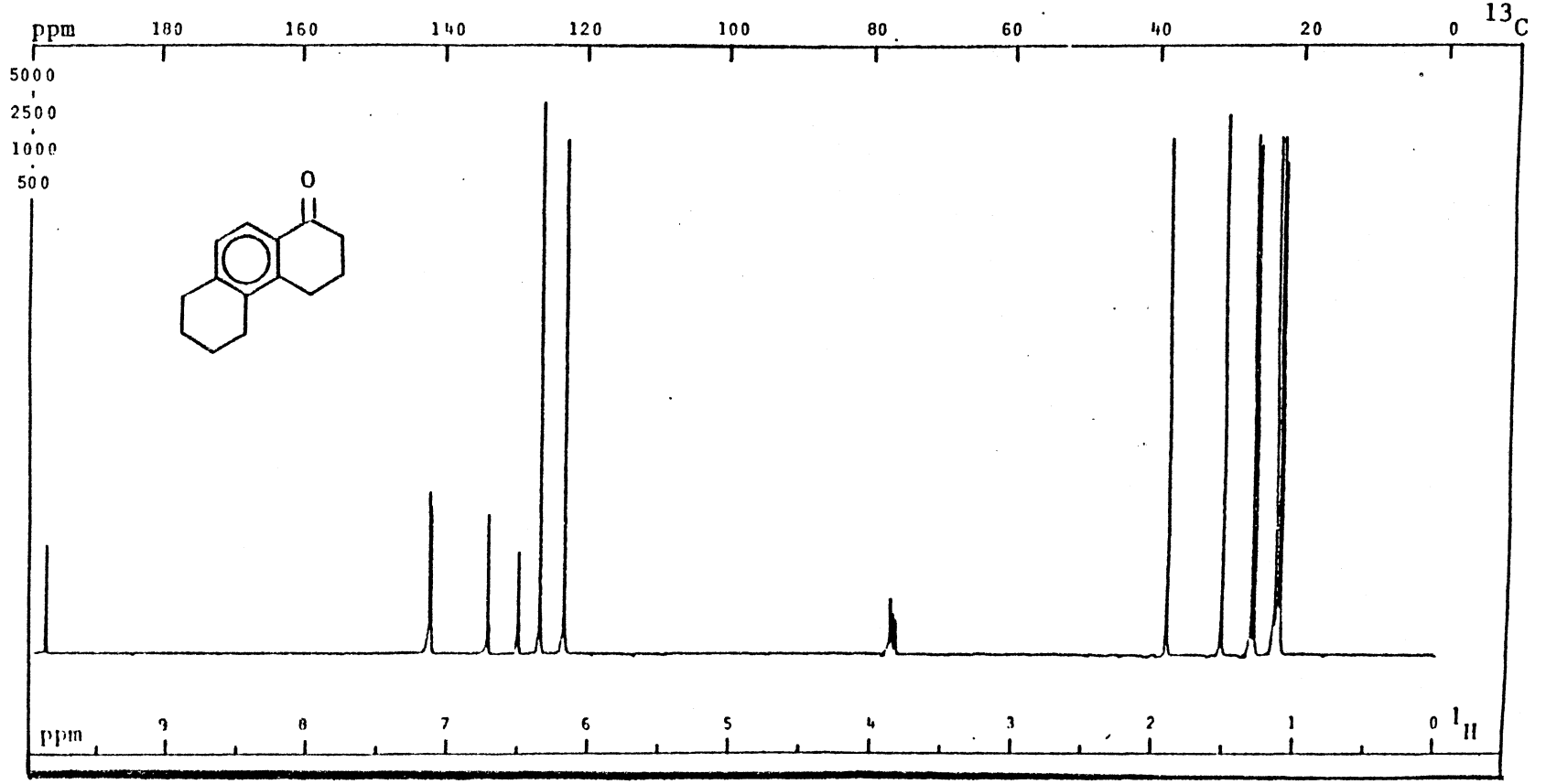
Spectrum 6. ^{13}C NMR of 6,6'-Dimethoxy-3,3',4,4'-tetrahydro-1,2-binaphthalen-1(2H)-one (47).



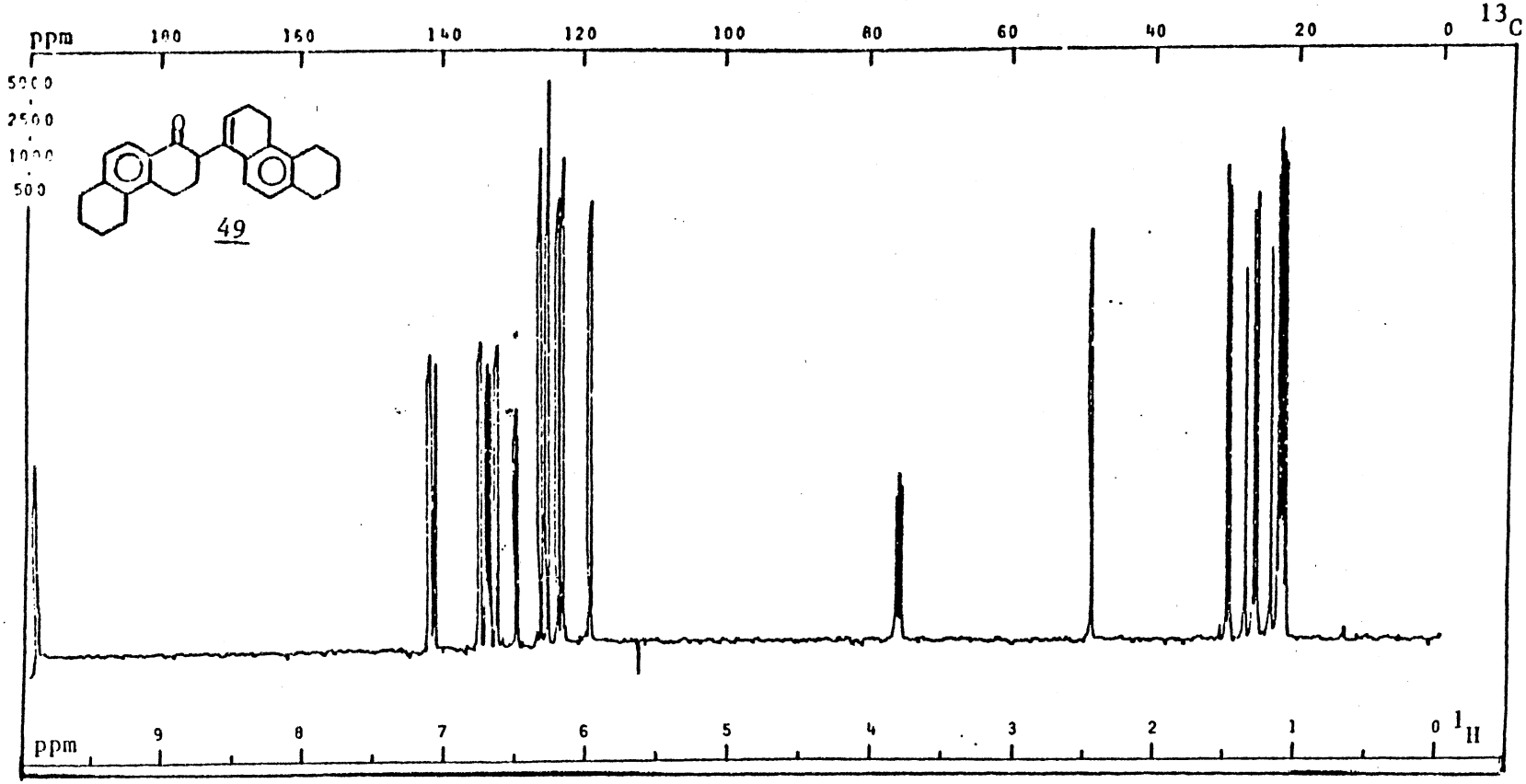
Spectrum 7. ^{13}C NMR of 3,4,5,6,7,8-Hexahydro-anthracen-(2H)-1-one.



Spectrum 8. ^{13}C NMR of 3,3',4,4',5,5',6,6',7,7',8,8'-Dodecahydro-1',2-bianthracen-1(2H)-one (48).



Spectrum 9. ^{13}C NMR of 3,4,5,6,7,8-Hexahydrophenanthrene-1(2H)-one.



Spectrum 10. ^{13}C NMR of 3,3',4,4',5,5',6,6',7,7',8,8'-Dodecahydro-1',2-biphenanthrene-1(2H)-one (49).

this carbon absorbs at 36.0 ppm, but for the corresponding dimer ketone (4), carbon-2 absorbs at 50.7 ppm, a difference of 14.7 ppm. This shift has been termed the "α-effect" and appears to be general for all classes of compounds although its magnitude differs in various families.

Spectra 3 and 4.

Spectrum 3 shows a carbonyl resonance of 196.6 ppm whereas the carbonyl resonance in spectrum 4 of the corresponding dimer ketone (46) appears at 198.6 ppm, a difference ($\Delta\delta$) of 2.0 ppm.

Spectra 5 and 6.

These ketones show ^{13}C carbonyl absorption for the monomer ketone, 6-methoxy-1-tetralone at 197.8 ppm in spectrum 5. The corresponding dimer ketone 47 has this absorption at 197.9 ppm in spectrum 6. These data show there is practically no change in chemical shift from that of monomer ketone. Such observation of insignificant changes in chemical shifts resulting from ring substitution at the para position have been noted.[101] This indicates that the electron density at the carbonyl carbon is not altered appreciably in comparing monomer and dimer ketone.

Spectra 7 and 8.

In the case of dimer ketone (48), the deshielding in spectrum 7 is again shifted 1.5 ppm for ^{13}C carbonyl absorption with respect to its corresponding monomer ketone.

Spectra 9 and 10.

Similarly, in the case of dimer ketone (49), as shown in spectrum 9, there is deshielding of 1.2 ppm for carbonyl absorption compared to its corresponding monomer ketone, spectrum 10.

In summary, it is interesting to note that for an electron-donating para substituted case, there is no deshielding effect, when a monomer ketone is converted to its corresponding dimer ketone. Another generalization for such a system is that, for all substituted 1-tetralone ring system the "α-effect" is in the same range ($\Delta\delta$ = 11.4 ± 0.3 ppm) while for 1-tetralone, the "α-effect" from monomer to dimer ketone, is higher ($\Delta\delta$ = 14.7 ppm)

To learn about ^{13}C carbonyl shielding, Gurudata and Stothers[100,101] recorded spectra of thirteen different β,γ-unsaturated ketones. They concluded that the effect of β,γ-double bond is not primarily operative through the bonding network but, instead, through space and therefore dependent on molecular geometry. This can be explained[102] as modes of overlap for p-orbitals of neighboring atoms as shown in Figure 14.

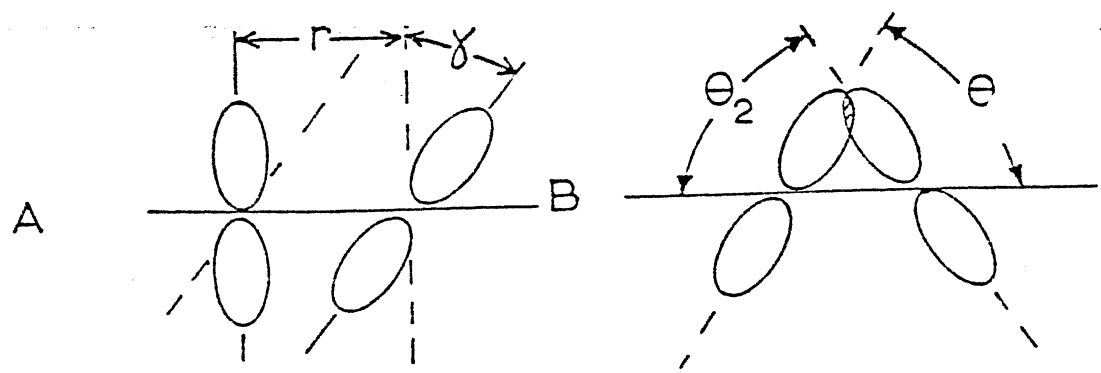


Figure 14. Modes of Overlap for p-Orbitals of Neighboring Atoms.

If the axes of the 2 p-orbitals lie in the parallel planes at a distance r, the overlap integral Sij is given by equation (1),

$$Sij = S\pi\pi Cos\gamma \qquad (1)$$

where γ is the angle between the axes (A in Figure 14). If the axes of the p-orbitals lie in a plane ($\gamma = 0$) but are tilted towards one another at angles θ_1 and θ_2, relative to the internuclear axis (B of Figure 14), the overlap can be resolved into $\sigma\sigma$ and $\pi\pi$ contributions, for which equation (2) can be written as

$$Sij = S\sigma\sigma Cos\ \theta_1\ Cos\ \theta_2 + S\pi\pi Sin\ \theta_1\ Sin\ \theta_2 \qquad (2)$$

If, in addition, γ is non-zero the second term will include a Cos γ factor.

For the case of two directly bonded sp^2-hybridized carbons, as in the case of α,β-unsaturated conjugative system, θ_1 and θ_2 are 90^o and the overlap integral is simply equation (1). This will also explain the effects of steric hindrance on carbonyl shieldings in α,β-unsaturated dimer ketones derived from 1-indanones described in preceeding discussions on page 54.

For the case of two sp^2-carbons separated by one sp^3-carbon, it is apparent that little π overlap is possible if the arrangement is a planar one. In case of non-planar conformation with the p-axes aligned (i.e. $\gamma = 0$), the overlap integral is given by equation (2). Interactions between the non-conjugated systems will be maximal in non-planar configuration or conformation and this will result in change in carbonyl absorption with β,γ conjugation relative to isolated carbonyl resonance in ^{13}C NMR.

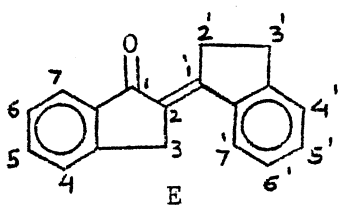
^{1}H NMR Data of Dimer Ketones of 1-Tetralones

Most chemists would expect that the double bond of a dimer ketone would be in conjugation with the carbonyl group rather than at the β,γ-position. That the latter is more common than realized is shown below.

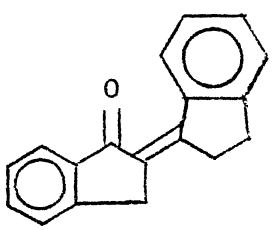
The regiochemistry of 1-tetralone dimer ketones was established through the study of their proton NMR spectra as shown in Table III. A distinct triplet for vinylic proton is observed around 5.7 ppm. A triplet around 3.8 ppm is for methine proton α to the carbonyl group. This clearly proves that the dimer product isolated from the self-condensation of 1-tetralones is the β,γ-unsaturated dimer ketone. An attempt to isomerize the β,γ-unsaturated dimer ketone (4) to the α,β-unsaturated isomer (40) using strong base under reflux in alcohol failed and no trace of (40) could be detected.

Spectral Assignments and Stereochemistry of the Dimer Ketones of 1-Indanones

As shown below in compound 39 carbons 1-7 are numbered on the indanone ring starting from the carbon of the carbonyl group. Numbers 1'-7' (as shown) refer to the carbons of the remaining ring of the dimer ketone.



E



Z

TABLE III

^{1}H NMR Data of Dimer Ketones of 1-Tetralones

Dimer Ketone	^{1}H NMR[a]	
	Vinyl[b]	Methine[c]
4	5.78	3.84
46	5.77	3.8
47	5.62	3.70
48	5.68	3.84
49	5.66	3.76

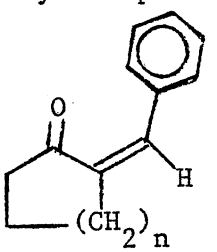
[a] δ from TMS.

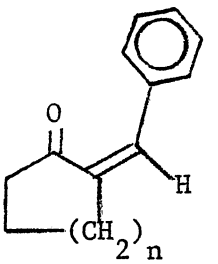
[b] Vinyl triplet, J = 4-5 Hz.

[c] Methine triplet, J = 6-7 Hz.

IR Analysis

It is normally possible to determine the stereochemistry of a tetra-substituted double bond conjugated with the carbonyl group using IR spectroscopy.[103] But in the case of aromatic ketones, for example, 2-benzylidene cyclopentanone 50a and 50b as well as 2-benzylidenecyclohexanones 51a and 51b, the problem is not simple to solve just by IR spectroscopy.





50a n=1
51a n=2

50b n=1
51b n=2

The carbonyl stretching frequency of the cis-isomer 50a is 15 cm^{-1} higher than that of the trans-isomer 50b. The difference between $\gamma_{C=O}$ and $\gamma_{C=C}$ is 60 cm^{-1} for the cis and 90 cm^{-1} for the trans isomer. The $\gamma_{C=C}$ band for the cis-isomer is very weak, whereas for the trans-isomer, it is as intense as the carbonyl stretching frequency. The dimer ketones (39, 52, 53, 54 and 55) were analyzed by IR spectroscopy. The difference between $\gamma_{C=O}$ and $\gamma_{C=C}$ did not show any trend either for cis or trans isomer; however, $\gamma_{C=C}$ band was intense enough to suggest that the carbon-carbon double bond may be trans.

^{1}H NMR Analysis

It is well known[104] that by means of the long range asymmetric

magnetic shielding of the carbonyl group, many structure determination have been carried out.[105] The zones of the positive and negative shielding of the carbonyl group are shown in Figure 15.

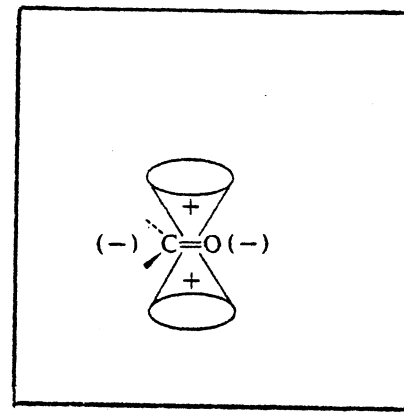
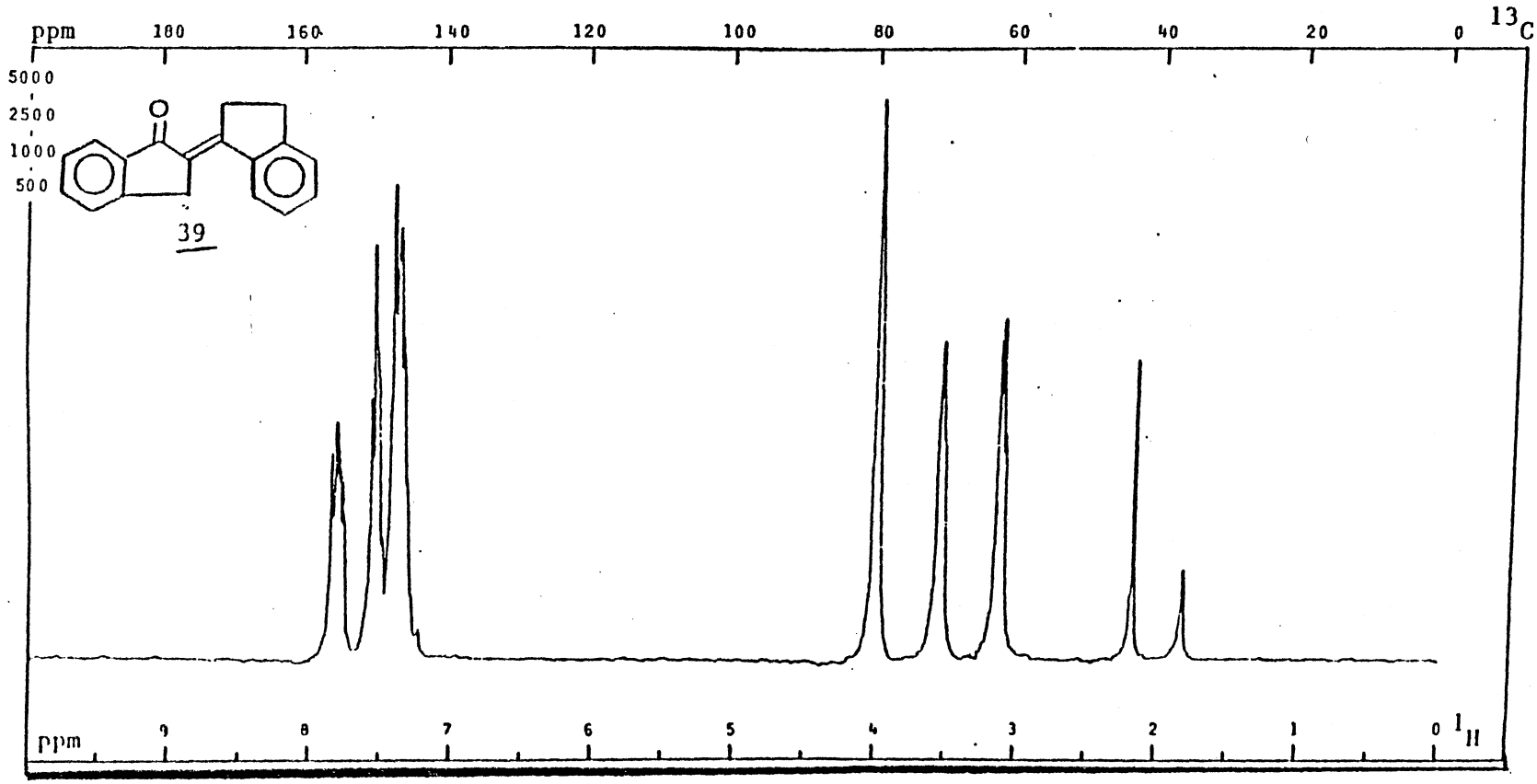
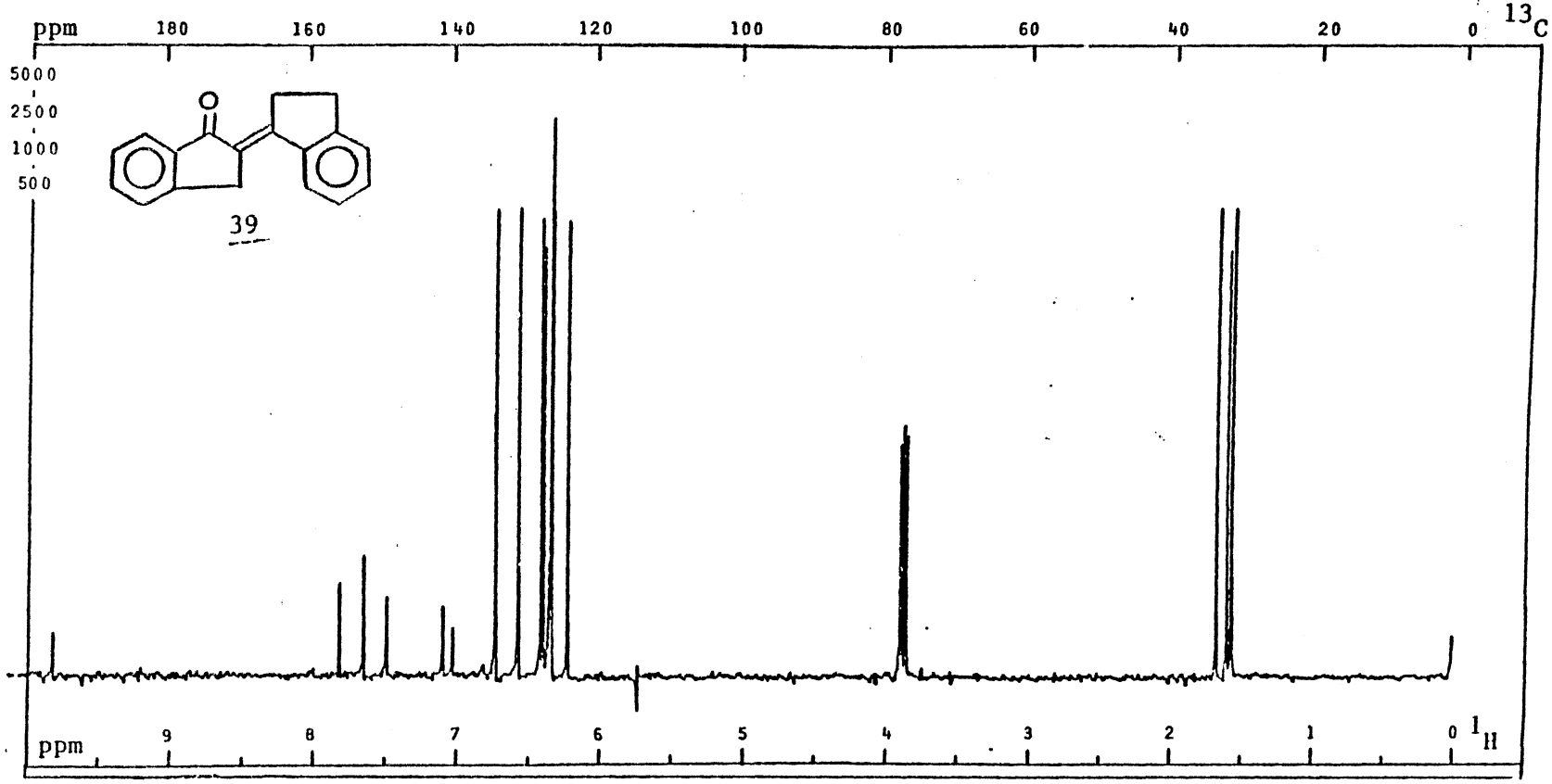


Figure 15. The Zones of Positive and Negative Shielding of the Carbonyl Group.

This fact is applicable in the system of dimer ketones derived from 1-indanones. For example, in the case of dimer ketone 39, out of eight aromatic protons, only one proton on C-7 should exhibit anisotropic deshielding, if the carbon-carbon double bond has trans configuration. Examination of spectrum-11, indicates that among all aromatic protons, one is distinct which absorbs at 7.7 ppm. Further observation of allylic protons of the dimer ketone 39 (spectrum-11) shows they are deshielded compared to normal allylic protons. This deshielding is not significant but still suggests the trans configuration of the double bond.



Spectrum 11. ^{1}H NMR of (E)2[2',3'-Dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one (39).



Spectrum 12. ^{13}C NMR of(E)2[2',3'-Dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one (39).

^{13}C NMR Analysis

^{13}C NMR is a powerful tool in the study of the stereochemistry of organic compounds. To prove that regiochemistry of dimer ketones (39, 52, 53, 54, 55) is different than dimer ketones of 1-tetralones, we recorded carbonyl absorption in ^{13}C NMR of these 1-indanone dimer ketones as shown in Table IV. It is evident from Table IV that compared to monomer ketones, all the dimer ketones show shielding of the carbonyl group. This is due to conjugated carbon-carbon double bond, as α,β double bond shifts the carbon absorption to higher field by electron release.[106] This is analogous to the fact that conjugated ketones are less reactive than corresponding saturated ketones. Indeed, the dimer ketone 39 failed to form oxime derivatives.

In summary (from Table IV), the shielding effect for all substituted dimer ketones of 1-indanones is higher with respect to dimer ketone 39. This may be rationalized in terms of hinderance for carbonyl group and aryl ring system attaining coplanarity.

Preparation and Single Crystal X-Ray Analysis of Dimer Ketone of 1-Indanone

We hoped to prove whether a dimer ketone derived from 1-indanone has the E or Z configuration as shown for dimer ketone 39 on page 47. To accomplish this, we considered IR, NMR and single crystal x-ray analysis. The IR and NMR studies were not sufficiently conclusive and therefore we sought an assignment through single crystal x-ray analysis. Unfortunately, none of the dimer ketones (52, 53, 54 or

TABLE IV

^{13}C NMR Data of Dimer Ketones of 1-Indanones

Dimer ketones of 1-indanones	^{13}C NMR (ppm from TMS) carbonyl[b]	$\Delta\delta$[a]
39	195.2 (206)	10.8
52	194.8 (206.5)	11.7
53	195.2 (206.8)	11.6
54	195.5 (207.4)	11.9
55	194.7 (206.3)	11.6

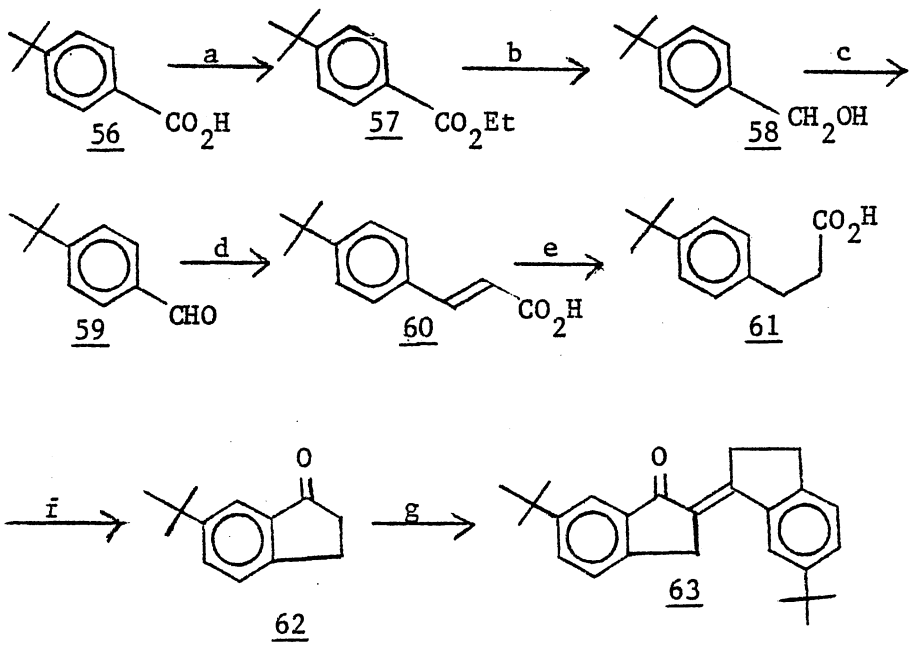
[a]Shifted value in ppm from monomer to dimer ketone.

[b]Shifted value of monomer ketone for carbonyl is noted in parentheses.

55) gave an adequate crystal for single crystal x-ray diffraction studies. However, the dimer ketone 39, from 1-indanone, gave a crystal which permitted a partial solution as follows.

Crystallization of 39 from a range of solvents yielded crystals of poor quality. From methanol, at room temperature, it was possible to crystallize yellow plates that tend to form at their major faces like misaligned slices of bread. Numerous crystals were photographed and were found unsuitable for data collection, showing broad diffraction peaks, very large standard deviations in cell dimensions, and weak diffraction. The crystal finally selected for single crystal X-ray diffraction studies was recognized to be of less than ideal quality by the large error in the a cell dimension, by the low percentage of observed to measured dots (31%) (33 observed reflections per nonhydrogen atom) and it was not anticipated that refinement would lead to accurate bond angles and distances. These expectations were borne out by the final refinement where lack of good agreement between equivalent distances in the two molecules of the asymmetric unit is clearly evident. However, the connectivity and orientation of the molecule at the double bond is clearly established and is the same in both molecules of the asymmetric unit. As this could not be determined by other physical measurements, the crystallographic results may be viewed as of some value. Thus these data strongly suggest that 2,3-dihydroinden-1-one ring is joined at the 2 position by a double bond to the 1' position of the 2,3-dihydroindene ring of E configuration as shown in structure 39. Since single crystal X-ray diffraction still remains the best choice for stereochemical assignment[107] of the dimer ketone from 1-indanones, we undertook the

synthesis of the dimer ketone 63 as shown in Figure 16. It was hoped that introducing a tert.-butyl group would disrupt the packing pattern in the crystal lattice sufficiently so that planarity would be less likely and thus a satisfactory crystal could result.



[a]EtOH, H^+, mol. sieve, Δ.
[b]DIBAH, toluene, -78 °C.
[c]2,2' BPCC, CH_2Cl_2, 25 °C.
[d]Malonic acid, pyridine, 45 °C.
[e]Pd/C, H_2, CH_3CO_2H.
[f]PPA, 85 °C.
[g]Basic alumina, cyclohexane, 80 °C.

Figure 16. Synthesis of 6-tert-Butyl-1-indanone.

Direct conversion of acid 56 to aldehyde 59 is not reliably selective, as most of the methods[104] available for this purpose seem to be lacking control due to severe conditions. So we thought to prepare ester 57. Step a in Figure 15 was carried out, by using molecular sieves[108] (3A Linde) which selectively absorbed water from a mixture of water and ethanol. This way of esterification results in quantitative yield (98%) and the technique is extremely simple to use. The usual extraction step is avoided because of direct isolation of ester 57 from the reaction mixture by distillation. Attempts to control metal hydride reduction of ester 57 to aldehyde 53 were not successful. Shorter time (sh) at lower temperature for reduction of ester 57 resulted in recovery of starting ester 57; while on the other hand longer time (8 h) at lower temperature gave benzyl alcohol 58 (yield 80%). Since compound 58 resulted, we decided to oxidize it to aldehyde 59 using 2,2'-bipyridinium chlorochromate (2,2'-BPCC).[100] It is easily and safely prepared by adding the readily available 2,2'-bipyridine at room temperature to an equimolar mixture of chromic anhydride and dilute HCl. Treatment of benzyl alcohol 58 with 2,2'-BPCC gave 49% yield of aldehyde 59, as shown in step c.

Aldehyde 59 was condensed with malonic acid using Knoevenagel reaction as shown in step d. Presence of catalytic amount of an amine (piperidine) is a must for the condensation to occur. Following the literature procedure,[110] quantitative yield (100%) of unsaturated acid 60 was obtained. Compound 60 was reduced to saturated acid 61 using catalytic hydrogenation. Catalytic hydrogenation was effected by shaking the solution of unsaturated acid 60 in glacial acetic acid

with 5% Pd/C under an atmosphere of hydrogen gas. A quantitative yield of saturated acid 61 (as shown in step e) was obtained. Using polyphospholic acid as a cyclizing agent, compound 61 was converted to 6'-ter butyl-1-indanone 62 as shown in step f. As outlined in Figure 7, using ultrasonic agitation, ketone 62 was converted to corresponding dimer ketone 63 (shown in step g of Figure 16).

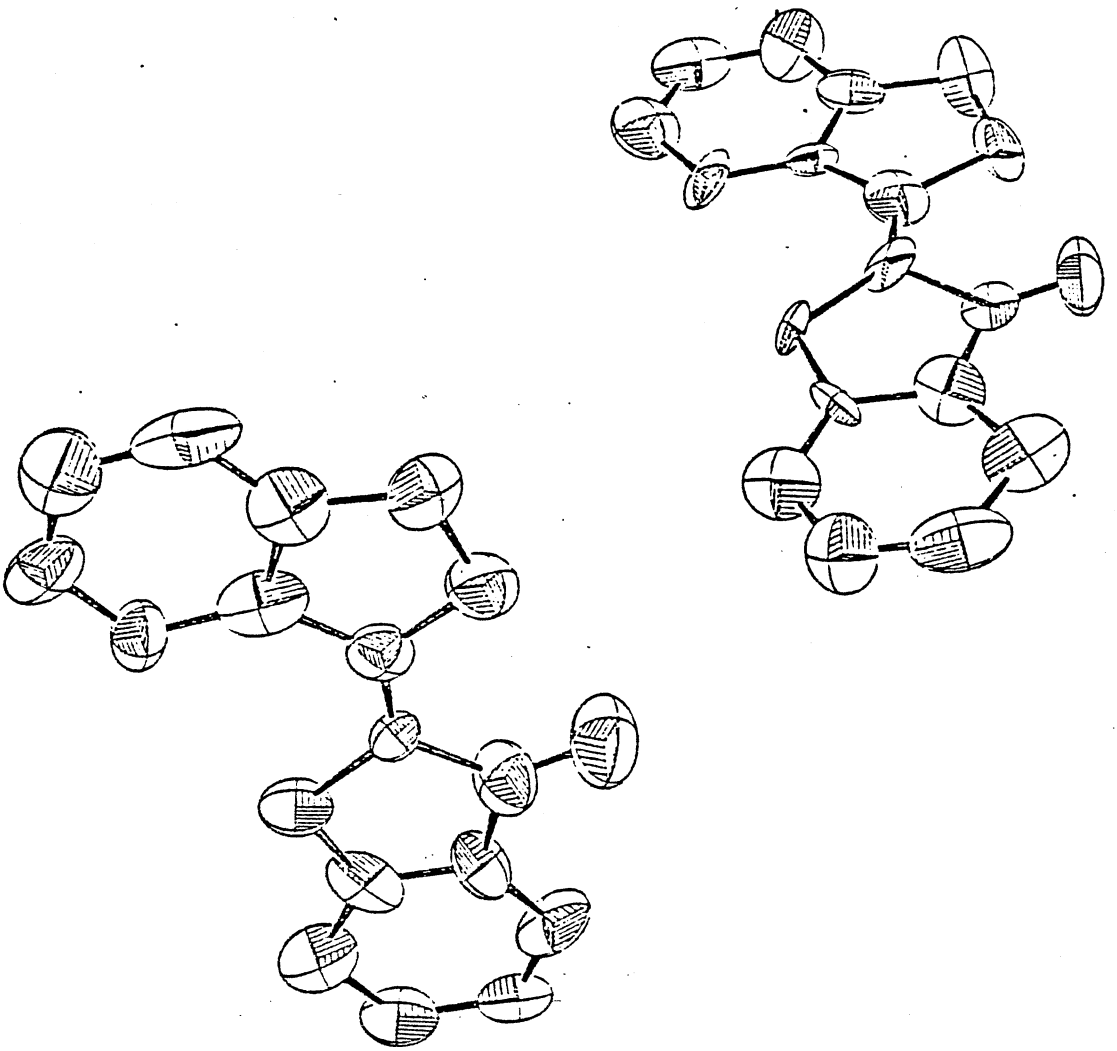


Figure 17. Single-crystal, X-Ray Analysis of 39.

TABLE V

Single Crystal X-Ray Data for 39

Formula	$C_{18}H_{14}O$
MWT	246.3
a	26.734(17)Å
b	19.006(8)
c	5.304(2)
α	90.0°
β	90.0
γ	90.0
V	2553.2(22)Å^3
F(000)	1040
μMoK_α	0.72 cm^{-1}
λMoK_α	0.71069Å
D_{calc}	1.281 g cm^{-3}
Z	8
Obs. refl.	1259
R	11.9%
Space group	$P2_12_12_1$

TABLE VI

Positional Parameters for 39

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
O1	0.3810(5)	0.1386(8)	1.0904(35)
C1	0.4271(7)	0.1458(10)	1.1367(42)
C2	0.4673(5)	0.1040(8)	1.0038(32)
C3	0.5182(7)	0.1345(10)	1.1229(36)
C3a	0.5005(7)	0.1895(9)	1.3201(42)
C4	0.5320(8)	0.2300(10)	1.4795(44)
C5	0.5055(8)	0.2760(10)	1.6553(39)
C6	0.4518(7)	0.2810(11)	1.6620(35)
C7	0.4251(8)	0.2411(11)	1.4952(44)
C7a	0.4484(6)	0.1939(10)	1.3274(42)
C1'	0.4620(7)	0.0546(10)	0.8199(36)
C2'	0.4125(7)	0.0300(11)	0.7181(40)
C3'	0.0757(7)	0.0264(11)	0.0139(43)
C3a'	0.4792(7)	-0.0313(10)	0.4989(42)
C4'	0.5097(9)	-0.0719(11)	0.3387(42)
C5'	0.5612(8)	-0.0688(12)	0.3629(49)
C6'	0.5815(8)	-0.0238(11)	0.5449(40)
C7'	0.5555(6)	0.0199(10)	0.7052(39)
C7a'	0.5023(8)	0.0157(9)	0.6816(41)
(O1)	0.1335(4)	0.2031(8)	0.2208(29)
(C1)	0.1763(6)	0.1987(10)	0.2584(36)
(C2)	0.2171(7)	0.2406(10)	0.1144(39)
(C3)	0.2667(5)	0.2199(10)	0.2330(33)
(C3a)	0.2536(6)	0.1630(9)	0.4337(34)
(C4)	0.2833(7)	0.1269(10)	0.5966(43)
(C5)	0.2624(8)	0.0768(11)	0.7705(50)
(C6)	0.2119(9)	0.0677(11)	0.7819(43)
(C7)	0.1763(8)	0.1043(10)	0.6167(46)
(C7a)	0.2024(7)	0.1530(10)	0.4454(44)
(C1')	0.2071(7)	0.2921(10)	-0.0606(40)
(C2')	0.1535(6)	0.3112(10)	-0.1499(38)
(C3')	0.1601(7)	0.3673(11)	-0.3705(50)
(C3a')	0.2178(7)	0.3766(10)	-0.3829(39)
(C4')	0.2424(9)	0.4250(12)	-0.5497(52)
(C5')	0.2949(10)	0.4250(12)	-0.5450(47)
(C6')	0.3226(8)	0.3801(11)	-0.3757(45)
(C7')	0.2959(7)	0.3348(11)	-0.2004(41)
(C7a')	0.2434(6)	0.3332(10)	-0.2053(33)

TABLE VII

Bond Angles (°) and Distances (Å) for 39

	Molecule A	(Molecule B)
C1-O1	1.26(2)	1.16(2)
C1-C2	1.49(2)	1.53(2)
C2-C1'	1.33(2)	1.34(3)
C2-C3	1.60(2)	1.51(2)
C3-C3a	1.52(3)	1.52(2)
C3a-C7a	1.40(3)	1.38(2)
C3a-C4	1.40(3)	1.34(3)
C4-C5	1.44(3)	1.40(3)
C5-C6	1.44(3)	1.36(3)
C6-C7	1.34(3)	1.45(3)
C7-C7a	1.38(3)	1.44(3)
C7a-C1	1.45(3)	1.46(3)
C1'-C2'	1.50(3)	1.55(2)
C1'-C7a'	1.48(3)	1.44(2)
C2'-C3'	1.52(3)	1.56(3)
C3'-C3a'	1.47(2)	1.55(3)
C3a'-C7a'	1.43(3)	1.40(3)
C3a'-C4'	1.38(3)	1.41(3)
C4'-C5'	1.38(3)	1.40(4)
C5'-C6'	1.37(3)	1.42(3)
C6'-C7'	1.35(3)	1.43(3)
C7'-C7a'	1.43(3)	1.40(2)
O1-C1-C2	124(2)	126(2)
C7a-C1-C2	110(1)	106(1)
C7a-C1-O1	126(2)	128(2)
C1-C2-C3	105(1)	107(2)
C1-C2-C1'	128(2)	123(2)
C1'-C2-C3	128(1)	129(2)
C2-C3-C3a	103(1)	105(1)
C3-C3a-C4	125(2)	124(2)
C3-C3a-C7a	112(2)	114(2)
C4-C3a-C7a	124(2)	122(2)
C3a-C4-C5	113(2)	120(3)
C4-C5-C6	123(2)	120(2)
C5-C6-C7	119(2)	125(2)
C6-C7-C7a	121(2)	110(2)
C7-C7a-C3a	120(2)	126(2)
C7-C7a-C1	130(2)	122(2)
C1-C7a-C3a	110(2)	112(2)
C2-C1'-C2	124(2)	123(2)
C2-C1'-C7a'	127(2)	126(2)
C2'-C1'-C7a'	109(2)	110(2)

TABLE VII (Continued)

	Molecule A	(Molecule B)
C1'-C2'-C3'	106(2)	106(1)
C2'-C3'-C3a'	106(2)	102(2)
C3'-C3a'-C7a'	111(2)	110(1)
C3'-C3a'-C4'	130(2)	130(2)
C4'-C3a'-C7a'	118(2)	120(2)
C3a'-C4'-C5'	128(2)	117(2)
C4'-C5'-C6'	119(2)	122(2)
C5'-C6'-C7'	126(2)	118(2)
C6'-C7'-C7a'	115(2)	120(2)
C7'-C7a'-C1'	131(2)	132(2)
C7'-C7a'-C3a'	121(2)	119(2)
C3a'-C7a'-C1'	108(2)	108(2)

CHAPTER III

EXPERIMENTAL

Reactions were carried out under inert atmosphere of either argon or nitrogen unless otherwise noted. Solvents were removed during workups by means of a rotatory evaporator. Melting points were determined with a Thomas Hoover capillary apparatus and were uncorrected. IR spectral data were obtained on a Perkin-Elmer 681 IR spectrometer. The ^{1}H and ^{13}C spectra were recorded as δ values or in parts per million (ppm), respectively, downfield from Me_4Si (TMS) as an internal standard. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Water was used as the sonic bath medium.

Ultrasonic Agitation in Basic Alumina Catalyzed Condensation of Ketones for Preparation of 3,3',4,4'-Tetrahydro-1',2-binaphthalen-1(2H)-one (4). A mixture of 36.5 g (0.25 mol) of α-tetralone, 100 ml cyclohexane and 125 g of activated basic alumina (0.5 g/mmol of ketone) was added to a 500 ml three-necked flask mounted in a sonic vibrator, under an inert atmosphere. Heating at 80 ^{o}C and agitation was continued for 24 h. The reaction mixture was then transferred to a Soxhlet apparatus containing basic alumina. The product was extracted with refluxing cyclohexane. Solvent and 1-tetralone were removed with steam distillation. The distillate was concentrated to obtain 1-tetralone (7.7 g).

The crude residue remaining from steam distillation was recrystallized using 2-propanol as the solvent which gave 20 g (62%) of dimer ketone 4: mp, 131-133 °C, orange 2,4-dinitrophenyl hydrazone: mp, 248-250 °C; ^{1}H NMR ($CDCl_3$) δ 8.24 (m, 1, Ar-H), 7.23-7.64 (m, 7, Ar-H), 5.88 (t, 1, vinylic), 3.89 (t, 1, C=C-CH), 2-3.2 (m, 8, $-CH_2$); mass spectrum (70 ev) m/e (rel. intensity) 274 (100), 146 (75), 129 (100), 43 (97), 29 (91); ^{13}C NMR ($CDCl_3$) ppm 198.63 (carbonyl), 136.71, 135.08, 133.62, 133.18, 132.83, 128.69, 127.90, 127.60, 127.41, 126.58, 125.97, 122.91, 50.71 (methine), 28.71, 28.21, 28.07, 27.99.

Ultrasonic Agitation in Basic Alumina Catalyzed Condensation of Ketones for Preparation of (E)-2[2',3'-Dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1-H-inden-1-one (39). A mixture of 6.6 g (0.05 mol) of 1-indanone, 40 ml cyclohexane and 25 g of activated basic alumina (0.5 g/mmol of ketone) was added to a 100 ml three necked flask mounted in a sonic vibrator under an inert atmosphere. Heating and agitation was continued for 24 h. The reaction mixture was then transferred to a Soxhlet apparatus containing basic alumina. The product was extracted with refluxing cyclohexane, the extract was concentrated and chromatographed through an alumina column to give 1.0 g of 1-indanone and 4.6 g (90%) of the dimer ketone 39. The crude product was recrystallized using 2-propanol to give 3.25 g (63%) of dimer ketone 39: mp 139-143 °C; ^{1}H NMR ($CDCl_3$) δ 7.6-7.7 (d, 1, ArH), 7-7.4 (m, 7, Ar-H), 3.7 (S, 2, $ArCH_2$), 3.2-3.5 (t, 2, $Ar-CH_2$), 2.8-3 (t, 2, allylic); mass spectrum (70 eV), m/e (rel. intensity) 240 (100), 245 (40), 217 (27), 215 (36), 202 (25), 116 (34), 115 (39), 107 (11),

101 (11), 77 (16); IR (KBr) (cm^{-1}), 1690 (carbonyl), 1590, 1620 (Aryl-H); ^{13}C NMR ($CDCl_3$) ppm 195.25 (carbonyl), 155.04, 151.73, 148.54, 139.55, 133.62, 130.43, 127.31, 126.29, 125.98, 125.94, 125.78, 123.62, 33.03, 31.56 and 30.94.

Ultrasonic Agitation in Basic Alumina Catalyzed Condensation of Ketones for Preparation of (E) and (Z)-1,3-Diphenyl-2-buten-1-one (44) and (45). Acetophenone (30 g, 0.25 mol), 50 mL of cyclohexane and 45 g (0.19 g/mmol of ketone) of activated basic alumina were combined and added to a 500 ml three necked flask mounted in a sonic vibrator. The experiment was carried out as described for 1-tetralone.

At 25 °C for 144 h: The product was extracted with refluxing ether using a Soxhlet apparatus. The extract was concentrated to give a crude oil (29.5 g), which on distillation (140 °C/0.4 mm) gave acetophenone (15.87 g) and 10.5 g (78%) of dimer ketones 44 and 45. ^1H NMR ($CDCl_3$) δ 7.1-8 (m, 10, Ar-H), 7.07 (s, 1, vinylic, 2.5-2.55 (s, 3, CH_3); mass spectrum (70 eV) m/e (rel. intensity) 222 (100), 221 (68), 105 (14), 77 (37); IR (KBr) (cm^{-1}), 1660 (C=O), 1450, 1600 (Aryl-H); ^{13}C NMR ($CDCl_3$) ppm 192.96 (Z isomer carbonyl), 191.63 (E isomer carbonyl), 154.96 (E, Ar), 152.25 (Z, Ar), 142.61 (E, Ar), 140.53 (Z, Ar), 139.27 (E, Ar), 137.96 (Z, Ar), 132.45, 129.19, 129.08, 128.99, 128.77, 128.68, 128.56, 128.49, 128.31, 128.79, 128.10, 127.98, 127.89, 127.68, 127.45, 127.33, 126.50, 125.42, 125.74, 124.14, 122.08, 121.96, 26.44 (methyl carbon of Z isomer) and 18.80 (methyl carbon of E isomer).

At 25 °C for 24 h: Extraction with refluxing ether, using a Soxhlet apparatus containing basic alumina, gave 28.0 g of crude oil. On distillation (140 °C/0.4 mm), 14.26 g of acetophenone and 8.07 g

(56%) of the dimer ketones 44 and 45 were obtained. ^{1}H NMR, IR and mass spectrum of this dimer ketones 44 and 45 were identical to that of an authentic sample.

At 80 °C for 24 h: After the reaction was complete, the reaction mixture was transferred to a Soxhlet apparatus containing alumina and extracted with refluxing ether. The extract was concentrated to obtain 28.5 g of crude oil, which on distillation (140 °C/0.4 mm) gave 15.6 g of acetophenone and 12.1 g (91%) of the dimer ketones 44 and 45. Its ^{1}H NMR, IR, ^{13}C NMR and mass spectrum were identical to that of an authentic sample.

Use of a Modified Sieve Shaker for Preparation of 3,3',4,4'-Tetrahydro-1',2-binaphthalen-1(2H)-one (4). A mixture of 36.5 g (0.25 mol) of 1-tetralone 100 mL, cyclohexane and 125 g of activated basic alumina (0.5 g/mmol of ketone) was added to a dry and clean stainless steel vessel mounted on the modified sieve shaker equipped with a reflux condenser. It was flushed with argon and then heated at reflux temperature (80 °C) with continuous shaking under an argon atmosphere for 24 h. The reaction mixture was allowed to cool, the vessel was disconnected from the apparatus and the contents were transferred to a Soxhlet apparatus containing 2 cm of Dicalite for extraction with cyclohexane. Extraction was continued overnight and the extract was steam distilled to give 7.7 g of recovered 1-tetralone. The residue from the steam distillation was dissolved in ether, dried ($MgSO_4$), and concentrated to give 18.9 g (70% based on recovered 1-tetralone) of crude dimer ketone 4. Recrystallization from 2-propanol gave material melting at 130-131 °C. The melting point of an admixture with authentic dimer ketone did not show a depression.

Application of the above procedure to the appropriate monomeric ketone gave the following dimeric ketones.

Use of a Modified Sieve Shaker for Preparation of (E)-2[2',3'-Dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one (39). Using the above procedure for workup of the reaction, 16.0 g (62%) of pure dimer ketone (39) was obtained. The melting point of an admixture with authentic dimer ketone did not show a depression.

Use of a Modified Sieve Shaker for Preparation of (E) and (Z)-1,3-Diphenyl-2-buten-1-one (44) and (45). Using the procedure described earlier, 58.5% (based on recovered monomer ketone) of a mixture of E and Z isomers of the dimer ketones 44 and 45 was obtained. It was isolated (after removal of monomer ketone) by distilling with superheated steam (156-200 ^{o}C). This dimer ketone gave satisfactory ^{1}H- and ^{13}C-NMR as well as mass spectral data.

Use of a Modified Sieve Shaker for Preparation of 7,7'-Dimethoxy-3,3',4,4'-tetrahydro-1',2-binaphthalen-1(2H)-one (46). After recrystallization with 2-propanol, 60% of pure dimer ketone (46) was obtained, mp 130-133 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 6.5-7.5 (m, 6, Ar-H), 5.6-5.9 (t, 1, vinylic), 3.6-3.9 (s, 6, methoxy); mass spectrum (70 eV), m/e (rel. intensity) 334 (100), 332 (13), 317 (10), 176 (48), 174 (31), 161 (33), 159 (33), 120 (84), 115 (26), 91 (17), 84 (14), 77 (88); IR (KBr) (cm^{-1}) 1680 (carbonyl), 1500, 1560, 1610; ^{13}C NMR ($CDCl_3$) ppm 198.51 (carbonyl), 158.20, 157.83, 136.33, 135.04, 134.65, 133.58, 129.76, 128.81, 128.04, 127.43, 121.52, 111.05, 109.91, 109.28, 55.35, 55.15, 50.45 (methine), 28.88, 27.04, 27.23 and 23.45.

Use of a Modified Sieve Shaker for Preparation of 3,3',4,4',5,5'-6,6',7,7',8,8'-Dodecahydro-1',1-bianthracen-1(2H)-one (48). Using the

above procedure, 81% (after recovering the monomer ketone) of dimer ketone (48) was obtained as pure yellowish white crystals; mp 160-162 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 7.8-7.9 (s, 1, Ar-H), 7.3 (s, 1, Ar-H), 7 (s, 1, Ar-H), 6.9 (s, 1, Ar-H), 5.8-5.9 (t, 1, vinylic), 3.8-3.9 (t, 1, methine), 2.6-2.9 (m, 12, benzylic), 2.2 (b, 4, methylene), 1.8 (m, 8, aliphatic); mass spectrum (70 eV), m/e (rel. intensity) 382 (100), 381 (67), 200 (89), 185 (55), 129 (62), 115 (35), 77 (21); ^{13}C NMR ($CDCl_3$) ppm 198.3 (carbonyl), 143.92, 141.20, 135.87, 135.72, 135.17, 134.70, 134.21, 131.10, 130.76, 129.14, 128.45, 127.95, 126.05, 123.74, 50.30 (methine), 29.81, 29.41, 29.14, 29.02, 28.81, 27.94, 27.22, 23.46, 23.39, 23.31, 23.11 and 22.92.

Use of a Modified Sieve Shaker for Preparation of 3,3',4,4',5,5',-6,6',7,7',8,8'-Dodecahydro-1',2-biphenanthrene-1(2H)-one (49). Using the above procedure, 92% (after recovering the monomer ketone) of dimer ketone 49 was obtained as pure white crystals: mp 137-138 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 7.7-8 (d, 2, Ar-H), 6.7-7 (d, 2, Ar-H), 5.4-5.7 (s, 1, vinylic), 3.6-3.9 (b, 1, methine), 2.4-2.8 (m, 10, methylene), 1.9-2.1 (m, 4, aliphatic), 1.3-1.8 (m, 10, aliphatic); mass spectrum (70 mV), m/e (rel. intensity) 382 (100), 380 (43), 378 (50), 200 (54), 141 (46), 100 (43), 77 (15); ^{13}C NMR ($CDCl_3$) ppm 198.86 (carbonyl), 142.92, 142.28, 135.92, 135.04, 134.78, 134.55, 133.58, 131.01, 130.84, 127.33, 126.34, 124.85, 124.24, 120.43, 49.68 (methine), 30.54, 30.08, 27.89, 26.72, 26.22, 24.30, 23.42, 23.13, 23.01, 22.80, 22.60 and 22.23.

Use of a Modified Sieve Shaker for Preparation of 6,6'-Dimethyl-(E)-2[2',3'-dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one (52). Using the above procedure, dimer ketone 52 was obtained. It was recrystallized using 2-propanol as solvent. That gave 68% of pure

dimer ketone 52: mp 169-170 °C; ^{1}H NMR ($CDCl_3$) δ 7.6-7.7 (d, 1, Ar-H), 7.2-7.5 (m, 5, Ar-H), 4 (s, 2, allylic), 3.6 (t, 2, benzylic), 3.1 (t, 2, allylic), 2.5 (s, 3, Ar-CH_3), 2.4 (s, 3, Ar-CH_3); mass spectrum (70 eV), m/e (rel. intensity) 274 (100), 259 (51), 163 (16), 111 (14), 107 (40), 81 (31); ^{13}C NMR ($CDCl_3$) ppm 195.33 (carbonyl), 154.79, 148.86, 145.88, 141.11, 139.70, 137.03, 136.32, 134.68, 131.43, 126.57, 126.27, 125.54, 125.33, 123.56, 32.67, 31.46, 21.56 and 21.18.

Use of a Modified Sieve Shaker for Preparation of 5,5'-Dimethyl-(E)-2[2',3'-dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one (53). The dimer ketone (53) was isolated by adopting the work-up procedure similar to that used earlier, which gave after recrystallization, 72% of dimer ketone 53: mp 157-160 °C; ^{1}H NMR ($CDCl_3$) δ 7.7 (d, 1, Ar-H), 7.3 (d, 1, Ar-H), 7.1-7.2 (m, 4, Ar-H), 3.9 (s, 2, allylic), 3.5 (t, 2, allylic), 3.1 (t, 2, benzylic), 2.4 (s, 3, methyl), 2.41 (s, 3, methyl); mass spectrum (70 eV), m/e (rel. intensity) 274 (100), 259 (42), 257 (11), 215 (15), 145 (31), 91 (5), 77 (5). IR (KBr) (cm^{-1}) 1695 (carbonyl), 1590, 1620 (Aryl-H). ^{13}C NMR ($CDCl_3$) ppm 194.83 (carbonyl), 154.44, 151.93, 148.94, 144.36, 140.88, 138.33, 137.47, 128.39, 127.90, 126.28, 126.21, 125.74, 125.63, 123.35, 32.83, 31.61, 30.72, 22.09 and 21.60. Anal. calcd. for $C_{20}H_{18}O$: C, 87.59; H, 6.56. Found: C, 87.42; H, 6.88.

Use of a Modified Sieve Shaker for Preparation of 4,4'-Dimethyl-(E)-2[2',3'-dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one-(54). The dimer ketone (54) was prepared by the procedure described for 4. It was recrystallized using 2-propanol to give a 73% yield of pure compound: mp 142-145 °C; ^{1}H NMR ($CDCl_3$) δ 7.1-7.7 (m, 6, Ar-H), 3.5-3.6 (m, 4, ArCH_2), 3.2 (t, 2, allylic), 2.35 (s, 3, Ar-CH_3), 2.25

(s, 3, $ArCH_3$); mass spectrum (70 eV), m/e (rel. intensity) 274 (100), 259 (50), 257 (15), 216 (23), 189 (13), 105 (20), 91 (13); ^{13}C NMR ($CDCl_3$) ppm 195.58 (carbonyl), 155.47, 150.68, 147.48, 140.65, 139.30, 135.46, 135.03, 134.97, 131.05, 127.44, 127.13, 127.07, 126.99, 123.39, 31.67, 31.42, 29.78, 18.86 and 17.89. Anal. calcd. for $C_{20}H_{18}O$: C, 87.54; H, 6.56. Found: C, 87.63; H, 6.9.

Use of a Modified Sieve Shaker for Preparation of 1,3,5-Triphenylbenzene. A mixture of 30 g (0.25 mol) of acetophenone, 50 ml cyclohexane and 25 g (0.2 g/mmol of ketone) of activated basic alumina was added to clean and dry stainless steel vessel mounted on the modified sieve/shaker. Argon was maintained during heating and shaking which was continued for 24 h. The reaction was carried out under pressure (25 lb/sq. inch) at 105-106 °C. The reaction mixture was cooled to room temperature and then transferred to a Soxhlet apparatus containing basic alumina. The product was extracted with refluxing ether. Solvent, acetophenone and dypnone were removed with steam distillation, which gave 6.9 g of acetophenone and 7.6 g (68.5%) of dypnone. The crude solid residue was recrystallized using hot ethanol to give 8.1 g (87.1%) of white crystals of 1,3,5 triphenyl benzene: mp 172-173 °C; ^1H NMR ($CDCl_3$) δ 7.4 (t, 3, Ar-H), 7.5 (t, 6, Ar-H), 7.7 (d, 6, Ar-H), 7.8 (s, 3, Ar-H); mass spectrum (70 eV) m/e (rel. intensity) 306 (60), 229 (10), 224 (20), 223 (100), 165 (10), 152 (5), 145 (10), 124 (8), 91 (10), 85 (5), 77 (100); ^{13}C NMR ($CDCl_3$) 128.83, 127.53, 127.34 and 125.16.

Using p-Toluenesulfonic Acid as a Catalyst for Preparation of 6,6'-Dimethoxy-3,3',4,4'-tetrahydro-1',2-binaphthalen-1(2H)-one (49). A mixture of 3.5 g (0.02 mol) of 6-methoxy-1-tetralone, 11.5 g (10.3 ml)

of ethylene glycol and p-toluenesulfonic acid (0.05 g) in 21.2 g (24.5 ml) of toluene was added to a two-necked, 100 mL flask equipped with a Dean-Stark trap. Stirring and heating was continued for 37 h, during this period, reaction mixture was heated reflux. In the Dean-Stark trap, the bottom layer was not very distinctly separate. After cooling the reaction mixture, the toluene phase was removed and washed with aqueous sodium bicarbonate solution and then with water. After drying ($MgSO_4$), solvent was removed to obtain 0.4 g (12%) of crude dimer ketone 47 which on recrystallization with hot 2-propanol gave 0.33 g (10%) of dimer ketone 47: mp 125-126 °C; ^{1}H NMR ($CDCl_3$) δ 8.1 (b, 1, Ar-H), 7.3 (s, 1, Ar-H), 6.9-7 (dd, 2, Ar-H), 6.7-6.8 (dd, 2, Ar-H), 5.6 (t, 1, vinylic), 3.85 (s, 3, methoxy), 3.8 (s, 3, methoxy), 2.8-3 (b, 1, methine), 2.75 (t, 2, allylic), 2.2-2.4 (m, 6, methylene); mass spectrum (70 eV) m/e (rel. intensity) 334 (100), 333 (20), 306 (26), 176 (32), 161 (26), 159 (52), 148 (49), 115 (36), 91 (30), 84 (30), 77 (31). ^{13}C NMR ($CDCl_3$) ppm 197.94 (carbonyl), 163.57, 158.26, 146.60, 138.84, 134.91, 130.02, 126.89, 126.71, 124.56, 124.35, 113.92, 113.21, 112.49, 110.83, 55.41, 55.18, 50.54 (methine), 28.78, 28.66, 28.24 and 23.10.

Using p-Toluenesulfonic Acid as a Catalyst for Preparation of 5,5'-Dimethoxy-(E)-2-[2',3'-dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one (55). Using the above procedure, 15% of dimer ketone 55 was obtained as pure white crystals: mp 186-188 °C; ^{1}H NMR ($CDCl_3$) δ 7.7 (d, 1, Ar-H), 7.4 (m, 3, Ar-H), 6.8-7 (m, 4, Ar-H), 3.7 (s, 3, OCH_3), 3.65 (s, 3, OCH_3), 3.9 (s, 2, benzyl allylic), 3.5 (t, 2, benzylic), 3 (t, 2, allylic); mass spectrum (70 eV) m/e (rel. intensity) 306 (100), 205 (40), 85 (17), 77 (15); ^{13}C NMR ($CDCl_3$) ppm 194.68

(carbonyl), 164.14, 161.64, 153.97, 153.36, 151.04, 133.72, 133.28, 126.86, 125.02, 124.43, 114.53, 114.01, 109.71, 109.41, 55.49, 55.38, 32.94, 31.69 and 31.01.

Use of Titanium Tetrachloride and Triethylamine for Preparation of 3,3',4,4'-Tetrahydro-1',2-binaphthalen-1(2H)-one (4). To 200 mL of olefin-free n-hexane, 69.9 g (56.0 mL, 0.5 mol) of $TiCl_4$ was added in an N_2 atmosphere. The mixture was cooled by an ice-salt water bath to -10 °C and a solution of 66 mL (72.5 g, 0.5 mol) of 1-tetralone in 850 mL CH_2Cl_2 was added rapidly, with vigorous stirring, to give a fluffy, yellow precipitate. Subsequently, a solution of 66 mL (72.5 g, 0.5 mol) of 1-tetralone and 148 mL (107.5 g, 1.1 mol) of triethylamine diluted to 850 mL with CH_2Cl_2 was added. The ensuing red-black solution was stirred at -10 °C for 40 min and then allowed to warm to room temperature. After 16 h, the black product was treated with 1.6 L H_2O in 3 portions, dried ($MgSO_4$) and concentrated. The product was washed with 200 mL of 2-propanol and the wash was filtered to give a combined yield of 96 g (70%) of the dimer ketone 4. Recrystallization from 1 L of 2-propanol gave 70 g of white crystals: mp 130-133 °C; ^1H NMR ($CDCl_3$) δ 8.1 (m, 1, Ar-H), 7.00-7.55 (m, 7, Ar-H), 5.77 (m, 1, vinyl H), 3.83 (t, 1, methine H), 3.00 (m, 2, methylene), 2.64-2.85 (m, 2, methylene), 2.1-2.45 (m, 4, methylene); mass spectrum (70 eV) m/e (rel. intensity) 274 (100), 146 (75), 129 (100), 43 (97), 29 (91); ^{13}C NMR ($CDCl_3$) ppm 198.63 (carbonyl), 136.71, 135.08, 133.62, 133.18, 132.83, 128.69, 127.90, 127.60, 127.41, 126.58, 126.58, 125.97, 122.91, 50.71 (methine), 28.71, 28.21, 28.07 and 27.99.

Use of Titanium Tetrachloride and Triethylamine for Preparation of (E)-2,[2',3'-Dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-

one (39). Using the above procedure and the reaction scale, 54% of pure dimer ketone 39 was obtained (no starting monomer ketone was recovered): mp 139-142 °C; ^{1}H NMR ($CDCl_3$) δ 7.6-7.7 (d, 1, Ar-H), 7-7.4 (m, 7, Ar-H), 3.7 (s, 2, $ArCH_2$), 3.2-3.5 (t, 2, Ar-CH_2), 2.8-3 (t, 2, allylic); mass spectrum (70 eV), m/e (rel. intensity) 246 (100), 245 (40), 115 (39), 77 (16); IR (KBr) cm^{-1}, 1690 (carbonyl), 1590, 1620 (Ar-H).

Use of Titanium Tetrachloride and Triethylamine for Preparation of (E) and (Z)-1,3-Diphenyl-2-buten-1-one (44) and (45). Using the above procedure and the reaction scale, 64% of a mixture of E and Z dimer ketones was obtained and purified by distillation: bp 140 °C (0.4 mm); ^{1}H NMR ($CDCl_3$) δ 7.1-8 (m, 10, Ar-H), 7.07 (s, 1, vinylic), 2.5 (s, 3, CH_3); mass spectrum (70 eV), m/e (rel. intensity) 222 (100), 221 (68), 105 (14), 77 (37); IR (KBr) cm^{-1}, 1660 (carbonyl), 1450, 1600.

Use of Titanium Tetrachloride and Triethylamine for Preparation of 7,7'-Dimethoxy-3,3',4,4'-tetrahydro-1',2-binaphthalen-1(2H)one (46). Using the above procedure and the reaction scale, 70% of pure dimer ketone 46 was obtained (no starting monomer ketone was recovered): mp 127 °C; ^{1}H NMR ($CDCl_3$) δ 6.5-7.5 (m, 6, Ar-H), 5.6-5.9 (t, 1, vinylic), 3.6-3.7 (s, 6, OCH_3); mass spectrum (70 eV), m/e (rel. intensity) 334 (100), 176 (48), 161 (33), 120 (84), 91 (17), 84 (44), 77 (88); IR (KBr) cm^{-1} 1680 (carbonyl); ^{13}C NMR ($CDCl_3$) ppm 198.51 (carbonyl), 158.20, 157.83, 136.33, 135.04, 134.65, 133.58, 129.76,128.81, 128.04, 127.43, 121.52, 111.05, 109.91, 109.28, 55.35, 55.15, 50.45 (methine), 28.88, 27.04, 27.23 and 23.45.

Use of Titanium Tetrachloride and Triethylamine for Preparation

of 6,6'-Dimethoxy-3,3',4,4'-tetrahydro-1',2-binaphthalen-1(2H)one (47). Using the above procedure and the reaction scale, 78% of pure dimer ketone 47 was obtained (no starting monomer ketone was recovered): mp 125-126 °C; ^{1}H NMR ($CDCl_3$) δ 8.1 (s, 1, Ar-H), 7.3 (s, 1, Ar-H), 6.9-7 (dd, 2, Ar-H), 6.7-6.8 (dd, 2, Ar-H), 5.6 (t, 1, vinylic), 3.0 (s, 3, OCH_3), 3.8 (s, 3, OCH_3), 2.8-3 (broad, 1, methine); mass spectrum (70 eV), m/e (rel. intensity) 334 (100), 306 (26), 176 (32), 159 (52), 148 (49), 115 (36), 84 (300), 77 (31); ^{13}C NMR ($CDCl_3$) ppm 197.94 (carbonyl), 163.57, 158.26, 146.60, 138.84, 134.91, 130.30, 126.89, 126.71, 124.56, 124,35, 113.92, 113.21, 112.49, 110.83, 55.41, 55.18, 50.54 (methine), 28.78, 28.66, 28.24 and 23.10.

Use of Titanium Tetrachloride and Triethylamine for Preparation of 3,3',4,4',5,5',6,6',7,7',8,8'-Dodecahydro-1',2-bianthracen-1(2H)one (48). Using the above procedure and the reaction scale, 74% of pure dimer ketone 48 was obtained (no starting monomer ketone was recovered): mp 160-163 °C; ^{1}H NMR ($CDCl_3$) δ 7.8 (s, 1, Ar-H), 7.3 (s, 1, Ar-H), 7 (s, 1, Ar-H), 6.9 (s, 1, Ar-H), 5.8 (t, 1, vinylic), 3.8 (t, 1, methine), 2.6-2.9 (m, 12, Ar-CH_2), 2.2 (b, 4, CH_2), 1.8 (m, 8, CH_2); mass spectrum (70 eV), m/e (rel. intensity) 382 (100), 200 (89), 129 (62), 115 (35), 77 (21); ^{13}C NMR ($CDCl_3$) ppm 198.30 (carbonyl), 143.92, 141.20, 135.87, 135.71, 135.18, 134.73, 134.28, 131.30, 130.77, 129.18, 128.50, 127.00, 126.04, 123.77, 50.10 (methine), 29.81, 29.44, 29.13, 29.10, 28.80, 27.91, 27.31, 23.44, 23.38, 23.30, 23.11 and 22.92.

Use of Titanium Tetrachloride and Triethylamine for Preparation of 3,3',4,4',5,5',6,6',7,7',8,8'-Dodecahydro-1',2-biphenanthrene-1(2H)-one (49). Using the above procedure and the reaction scale, 71% of pure dimer ketone 49 was obtained (no starting monomer ketone was

recovered): mp 140-143 °C; ^{1}H NMR ($CDCl_3$) δ 7.7-8 (d, 2, Ar-H), 6.9 (d, 2, Ar-H), 5.4-5.7 (s, 1, vinylic), 3.6-3.9 (t, 1, methine), 2.4-2.8 (m, 10, CH_2), 1.3-2.1 (m, 14, CH_2); mass spectrum (70 eV), m/e (rel. intensity) 382 (100), 380 (43), 200 (54), 141 (46), 77 (15); ^{13}C NMR ($CDCl_3$) ppm 198.70 (carbonyl), 142.92, 142.28, 135.92, 135.04, 134.78, 134.55, 133.58, 131.01, 130.88, 127.34, 126.31, 124.88, 124.22, 120.41, 49.80 (methine), 30.51, 30.10, 27.81, 26.72, 26.22, 24.31, 23,43, 23.17, 23.05, 22.83, 22.62 and 22.22.

Use of Titanium Tetrachloride and Triethylamine for Preparation of 5,5'-Dimethoxy-(E)-2-[2',3'-dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one (55). Using the above procedure and the reaction scale, 84% of pure dimer ketone 55 was obtained (no starting monomer ketone was recovered): mp 186-188 °C; ^{1}H NMR ($CDCl_3$) δ 7.7 (d, 1, Ar-H), 7.5 (m, 3, Ar-H), 6.8-7 (m, 4, Ar-H), 3.7 (s, 3, OCH_3), 3.6 (s, 3, OCH_3), 3.9 (s, 2, benzyl allylic), 3.5 (t, 2, benzylic), 3.1 (t, 2, allylic); mass spectrum (70 eV), m/e (rel. intensity) 306 (100), 291 (39), 205 (40), 124 (18), 85 (17), 77 (15); ^{13}C NMR ($CDCl_3$) ppm 194.68 (carbonyl), 164.14, 161.64, 153.97, 153.36, 151.04, 133.72, 133.28, 126.86, 125.02, 124.43, 114.53, 114.01, 109.71, 109.41, 55.49, 55.38, 32.94, 31.69 and 31.01.

Esterification of 4-Tert Butyl Benzoic Acid (56). A mixture of 80.0 g (0.45 mol) of 4-tert. butyl benzoic acid (56), 124 g (2.7 mol) of anhydrous ethanol and 1.3 mL of sulfuric acid was placed in a 500 mL two-necked, round bottomed flask fitted with a thermometer and Soxhlet extractor containing 81 g of conditioned Linde 3A° molecular sieve. The Soxhlet extractor was fitted with a high capacity condenser. Anhydrous ethanol was added until the molecular sieves were

covered. The flask contents were heated at reflux temperature (a range from 76.2 °C to 78.5 °C) and stirred with a magnetic bar for 15 h. Some of the alcohol was distilled into the Soxhlet chamber and retained there. The flask was cooled and 5 g of anhydrous sodium carbonate were added with stirring to neutralize the sulfuric acid. The suspension was filtered and ethanol was removed by rotatory evaporation. The residue was dissolved in ether (3 x 50 ml) and the resulting organic layer was treated with 1N KOH solution (3 x 50 ml) to remove unreacted acid. The ether layer was separated, washed with 1 N KOH solution (3 x 50 ml), dried ($MgSO_4$) and concentrated to give 88 g (95%) of crude ethyl 4-tert butyl benzoate (57) which was purified by distillation at 100 °C/1.2 mm; ^1H NMR ($CDCl_3$) δ 7.5-8 (dd, 4, Ar-H), 4.4 (q, 2, CH_2), 1.4 (t, 3, CH_3), 1.3 (s, 9, t-butyl); mass spectrum (70 eV), m/e (rel. intensity) 206 (100), 191 (70), 178 (36), 161 (49), 146 (39), 135 (78), 133 (69), 107 (15), 105 (32), 102 (18), 91 (63), 77 (60); IR (KBr) (cm^{-1}) 3010 (Aryl C-H), 2980 (aliphatic C-H), 1710 (conjugated C=O), 1605 (aromatic), 1300-1500 (tertiary butyl), 830 (para substitution); ^{13}C NMR ($CDCl_3$) ppm 166.17 (carbonyl), 156.01, 129.18, 127.56, 124.95, 60.32, 34.71, 30.82 and 14.10.

Diisobutyl Aluminum Hydride (DIBAH) Reduction of Ethyl 4-tert. Butylbenzoate (57). Ethyl ester (57) (82.4 g, 0.4 mol), under a nitrogen atmosphere, was mixed in 800 mL of dry toluene in a 2 L, three necked flask fitted with a mechanical stirrer and a thermocouple. A solution of 61.2 g (0.44 mol) of DIBAH in 500 ml toluene was added dropwise at -78 °C over a period of 3 h with continuous stirring. When the addition was complete, the mixture was stirred at -78 °C for an additional 5 h. The reaction mixture was allowed to warm to 0 °C

and 150 ml of cold methanol was added slowly to the reaction mixture with continuous stirring. A mixture of 150 mL of methanol and 150 mL of ice-water was added with stirring to reaction mixture. The aluminum salts which formed were decomposed through addition of 5% HCl. The product was extracted with ether and evaporation gave 60.0 g (91.5%) of 4-tert-butylbenzyl alcohol: bp 140 °C (20 mm); ^{1}H NMR 8.1 (d, 2, Ar-H), 7.8 (d, 2, Ar-H), 4.5 (s, 2, $ArCH_2O$), 1.3 (s, 9, t-butyl); ^{13}C NMR ($CDCl_3$) ppm 150.39, 135.24, 127.48, 125.14 (aromatics), 71.72 ($ArCH_2$), 34.39 (t-butyl-c), 31.23 (t-butyl); mass spectrum (70 eV), m/e (rel. intensity) 164 (100), 163 (80), 148 (90), 117 (60), 92 (95), 91 (50) and 77 (60).

Oxidation of 4-Tert-butylbenzyl Alcohol (58). A solution of 6.12 g (37.3 mmol) of (58) in 100 mL CH_2Cl_2 was added to a stirred solution of 2,2'BPCC (33.7 g, 0.1 mol) in 150 ml CH_2Cl_2. The mixture was stirred at room temperature for 4 h. When the oxidation was complete, the mixture was diluted with ether and filtered through Dicalite. The filtrate was washed with 5% HCl and 10% Na_2CO_3 solution. Evaporation of solvent gave 3.0 g (49%) of 4-tert.-butylbenzaldehyde. It was purified by distillation: 112-113 °C/13 mm; ^{1}H NMR ($CDCl_3$) δ 1.3 (s, 9, t-butyl), 7.8 (d, 2, Ar-H), 8.1 (d, 2, Ar-H), 10 (s, 1, CHO); ^{13}C NMR ($CDCl_3$) ppm 191.71 (carbonyl), 158.20 and 129.62 (of ArC), 127.57, 125.95, 125.88, 125.18 (ArC), 34.42 ($ArC(CH_3)_3$), 31.33 (t-butyl); mass spectrum (70 eV), m/e (rel. intensity) 162 (100), 161 (18), 148 (10), 147 (70), 91 (40), 85 (70), 83 (90) and 77 (15).

Preparation of p-tert-Butyl Cinnamic Acid (60). p-tert-Butyl benzaldehyde (25 g, 0.15 mol) and 75 mL of pyridine were placed in a 3-L, two necked, round-bottomed flask fitted with a condenser and

thermometer. The solution was warmed to 50 °C and malonic acid (39 g, 0.37 mol) was added in portions, with magnetically stirring. Heating was continued and at 80-85 °C piperidine (1.5 mL) was added. The mixture was stirred for 1 h and then for 3 h at 100-105 °C. The reaction was cooled to 25 °C and pyridine was evaporated under the reduced pressure. The residue was diluted with water and acidified with 1:1 HCl until acidic. The solid product was filtered by suction, washed with 3 x 300 mL portions of water and purified by crystallization to give 29.1 g (92%) of white, crystalline 60: mp 192-193 °C; ^{1}H NMR ($CDCl_3$) δ 7.5 (dd, 4, Ar-H), 7.8 (d, 1, vinylic), 6.5 (d, 1, vinylic), 1.39 (s, 9, t-butyl); ^{13}C NMR ($CDCl_3$) ppm 172.51, 154.35, 146.89, 131.35, 128.24, 125.94, 116.45, 34.94, 31.14; mass spectrum (70 eV), m/e (rel. intensity) 204 (100), 189 (98), 161 (58), 128 (44), 115 (44), 102 (23), 77 (31); IR (KBr) cm^{-1} 2990 (CO_2H), 1690 (CO).

Catalytic Hydrogenation of p-tert-Butyl Cinnamic Acid (60). The catalytic hydrogenation of unsaturated acid (60) was carried out using a Parr Model 3920 hydrogenation apparatus. A 29.1 g (0.15 mol) sample of 60 was added to a stainless steel hydrogenation vessel containing 300 mL of acetic acid and 1.5 g of 5% Pd/C catalyst. The vessel was evacuated, hydrogen was introduced, and then shaken (Parr apparatus) at 45-50 psig and 50-60 °C until hydrogen uptake ceased (0.5 h). Excess hydrogen was vented and the vessel contents were filtered through Dicalite to remove the catalyst. The filtrate was diluted with water to precipitate the product as white solid. The product was filtered and purified by recrystallization using 2-propanol to give 26.5 g (90%) of compound 61: mp 102-115 °C; ^{1}H NMR ($CDCl_3$) δ 7.3 (dd, 4, Ar-H), 2.9 (t, 2, $ArCH_2$), 2.7 (t, 2, CH_2), 1.3 (s, 9,

t-butyl); ^{13}C NMR ($CDCl_3$) ppm 179.28, 149.19, 137.08, 127.90, 125.44, 114.08, 35.59, 34.39 and 31.49; IR (KBr) cm^{-1} 3005 (CO_2H), 1710 (CO); mass spectrum, m/e (rel. intensity) 206 (100), 192 (77), 132 (36), 131 (20), 117 (46), 91 (41).

Cyclization of p-tert-Butylhydrocinnamic Acid (61). Polyphosphoric acid (PPA) (50 mL) was heated in a 250 mL, 3-necked flask fitted with a mechanical stirrer, and a thermometer; the third neck being open. When the temperature of the PPA reached 80 °C, 5 g (0.025 mol) of acid 61 was added in small amounts over a period of 15 min. The mixture was stirred at 80-85 °C for 1.5 h. The cooled mixture was poured over 150 g of ice to hydrolyze the PPA. The solution was extracted twice with 20 mL portions of ether. The combined ether extracts were washed with saturated $NaHCO_3$ solution (no reacted 61 was recovered from this) and then with water. The ether layer was filtered through Dicalite and dried ($MgSO_4$). The solvent was removed and the yellow oil was distilled (Kugelrohr, 145-150 °C, 3 mm) to give 3.8 g (76%) of colorless oil, which solidified on standing: ^1H NMR ($CDCl_3$) δ 7.4 (s, 1, Ar-H), 7.3 (d, 2, Ar-H), 3.9 (d, 2, CH_2), 3.3 (d, 2, CH_2), 1.3 (s, 9, t-butyl); ^{13}C NMR ($CDCl_3$) ppm 207.29 (carbonyl), 152.29, 150.66, 136.89, 132.42, 126.25, 119.85, 36.59, 34.73, 31.31, 25.28.

Preparation of 6,6'-Ditert Butyl-(E)-2[2',3'-dihydro-1'H-inden-1-ylidene]-2,3-dihydro-1H-inden-1-one (63). A mixture of 3.6 g (0.02 mol) of 6-tert-butyl-1-indanone (62), 25 ml cyclohexane and 25 g of activated basic alumina (0.5 g/mmol of ketone) was added to a 100 ml three-necked flask mounted in a sonic vibrator, under an inert atmosphere. Heating at 80 °C and agitation was continued for 24 h. The reaction mixture was then transferred to a Soxhlet apparatus containing basic

alumina. The product was extracted with refluxing cyclohexane, the extract was concentrated and chromatographed through an alumina column to give 0.5 g of 6-tert-butyl-1-indanone and 2.0 g (65%) of the dimer ketone 63: mp 145 °C; ^{1}H NMR ($CDCl_3$) 8.7-9 (dd, 2, Ar-H), 7.4-7.6 (m, 4, Ar-H), 4.1 (s, 2, CH_2), 3.7 (t, 2, CH_2), 3.2 (t, 2, CH_2), 1.4 (s, 9. t-butyl).

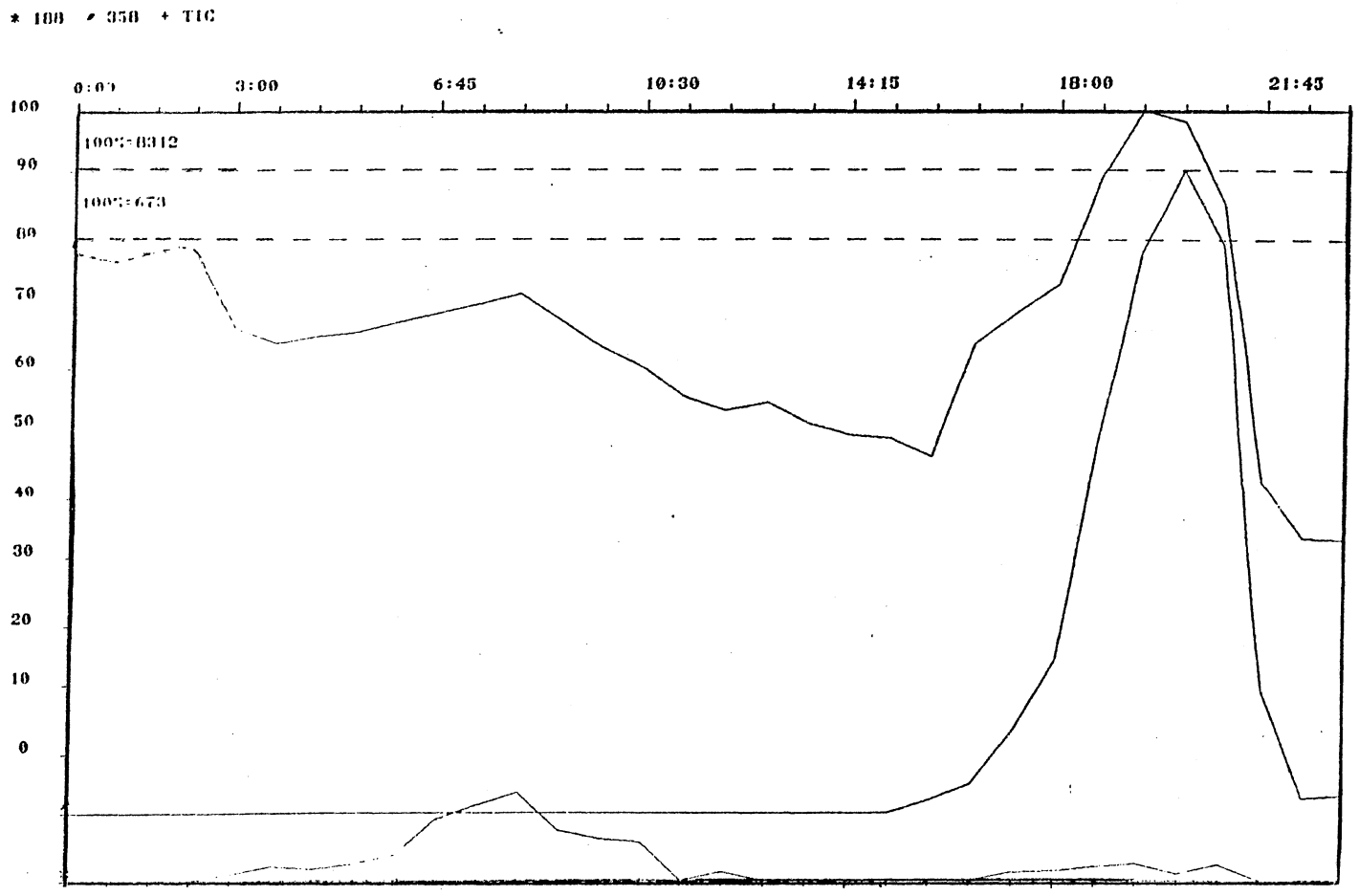


Figure 18. Cross Scan Report of Dimer Ketone 63.

REFERENCES

1. Wurtz, A. Bull. Soc. Chim. France 1982, 17, 436.

2. Jung, M. E. Tetrahedron 1976, 32, 1.

3. March, J. "Advanced Organic Chemistry" McGraw Hill, N.Y. 1977, 850.

4. Schmidt, J. G. Ber. 1880, 13, 2342.

5. Claisen, L. Ann. 1899, 30C, 322.

6. Nielsen, A. T. and Houlihan, W. J. Org. Reactions 1979, 16, 1.

7. Kunin, R. "Ion Exchange Resins," Wiley, N.Y. 1950, 1.

8. Okamoto, G. Bull. Chem. Soc. Jpn. 1966, 39, 2778.

9. Hauser, C. R. J. Amer. Chem. Soc. 1953, 75, 1068.

10. Hauser, C. R. J. Amer. Chem. Soc. 1967, 89, 4566.

11. Geissman, T. A. Org. Reactions 1944, 2, 94.

12. Schurink, H. B. J. Org. Syntheses 1941, Coll. Vol. 1, 425.

13. Stork, G. and d'Angelo, J. J. Amer. Chem. Soc. 1974, 96, 7114.

14. Claisen, L. Ber. 1887, 20, 655.

15. Nielsen, A. T. and Houlihan, W. J. Org. Reactions 1979, 16, 112.

16. Burnham, J. W.; Melton, R. G.; Eisenbraun, E. J.; Keen, G. W. and Hamming, M. C. J. Org. Chem. 1973, 38, 2783.

17. Springer, J. M.; Hinman, C. W.; Eisenbraun, E. J.; Flanagan, P. W. K. and Hamming, M. C. J. Org. Chem. 1970, 35, 1260.

18. Muzart, J. Synthesis 1982, 20, 60.

19. Plesek, J. Chem. Listy 1956, 50, 246. [C.A., 1956, 50, 7732.]

20. Varech, D.; Ouannes, C. and Jacques, J. Bull. Soc. Chim. France 1965, 1662.

21. Gentry, R. E. and Burtner, R. R., U.S. Patent 2836624, 1958. [C.A., 1958, 52, 17222.]

22. Chenault, J. and Sainson, C. C. R. Acad. Sci. 1978, 287, 545.

23. Kanaoka, Y.; Sato, E.; Yonemitsu, O. and Ban, Y. Tetrahedron Lett. 1964, 35, 2419.

24. Diels, O.; Blanchard, W. M. and Heyden, H. Ber. 1914, 47, 2355.

25. Wayne, W. and Adkins, H. J. Amer. Chem. Soc. 1940, 62, 3401.

26. Moore, H. W. and Snyder, H. R. J. Org. Chem. 1963, 28, 535.

27. Mitchell, J. A. and Reid, E. E. J. Amer. Chem. Soc. 1931, 53, 330.

28. Senderens, J. B. Bull. Soc. Chim. France 1908, 823.

29. Colonge, J. Compt. Rend. 1933, 196, 1414.

30. Bianchetti, G; Dalla Croce, P. and Pocar, D. Tetrahedron Lett. 1965, 13, 2039.

31. Taboury, F. and Gudchot, M. Compt. Rend. 1919, 62, 169.

32. Dubois, J. E. Bull. Soc. Chim. France 1955, 272.

33. Mastagli, P. and Durr, G. Bull. Soc. Chim. France, 1955, 268.

34. Dietrich, W. German Patent 857960, 1952. [C.A., 1953, 47, 11240.]

35. Conant, J. B. and Tuttle, N. Org. Syntheses 1941, Coll. Vol., 1, 345.

36. Baeyer, Ann. 1866, 140, 297.

37. Landa, S. and Sesulka, V. Chem. Listy 1957, 51, 1159. [C.A., 1957, 51, 13814.]

38. Adams, R. and Hufferd, R. W. Org. Syntheses 1941, Coll. Vol., 1, 759.

39. Wallach, O. Ber. 1907, 40, 70.

40. Wenkert, E.; Bhattacharya, S. K. and Wilson, E. M. J. Org. Chem. 1964, 29, 5617.

41. Volkova, N. V. and Yasnikov, A. A. Dokl. Akad. Nauk USSR 1963, 149, 94. [C.A., 1963, 59, 5011.]

42. Cologne, J. Bull. Soc. Chim. France 1934, 1101.

43. Hine, J.; Houston, J. G.; Jensen, J. H. and Mulders, J. J. Amer. Chem. Soc. 1965, 87, 5050.

44. Noyce, D. S. and Snyder, L. R. J. Amer. Chem. Soc. 1959, 81, 624.

45. Noyce, D. S. and Reed, W. L. J. Amer. Chem. Soc. 1959, 81, 624.

46. Schappell, F. G. and Pines, H. J. Org. Chem. 1966, 31, 1735.

47. Heathcock, C. H., "Comprehensive Carbanion Chemistry," Elsevier, 1981, Vol. II, 1.

48. Hassner, A. H. and Mead, T. C. Tetrahedron Lett. 1962, 9, 1223.

49. Noyce, D. S. and Jorgenson, M. J. J. Amer. Chem. Soc. 1961, 83, 2525.

50. Lutz, R. E. and Slade, L. T. J. Org. Chem. 1961, 26, 4888.

51. Dubois, J. E. and Dubois, M. Bull. Soc. Chim. France 1969, 355.

52. Masamune, S.; Mori, S.; van Horn, D. and Brooks, D. W. Tetrahedron Lett. 1978, 1665.

53. Jeffrey, E. A.; Meisters, A. and Mole, T. J. Organometallic Chem. 1974, 74, 373.

54. Heng, K. K. and Smith, R. A. J. Tetrahedron, 1979, 425.

55. Izawa, T. and Mukaiyama, T. Chem. Lett., 1978, 409.

56. Mukaiyama, T. Angew. Chem. Int. Ed. Engl. 1977, 16, 817.

57. Barot, B. C.; Sullins, D. W. and Eisenbraun, E. J. Synthetic Commun. 1984, 14, 397.

58. Mazza, L. J. and Guarna, A. Synthesis, 1980, 41.

59. Holba, A. G.; Premasager, V.; Barot, B. C. and Eisenbraun, E. J., Unpublished results.

60. McMurry, J. E. Acc. Chem. Res. 1974, 7, 281.

61. Jones, G. Org. Reactions, 1967, 15, 204.

62. Han, B. H. and Boudjouk, P. Tetrahedron Lett. 1982, 23, 1643.

63. Han, B. H. and Boudjouk, P. Tetrahedron Lett. 1981, 22, 275.

64. Han, B. H. and Boudjouk, P. J. Org. Chem. 1982, 47, 5030.

65. Han, B. H. and Boudjouk, P. J. Org. Chem. 1982, 47, 751.

66. Han, B. H. and Boudjouk, P. J. Amer. Chem. Soc. 1982, 104, 49.

67. Repic, O. and Vogt, S. Tetrahedron Lett. 1982, 23, 2729.

68. Yamawaki, J.; Ando, T. and Hanafusa, T. Chemistry Lett. 1983, 37.

69. Ando, T.; Kawate, T. and Hanafusa, T. Synthesis, 1983, 637.

70. Miyake, M.; Uematsu, R. and Nomura, M. Chemistry Lett. 1984, 535.

71. Kitazume, T. and Ishikawa, N. Chemistry Lett. 1981, 1679.

72. Davidson, R. S.; Patel, A. M. and Safdar, A. Tetrahedron Lett. 1983, 24, 5907.

73. Reeves, W. P. and McClusky, J. V. Tetrahedron Lett. 1983, 24, 158.

74. Luche, J. L. and Damiano, J. C. J. Amer. Chem. Soc. 1980, 102, 792.

75. Mason, T. J.; Lorimer, J. P. and Mistry, B. P. Tetrahedron Lett. 1982, 23, 5362.

76. Raucher, W. and Klein, P. J. Org. Chem. 1981, 46, 3558.

77. Regen, S. L. and Singh, A. J. Org. Chem. 1982, 47, 1587.

78. Prakash, S. and Pandey, J. D. Tetrahedron 1965, 21, 903.

79. Moon, S.; Duchin, L. and Cooney, J. V. Tetrahedron Lett. 1979, 20, 391.

80. Luche, J.-L.; Petrier, C.; Lansard, J.-P. and Greene, A. B. J. Org. Chem. 1983, 48, 3837.

81. Kabalka, G. W.; Pagni, R. M.; Bridwell, P.; Walsh, E. and Hassaneen, H. M. J. Org. Chem. 1981, 46, 1513.

82. Posner, G. H. and Rogers, D. Z. J. Amer. Chem. Soc. 1977, 99, 8208.

83. Available from "Aldrich Chemical Co." Milwaukee, Wisconsin 53233, Catalog No. 19944-3.

84. Russel, A. S., "Aluminum Properties," Alcoa-Aluminum Company of America, Pittsburg, PA.

85. Abdullaev, A. I. and Farkhadov, T. S. Gazov. Prom-St. USSR, 1979, 4, 16. [C.A., 1980, 92, 46838g.]

86. Frankel, I. and Juergens, E. Govt. Rep. Announce. Index (U.S.) 1980, 80, 4065. [C.A., 1981, 94, 144793z.]

87. Nuriev, A. N., USSR Pat. 549,421, 1974. [C.A., 1977, 86, p. 191960w.]

88. Koho, K. T. Jpn. Pat. 80152517, 1980. [C.A. 1981, 95, p. 9337.]

89. Koho, K. T. Jpn. Pat. 8118689, 1981. [C.A. 1981, 94, p. 177841s.]

90. Zenz, D. R. Govt. Rep. Announce. Index (U.S.), 1977, 77, 184. [C.A. 1977, 87, 43745k.]

91. Posner, G. H. Angew. Chem. Int. Ed. Engl. 1978, 17, 487.

92. Handbook of Chemistry and Physics, CRC Press, Boca Raton, Fl.

93. Orchin, M.; Reggel, L. and Friedel, R. A. J. Amer. Chem. Soc. 1949, 71, 2743.

94. Retcofsky, H. L.; Reggel, L. and Friedel, R. A. Chem. Ind., 1969, 617.

95. Muzart, J. Synthesis, 1982, 60.

96. Internal Dimension of the Sonic Apparatus Tank of Branson Ultrasonic Cleaner, Model B220H, 185 Watts are (24 1 x 15 w x 10 h).

97. Weissler, A. and Hine, E. J. J. Amer. Acoust. Soc. 1961, 33, 130.

98. Repic, O.; Lee, P. G. and Giger, U. Org. Prep. and Proc. Int. 1984, 16, 25.

99. Eisenbraun, E. J. and Hall, H. Chem. and Ind. 1970, 1535.

100. Gurudata and Stothers, J. B. Can. J. Chem., 1969, 47, 3601.

101. Buchanan, G. W.; Stothers, J. B. and Wo, S. Can. J. Chem. 1969, 47, 3113.

102. Woods, W. G.; Carboni, R. A. and Roberts, J. D. J. Amer. Chem. Soc. 1956, 78, 5653.

103. Hassner, A. and Mead, T. C. Tetrahedron, 1964, 20, 2201.

104. Sicher, J. "Progress in Stereochemistry," Butterworth, London, 1962, 3.

105. Kupchan, S. M.; Eakin, M. A. and Thomas, A. M. J. Med. Chem. 1971, 14, 1147.

106. Stothers, J. B. and Lauterbur, P. C. Can. J. Chem. 1964, 42, 1563.

107. Bordner, J.; Thiessen, W. E.; Bates, H. A. and Rapoport, H. J. Amer. Chem. Soc. 1975, 97, 6008.

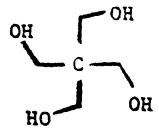
108. Harrison, H. R.; Haynes, W. M.; Arthur, P. and Eisenbraun, E. J. Chem. & Ind. 1968, 45, 1568.

109. Fujisawa, T.; Mori, T.; Tsuge, S. and Sato, T. Tetrahedron Lett. 1983, 24, 1543.

110. Jones, G. Org. Reactions, 1967, 15, 599.

APPENDIX

GLOSSARY OF STRUCTURES



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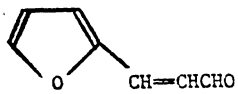

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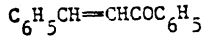

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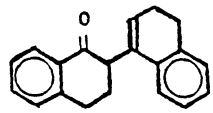

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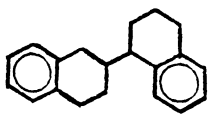

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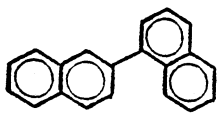

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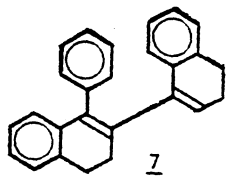

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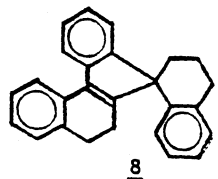

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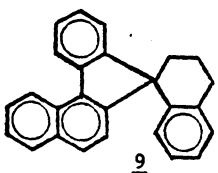

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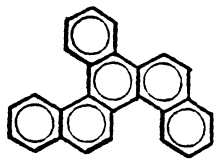

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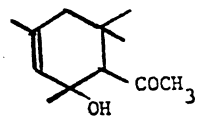

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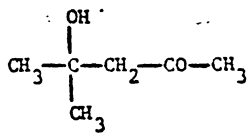

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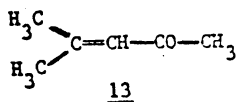

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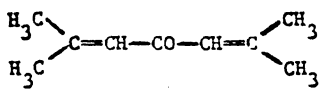

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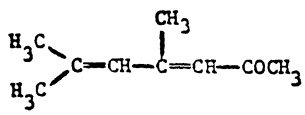

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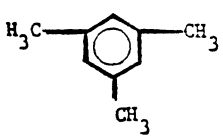

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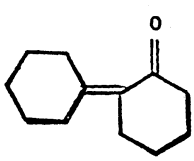

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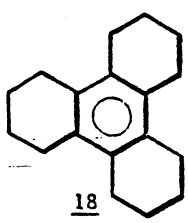

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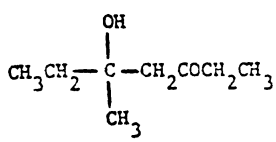

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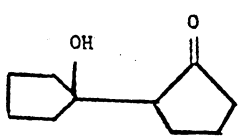

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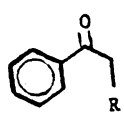

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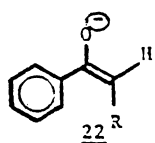

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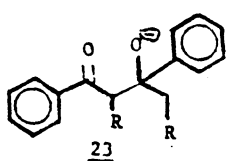

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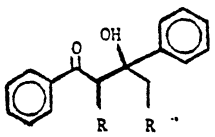
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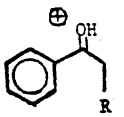
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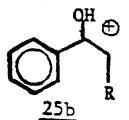
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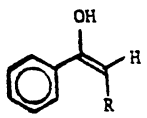
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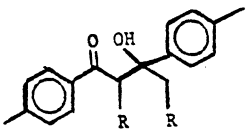
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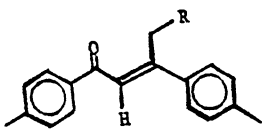
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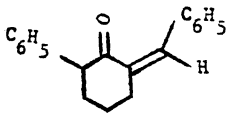
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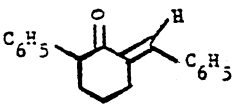
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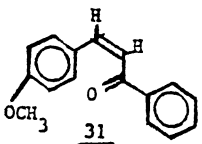
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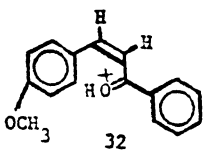
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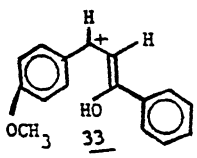
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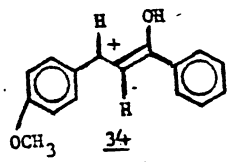
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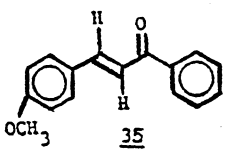
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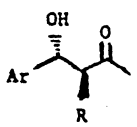
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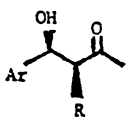
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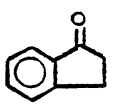
Ar = Aryl
M = Metal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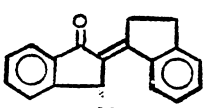
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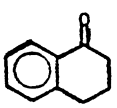
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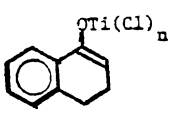
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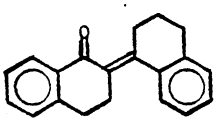
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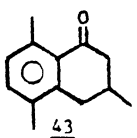
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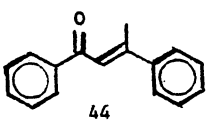
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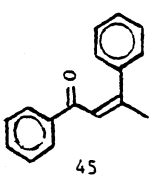
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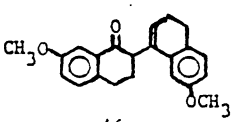
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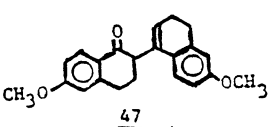
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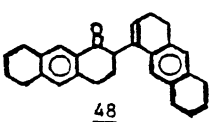
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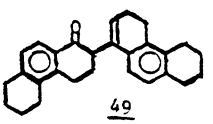

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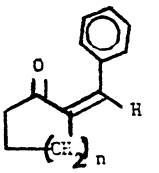

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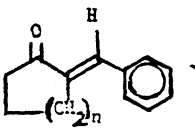

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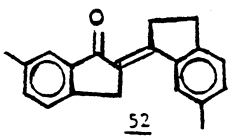

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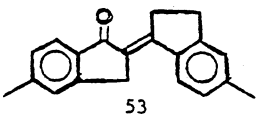

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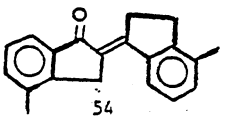

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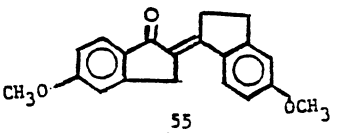

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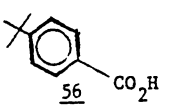

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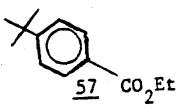

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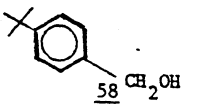

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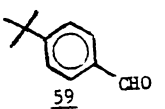

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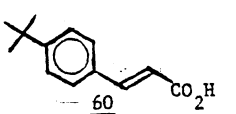

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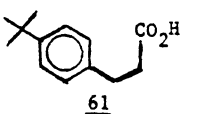

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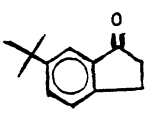

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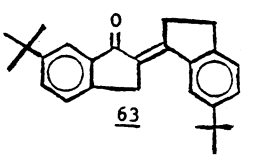

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VITA

Bhalchandra Chimamlal Barot

Candidate for the Degree of

Doctor of Philosophy

Thesis: ALUMINA CATALYZED SELF-CONDENSATION OF KETONES

Major Field: Chemistry

Biographical:

Personal Data: Born in Vijapur, India on October 8, 1951, the son of Mr. and Mrs. Chimanlal Barot.

Education: Received Bachelor of Science degree in Chemistry from University of Bombay, Bombay, India in June, 1973; Master of Science degree in Chemistry from Gujarat University, Ahmedabad, India in June, 1975; Master of Science degree in Chemistry from University of Georgia, Athens, Georgia in June, 1982; completed requirements for the Doctor of Philosophy degree at Oklahoma State University in December, 1984.

Professional Experience: Graduate Teaching Assistant, Oklahoma State University (1982-1984), University of Georgia (1979-81), Dow Chemical Scholarship (Summer 1982 and 1983); Graduate Research Assistant, Oklahoma State University (Summer, 1984).