Photolysis Pathways Of Some 2-alkylbenzophenones.

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PHOTOLYSIS PATHWAYS OF SOME 2-ALKYLBENZOPHENONES

by

Emory W.illiam Sarver

A DISSERTATION
Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy

Lehigh University
1969

This dissertation is respectfully submitted to the Graduate Faculty of Lehigh University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Emory W. Sarver

Emory W. Sarver

CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Feb. 10, 1969
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This thesis is dedicated to the author's wife, Judy, without whose encouragement and understanding this work would have been very difficult.

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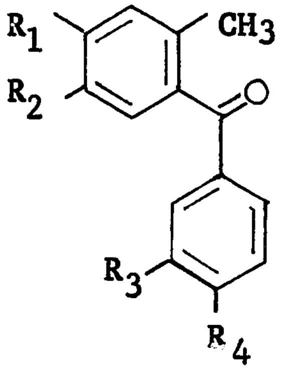
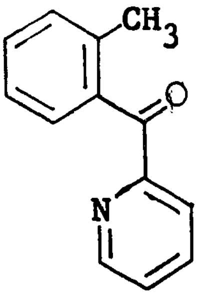
TABLE OF CONTENTS

ABSTRACT

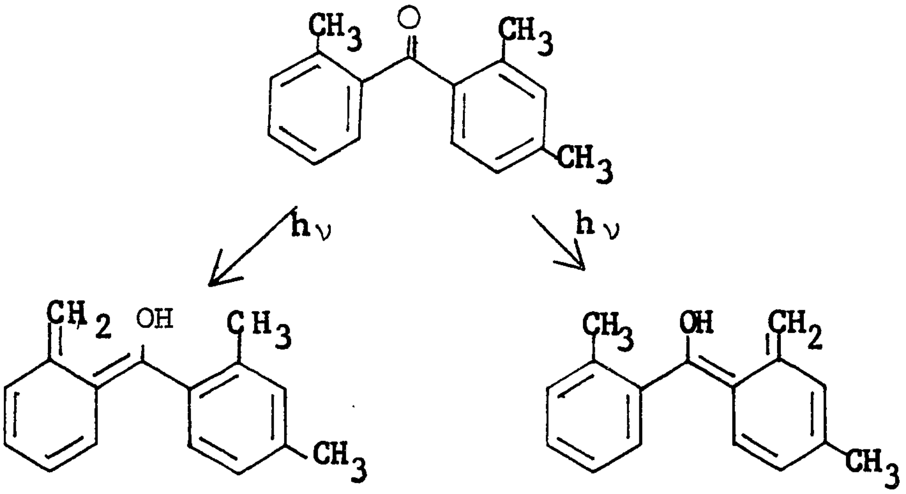
Current theories on the photochemical reactivity of o-alkylbenzophenones have suggested that these systems should be inert to intermolecular hydrogen abstraction. Several examples of this hitherto unreported photopinacolization reaction have been uncovered and the synthetic merit of the process has been established. The reaction is not limited to benzophenones but can also occur with appropriately substituted phenyl pyridyl ketones. Some steric and electronic limitations on photopinacolization have been inferred from the structures of ketones found to be inert to this process. A quantum yield determination for the photoreduction of 2,4-dimethylbenzophenone (Φ = 0.03) indicates that pinacol formation in this family is less than one-thirtieth in efficiency compared to the parent benzophenone.



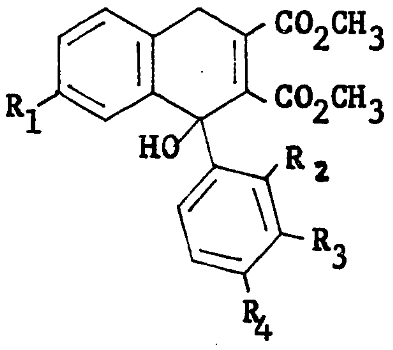


a. $R_1=CH_3, R_2=R_3=R_4=H$
b. $R_1=H, R_2=CH_3, R_3=R_4=H$
c. $R_1=R_2=H, R_3=R_4=CH_3$
d. $R_1=R_2=R_3=R_4=H$

Many examples of intramolecular hydrogen abstraction (photoenolization) by electronically excited ketone carbonyls in o-alkylbenzophenones, have been studied. Detection of photoenols has been effected by chemical trapping with dimethyl acetylenedicarboxylate and by a deuterium exchange process with CH_3OD. An experiment with an unsymmetrical ketone, 2,2',4'-trimethylbenzophenone, has indicated that dienophilic trapping onto the two different o-methyl functions is not equivalent. The deuteration of an ortho methyl group has been found to proceed smoothly past the point of incorporation of one deuterium with zero order kinetics.



An analysis of the mass spectral cracking patterns for four pure 2,3-dicarbomethoxy-1,4-dihydro-1-aryl-1-naphthols has revealed cracking patterns of two types. High mass fragments have been mass-assigned and plausible structural possibilities have been indicated.



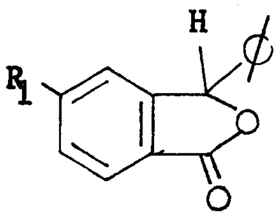
a. $R_1=CH_3, R_2=R_3=R_4=H$

b. $R_1=R_2=R_3=R_4=H$

c. $R_1=H, R_2=CH_3, R_3=R_4=H$

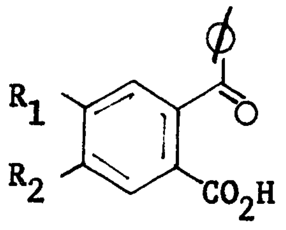
d. $R_1=R_2=H, R_3=R_4=CH_3$

The photooxidation of 2-methyl, 2,4-dimethyl- and 2,5-dimethylbenzophenone has been demonstrated. It has been proposed that the mechanism involves trapping of the photoenol species by molecular oxygen and transformation of this transient peroxide into 3-phenylphthalides and 2-benzoylbenzoic acids. Phthalide formation represents the oxidation of the o-methyl moiety to a carboxylate with concomitant reduction of the ketonic carbonyl to the hydrol oxidation state. A mechanism which involves a second enolization and oxygen trapping has been suggested to explain the formation of the 2-benzoylbenzoic acids.



a. R_1=H

b. R_1=CH_3

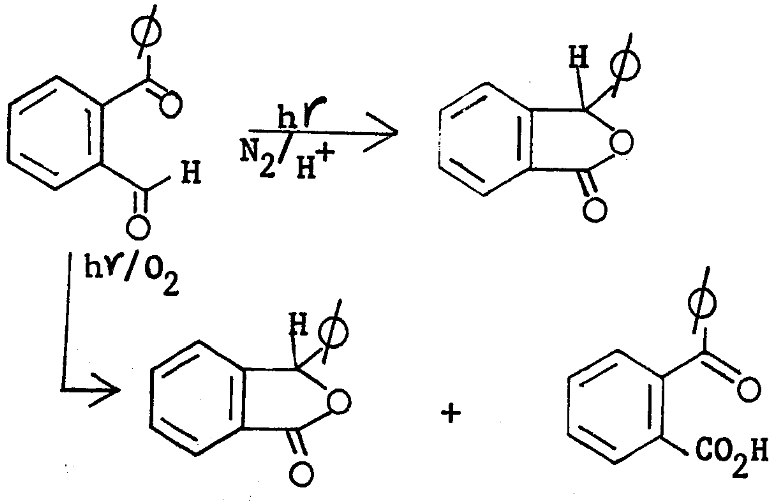


a. R_1=R_2=H

b. R_1=CH_3,R_2=H

c. R_1=H,R_2=CH_3

Another proposed intermediate in the photooxidation of o-methyl ketones, i.e., the 2-benzoylbenzaldehyde, has been independently prepared and photolyzed in oxygen-free media. Evidence based on mechanistic logic and spectroscopic detection of aldehyde absorptions in the infrared spectra of crude photooxidation products has suggested the intermediacy of this ketoaldehyde. Catalytic amounts of protonic acid have been found to encourage non-oxidative transformation of this benzoylbenzaldehyde into the 3-phenylphthalide. Photolysis of this ketoaldehyde in oxygen stream has given rise to both the phthalide and the benzoylbenzoic acid.



INTRODUCTION

A. Photoreduction: Intermolecular Hydrogen Abstraction

Any introduction to photochemistry would be incomplete without first stating that in 1900 G. Ciamician and P. Silber initiated the field by reporting the photoreduction of benzophenone to benzopinacol. The reaction was carried out in several solvents, but 2-propanol was the most successful and ever since has been the most popular solvent for reduction studies. Ciamician reported that 2-propanol was oxidized to acetone and that benzophenone was photoreduced to pinacol. Many investigators since the Ciamician-Silber contributions have demonstrated that both diaryl and aryl alkyl ketones show identical photochemical behavior although alkyl aryl and aliphatic ketones undergo bimolecular photoreduction at a much slower rate. All the early work has been summarized by Schönberg.[2,3]

The currently accepted mechanism for the photopinacolization reaction was derived from the work of Pitts and Hammond.[4,5,6,7,8] The initial step was shown to be an excitation of the carbonyl to an excited singlet state which then is transformed by intersystem crossing to an excited triplet.

$$(C_6H_5)_2CO \;+\; h\nu \longrightarrow (C_6H_5)_2CO^* \qquad (S_1) \tag{1}$$

$$(C_6H_5)_2CO^* \quad (S_1) \xrightarrow[\text{Crossing}]{\text{intersystem}} (C_6H_5)_2CO^* \qquad (T_1) \tag{2}$$

$$(C_6H_5)_2CO^* \quad (T_1) + (CH_3)_2CHOH \longrightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2\dot{C}OH \tag{3}$$

$$(C_6H_5)_2CO + (CH_3)_2\dot{C}OH \longrightarrow (C_6H_5)_2\dot{C}OH + (CH_3)_2CO \tag{4}$$

$$2(C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2COH\text{-}COH(C_6H_5)_2 \tag{5}$$

This mechanism shows very convincingly that the limiting quantum yield to be expected is two[6] for the disappearance of benzophenone and one for appearance of acetone or pinacol.

Phosphorescence and fluorescence studies have shown that benzophenone in an alcohol-ether glass at 77°K does not fluoresce and that its triplet state is as long lived as 4.3×10^{-3} sec.[9] Fluorescence has not been observed for benzophenone when it was excited at 3660A, but phosphorescence was observed to be the primary process. Hammond[10] has observed that the quantum yield for intersystem crossing (Φ_{ISC}) $S_1 \rightsquigarrow T_1$ was 0.99. This evidence indicated that the conversion to the excited triplet was quantitative upon excitation. The second mechanistic step was conjectured to be the abstraction of the carbinyl hydrogen by the excited triplet which has been characterized as a diradical by Zimmerman.[11] The dimethyl ketyl radical was observed to be so energetic that it spontaneously surrendered its hydroxyl hydrogen to an unexcited benzophenone to form the diphenylhydroxymethyl ketyl radical. Since no acetone pinacol was found in the products isolated, it was concluded that the dimethylhydroxymethyl radical had insufficient lifetime to dimerize. The only isolated product derived from 2-propanol was acetone.

The photoreduction process has been shown to be dependent on the $\pi^* \leftarrow n$ carbonyl absorption, also characterized as the "R" or radical band in the 300 mμ range of the uv spectrum. This band undergoes a hypsochromic shift in polar, hydrogen bonding solvents when compared to the same spectrum in a non-polar, non-hydrogen bonding solvents. The extinction coefficient of this band is also observed to be very low in intensity, often less than 100.[12]

Reaction (4) was shown to be extensively supressed when the benzophenone was present in very low concentration (8×10^{-6}M).[13] The process that was observed was (6) which replaced step (4).

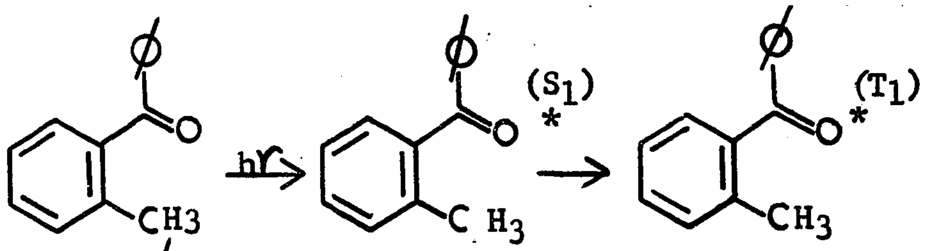
$$2(CH_3)_2\dot{C}OH \longrightarrow (CH_3)_2CO + (CH_3)_2CHOH \qquad (6)$$

However, when the benzophenone was present in higher concentrations (1×10^{-1} M), reaction (4) once again acted as a primary reaction path. It was concluded that the quantum yield of photoreduction was primarily a function of the concentration of 2-propanol and lay within the limits of unity and two for benzophenone disappearance.

A "para" substituent effect has been observed for photoreduction by Porter.[14] He studied the case of 4-hydroxybenzophenone which photoreduces in 2-propanol at a rate of 2×10^{-2} moles einstein^{-2} which is extremely slow compared to benzophenone. Pitts[16] has also described cases in which other "para" substituents, i.e. the $-NH_2$, $-C_6H_5$ and $-N(CH_3)_2$ groups diminished the rates of photoreduction.

B. Photoenolization: Intramolecular Hydrogen Abstraction Deuterium Exchange Method

Pitts[16] observed that the quantum yield of pinacol formation (Φ pinacol) was 0.00 for pinacolization of 2-hydroxybenzophenone. At the same time, however, he found that 2-methoxybenzophenone and 2-benzoylbenzoic acid underwent photoreduction in good yields. It was concluded from this evidence that the ortho hydrogen was responsible for diminishing or completely inhibiting formation of the pinacol. Yang[17] found that 2-methylbenzophenone was not photoreduced. He postulated that there was an intramolecular hydrogen abstraction of the excited carbonyl to form an enol species (8).



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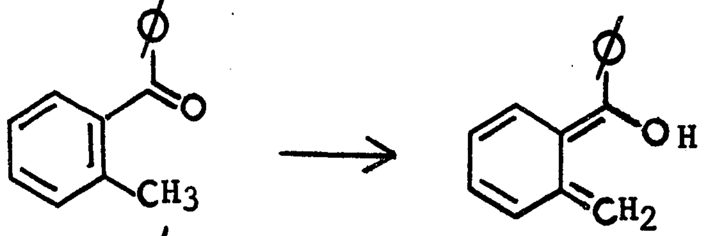

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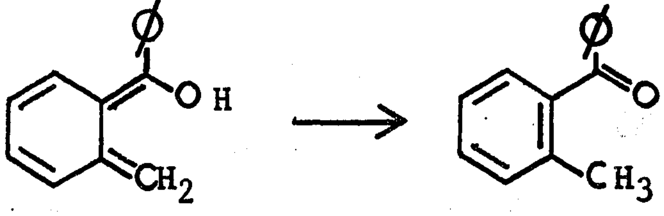
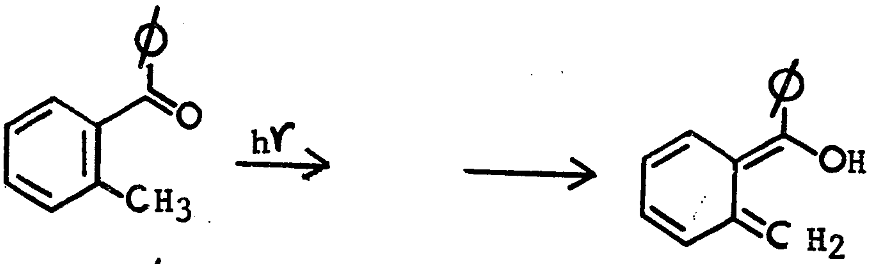


(9)

In order to demonstrate that this was indeed the reversible reaction which was inhibiting photoreduction, he devised two confirmatory experiments. The first experiment was an irradiation of 2-methylbenzophenone in deuteromethanol-d_1 to show deuterium incorporation in the ketone (9).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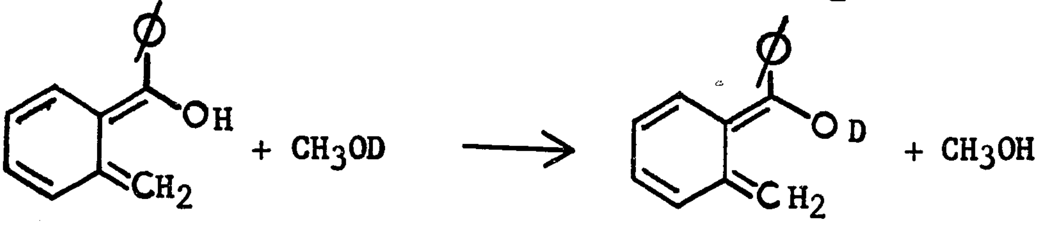
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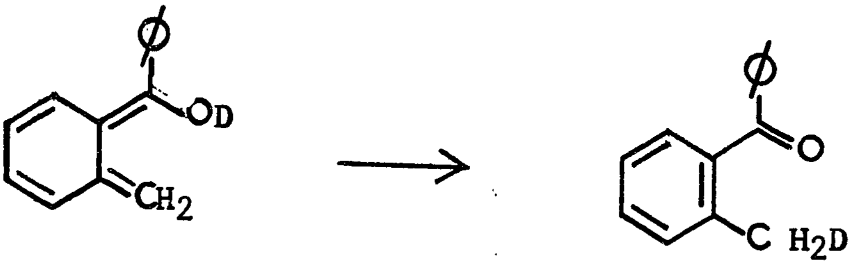
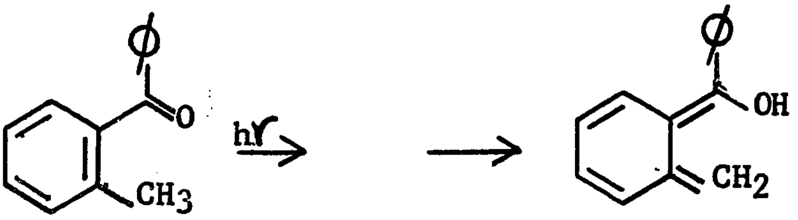

(12)

I

Compound I was recovered from the reaction and identified by physical properties. The deuterium incorporation was shown by mass spectroscopy to be unity.

Trapping Methods

Yang also reported a Diels-Alder reaction of the photoinduced diene of 2-methylbenzophenone with the dieneophile dimethyl acetylenedicarboxylate. He reported high conversion to an addition adduct which was demonstrated to be (II).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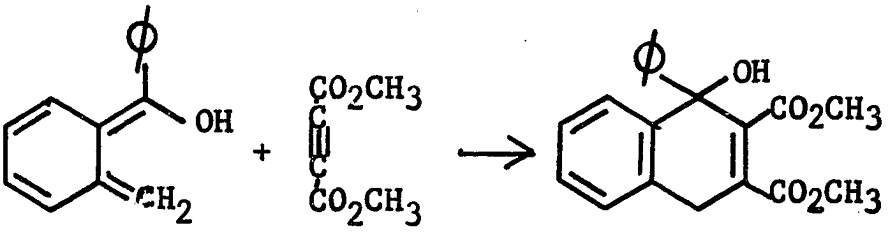
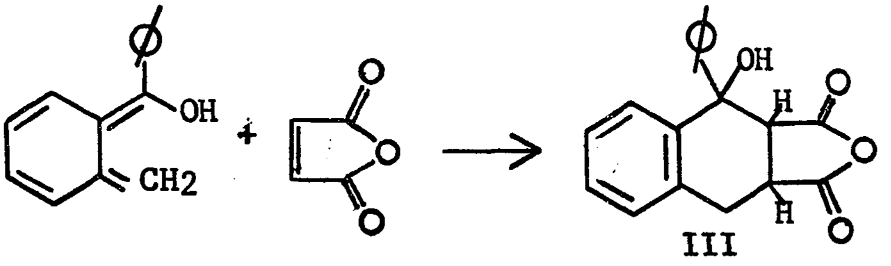

II

(14)

According to Yang these two experiments constitute the definitive proof that photoenolization is an efficient process ($\Phi = 0.5$) which completely suppresses external hydrogen abstraction, photoreduction. Porter[14] has shown that the main condition necessary for photoenolization to retard or suppress photopinacolization was that the α carbon of the ortho substitution must possess at least one hydrogen and that there was no steric crowding of the carbonyl by the "ortho" substituent. These two key requirements were indicated when 2-t-butylbenzophenone was found not only to photoreduce but to do so with reasonable quantum efficiency ($\Phi = 0.5$).

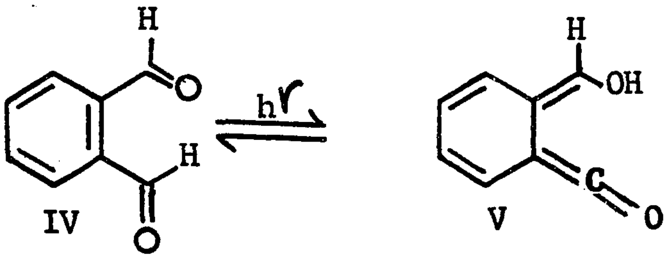
Recently Nerdel and Brodowski[18] employed another trapping agent maleic anhydride. They recovered from their reaction with 2-methylbenzophenone an 80% yield of III.



(15)

Other dienophilic trapping agents have been tried without success in this research program, but several o-methyl, di- and tri- substituted ketones have been trapped by Heindel, Lemke, and Pfau.[19]

Cohen[20] has trapped another photoenol from an excited carbonyl of o-phthalaldehyde IV. The enol (V) reacted with maleic anhydride to form an intermediate VI which was not isolated, but was treated with alkali followed by diazomethane to give VII and VIII.



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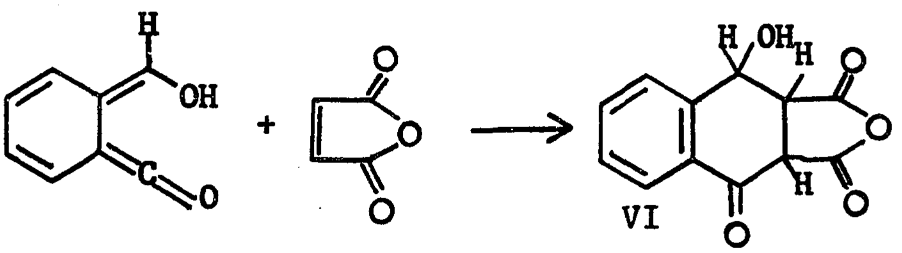

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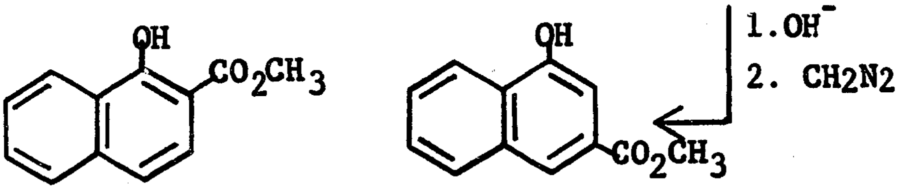
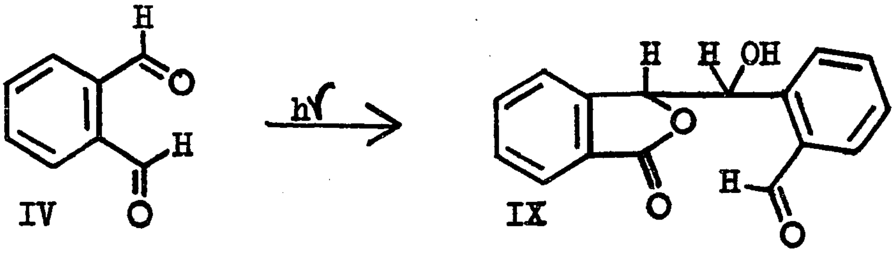


VII VIII (18)

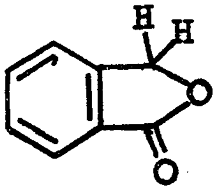
C. Photocycloaddition Reaction: Phthalide Formation

Schönberg and Mustafa[21] carried out sunlight irradiations of o-phthalaldehyde in inert solvents such as cyclohexane and reported a crystalline product for which they assigned structure IX.



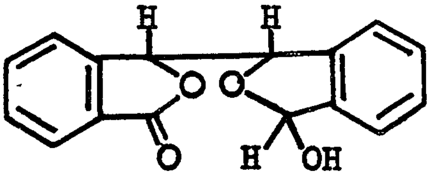
IV IX (19)

Schönberg postulated as an intermediate the phthalide X which would be expected to react with o-phthaladehyde to give product IX under the influence of light.



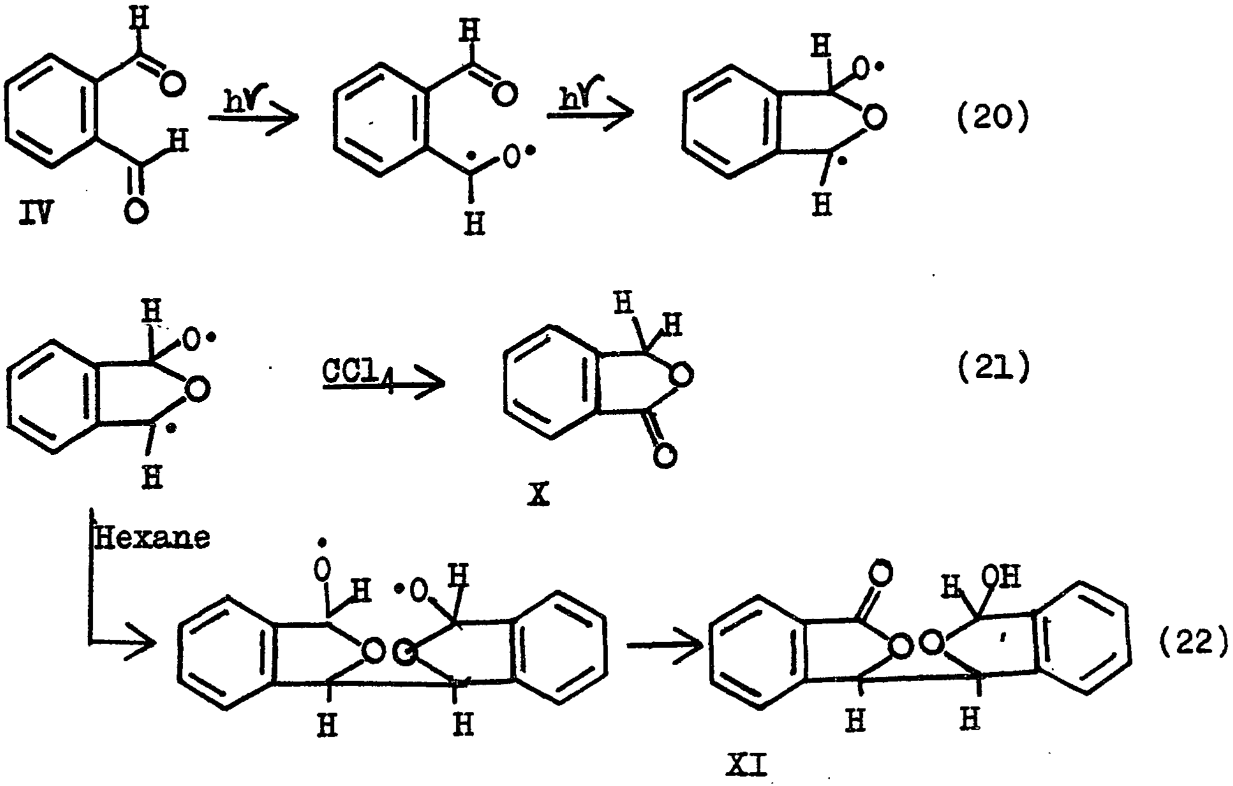
X

Kagan[22] reinvestigated the work of Schönberg and found that the irradiation of o-phthalaldehyde in carbon tetrachloride gave a high yield of the phthalide X. It was also ascertained that in hydrocarbon solvents such as hexane the product described by Schönberg could be isolated in high yields along with small amounts of the phthalide. Spectroscopic investigations of the dimeric product assigned structure IX by Schönberg showed the correct formulation to be XI.

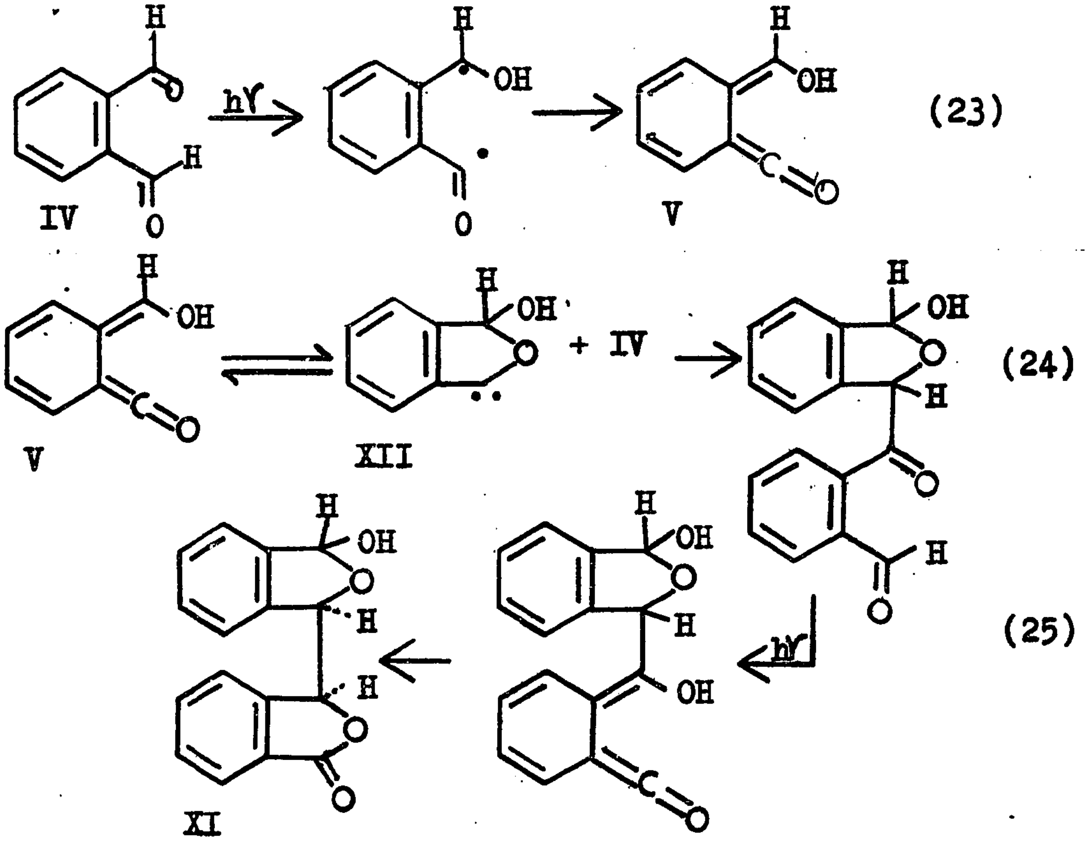


XI

Kagan explained the formation of the products by the mechanism outlined in sequence (20, 21, 22).



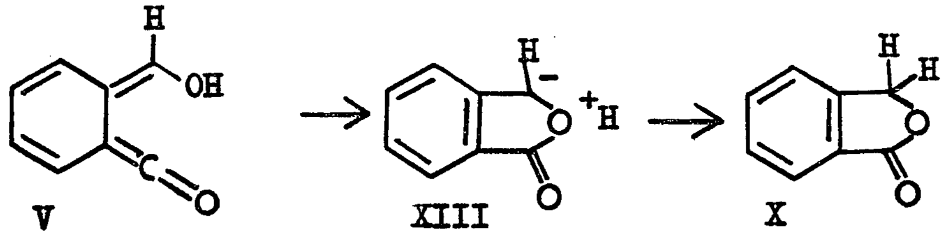
Cohen, Pinhey and Smith[20] have proposed a different process which they claim to be more consistent with the facts. Their postulated mechanism is shown in sequence (23, 24, 25).



As was stated earlier maleic anhydride is capable of trapping the photoenol ketene V in a Diels-Alder reaction. The carbene XII was postulated because Staab[23,24,25] demonstrated it to be an intermediate in the related photodimerization of benzocyclobutene-1,2-dione.[26] Yates[27] likewise showed it to be an intermediate in the photoaddition of a bicycloketone to alcohols.

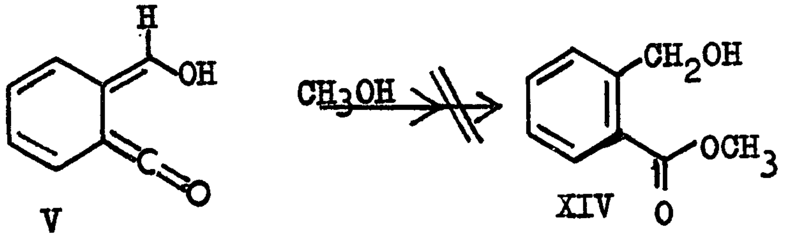
Besides the trapping of the enol ketene V, Cohen[23] also established that the amount of phthalide X produced was greatly increased by the addition of catalytic quantities of acid.

Pappas[28] expanded Cohen's results by postulating a different intermediate XIII in the phthalide mechanism.



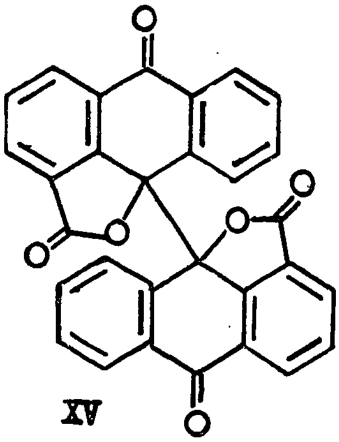
(26)

He reported but did not explain a special solvent effect in which chloroform and carbon tetrachloride promoted nearly quantitative production of phthalide, while benzene and 2-propanol retarded the conversion to phthalide. Pappas tried to generate the methyl hydroxy ester XIV from the enol ketene intermediate V but was unsuccessful in this and also in attempts to trap V as the isopropyl ester.



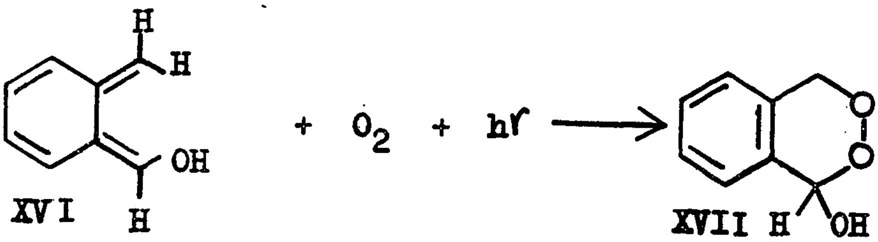
(27)

Recently Yates[29] published the results of a study of the air oxidation of 1-methylanthraquinone catalyzed by ultraviolet irradiation. One product he isolated was described as the dilactone XV together with anthraquinone-1-carboxylic acid. Yates further reported that 2-methyl-



XV

acetophenone was photooxidized to 3-methyl-phthalide and a cyclic peroxide XVII which was an oxygen adduct of the enol XVI.

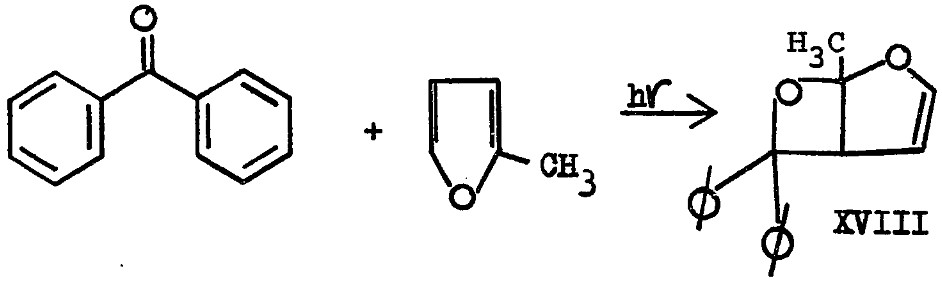


XVI XVII (28)

Photoaddition Reactions

A. Oxetane Formation

Rivas[30] described the photoreaction of benzophenone with furan and substituted furans and reported rapid and quantitative oxetane formation.

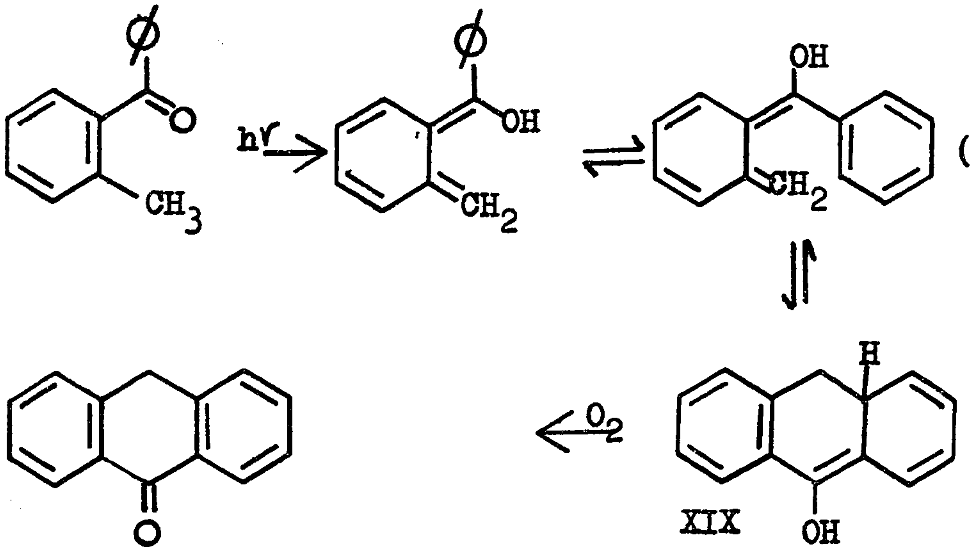


(29)

The sole product XVIII, derived from 2-methylfuran, was found by nmr to be the isomer shown. This reaction has been shown to be very general for excited diaryl ketones and many oxetane syntheses have been reported.[31]

B. Elbs Reaction

Ullman[32] has indicated that the enol formed when 2-methylbenzophenone undergoes intramolecular hydrogen abstraction should exist in equilibrium with a cycloaddition compound XIX. While the enol form would be expected to be the preferred tautomer, the cycloaddition compound, however, could react with oxygen to form a molecule of anthrone which Ullman isolated in a 1% yield.

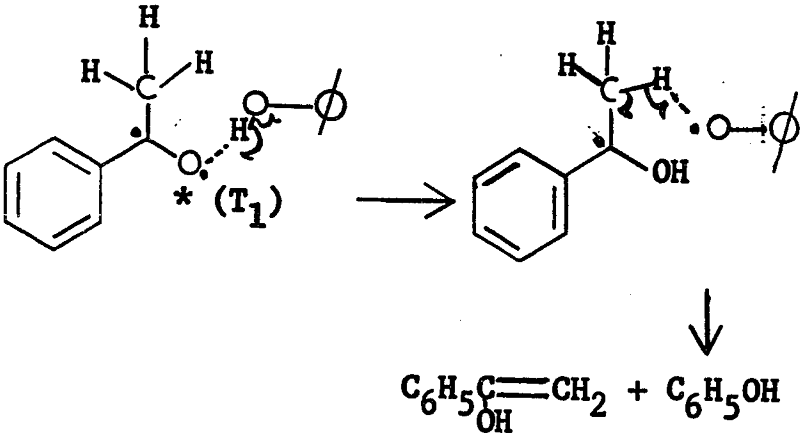


(30)

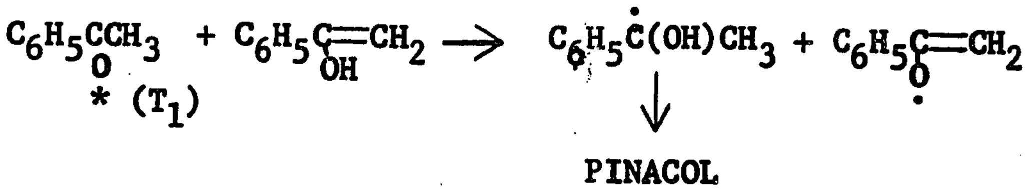
(31)

Photoredox Reactions of Acetophenone

A unique phenol-catalyzed redox reaction of acetophenone was recently reported by H. D. Becker.[33] Acetophenone underwent autoredox to an equimolar quantity of acetophenone pinacol and 1,2-dibenzoylethane. The reaction was described by mechanism (32), in which phenol serves as a hydrogen atom transfer agent.



(32)

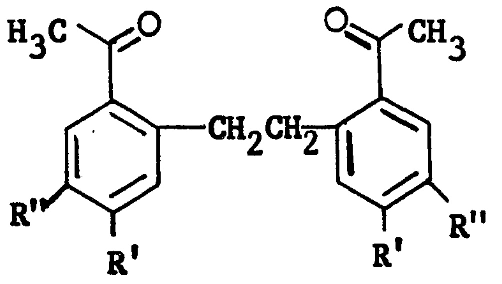


$$C_6H_5\underset{\underset{*\,(T_1)}{O}}{C}CH_3 + C_6H_5\underset{OH}{C}{=}CH_2 \longrightarrow \underset{\underset{\text{PINACOL}}{\downarrow}}{C_6H_5\dot{C}(OH)CH_3} + C_6H_5\underset{\dot{O}}{C}{=}CH_2 \qquad (33)$$

$$2C_6H_5\overset{O}{\overset{\|}{C}}CH_2\cdot \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}C_6H_5 \qquad (34)$$

XX

However, with ortho-methyl ketones a second type of redox reaction was observed in which radical coupling across the ortho positions yielded bibenzyl-like products XXI mixed with the expected pinacols.



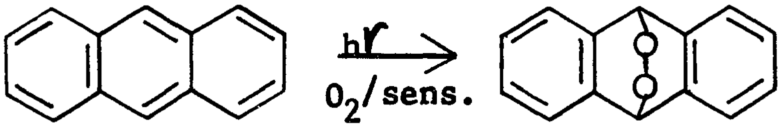
a. R'=H,R''=CH_3

b. R'=CH_3,R''=H

XXI

Photo-oxidation of Dieneoid Compounds

Schenck[34] has demonstrated that oxidation of dienes by excited oxygen is a general photoreaction for a wide variety of conjugated systems, (35,36,37).



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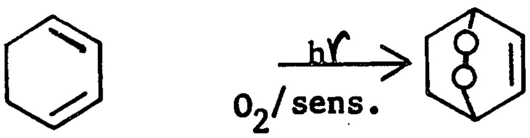

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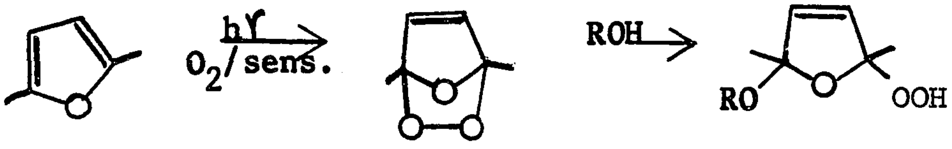

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XXII XXIII

Since the reactions were normally carried out in alcoholic media the "pseudo-ozonide" intermediates XXII might undergo ring-opening to hydroperoxides XXIII. Schönberg[35] postulated a mechanistic explanation which proposes a complex between the sensitizing molecule (sens.) and the oxygen which transfers energy to the dienic acceptor (A) in a subsequent step. Wavelength studies ruled out the possibility of a direct excitation of oxygen.

$$\text{Sens} \xrightarrow{h\nu} {}^{1}\text{Sens} \qquad (38)$$

$$^{1}\text{Sens} \longrightarrow {}^{3}\text{Sens} \qquad (39)$$

$$^{3}\text{Sens} + {}^{3}O_2 \longrightarrow \text{Sens}\ldots O_2 \qquad (40)$$

$$\text{Sens}\ldots O_2 + A \longrightarrow \text{Sens} + AO_2 \qquad (41)$$

$$^{3}\text{Sens} + {}^{3}O_2 \longrightarrow \text{Sens} + {}^{1}O_2 \qquad (42)$$

$$^{1}O_2 + A \longrightarrow AO_2 \qquad (43)$$

Kantsky[36] has proposed a similar mechanism which differed only in that no sensitizer-oxygen complex was postulated. According to this theory the sensitized molecule transferred its energy directly to the unexcited oxygen promoting the oxygen to a singlet state which then underwent addition to the acceptor (42,43).

Foote[37] has recently revealed a novel method of producing singlet excited oxygen. By the addition of sodium hypochlorite to a methanol solution of hydrogen peroxide, he was able to reproduce the reactions of Schenck (35,36, 37) in a nonphotochemical system.

RESULTS AND DISCUSSION

Photoreduction of 2-Alkylbenzophenones

The literature of organic photochemistry is devoid of reduction studies on o-alkylbenzophenones. Early work, summarized in a recent article by Pitts[38], gave the impression that benzophenones bearing ortho-hydroxy, amino, or alkyl functions were inert to normal bimolecular photoreduction. Pitts[16] and Yang[17] explained this inhibition of photoreduction by postulating a preferential internal hydrogen abstraction by the photoactivated carbonyl (see Introduction).

This work clearly demonstrates that photopinacolization of o-alkylbenzophenone does occur in solvents capable of effective hydrogen atom donation, e.g., 2-propanol. The generality of the reaction has been demonstrated in five cases. Thus, irradiation of .05 M solutions of the following ketones in 2-propanol gave excellent conversion to the corresponding diols. As a synthetic method for these materials the technique rivals any of the available metallic reductant systems.

TABLE 1 Photoreduction of "ortho" Substituted Ketones

Ketone		Pinacol	
	Hrs hν	% Yield	m.p.
2-methylbenzophenone	20 hrs	33	144-145°
2,4-dimethylbenzophenone	12 hrs	40	179-180°
2,5-dimethylbenzophenone	15 hrs	50	142-143°
2,3',4'-trimethylbenzophenone	10 hrs	33	139-141°
3-methyl-4-benzoylpyridine	18 hrs	40	170-171°

Utilization of the magnesium-iodine reduction procedure, normally one of the best for promoting pinacol formation, gave only a 31% pinacolization of 2,4-dimethylbenzophenone. By photolytic techniques a clean conversion to a readily isolated diol is available. The product isolation is facilitated by the pronounced insolubility of the high melting pinacolic products in the irradiation solvent. Accurate solubility measurements demonstrated that less than 5.5 x 10^{-4} moles of 2,4-dimethylbenzpinacol dissolve in 2-propanol at room temperatures. This feature, while conducive to facile isolation of product,contributes to experimental difficulties in carrying out the irradiation experiments. In alkylbenzophenone concentrations greater than 0.025 M in 2-propanol, the diols precipitate from the reaction mixture during the photolysis and coat the walls of the reaction vessel. With solid pinacol as an effective light-reflecting agent, continued photoreduction proceeds at a much slower rate. In addition, the alternate product of photopinacolic reduction, *i.e.*, acetone, contains a carbonyl chromophore which can compete for light with unreduced benzophenone as the irradiation proceeds. The cummulative effect of these two inhibitory effects on photoreduction can be illustrated by the one-stage vs two-stage reduction of 2,4-dimethylbenzophenone.

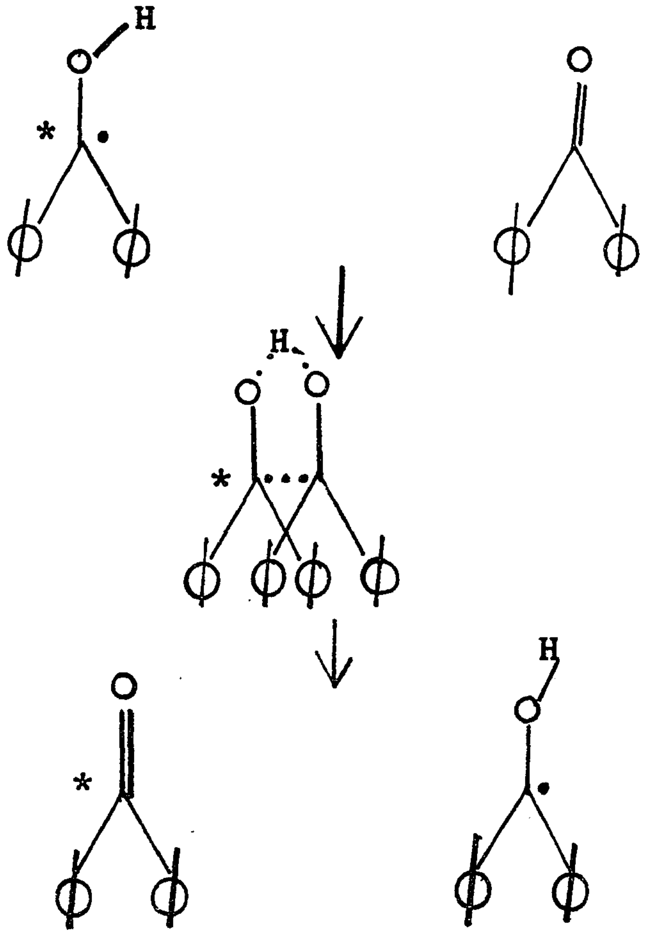
When a 0.05 M solution of 2,4-dimethylbenzophenone was irradiated for 12 hours and pinacol precipitation was allowed to continue unimpeded, a 28% conversion to diol product was observed. If, however, the precipitated diol was removed at six hours, acetone evaporated in vacuo and the unreduced ketone re-irradiated with acetone-free 2-propanol for an additional six hours, a total of 55% conversion to pinacol was obtained.

Although hydrogen abstraction from 2-propanol by photoexcited benzophenone constitutes a crucial step in the reduction mechanism, it is of interest to note that the rate of diol formation appears to be more rapid in alcohol medium. Thus, the 20 hour exposure of a 0.14 M solution of 2-methylbenzophenone in pure 2-propanol produced a 33% diol yield. A more diluted (0.05 M) solution of 2-methylbenzophenone in 1:1 2-propanol:benzene gave a 47% diol yield in equivalent time. This effect is especially surprising when one considers that the bimolecular coupling of two $Ar_2\dot{C}-OH$ radicals is the necessary product-forming step in the accepted pinacolic reduction mechanism.[4,5] This process should be facilitated in more concentrated 2-methylbenzophenone solutions.

TABLE 2 2-Propanol Concentration Effect on Quantum Yield[39]

2-Propanol M	Diluent	Rel rate
10.5	Benzene	1.4
5.2	Benzene	1.5
1.0	Benzene	1.6

Cohen has observed a very similar solvent effect in the photolysis of benzophenone itself. As long as 2-propanol and benzophenone were present in at least equimolar quantities, the rate of pinacol formation diminished with <u>increasing</u> alcohol concentration.[39] The inert diluent for the 2-propanol could be either benzene or an aliphatic hydrocarbon but not t-butyl alcohol. The explanation for these results lies in the demonstrated intermediacy of a very efficient light-absorbing transient species which has been postulated by Backstrom to be a charge-transfer complex.[40]



(44)

Franzen[41] has been more explicit in defining the nature of this non-isolated intermediate. By spectroscopic studies with radio-labeled benzhydrol, Franzen proposed that the transient was a 1:1 complex of $\mathrm{Ar_2CO}$ + $\mathrm{Ar_2\underset{\bullet}{C}{-}OH}$. All diarylhydroxymethyl radicals produced during the photolysis immediately complexed with un-activated $\mathrm{Ar_2CO}$. This tight-complex explained the absence of mixed pinacol formation between $\mathrm{Ar_2\underset{\bullet}{C}{-}OH}$ and the other radical present in the medium, $\mathrm{(CH_3)_2\underset{\bullet}{C}{-}OH}$ since this latter non-resonance stabilized radical suffered loss of a second H atom before it could unite with the diarylhydroxymethyl radicals.

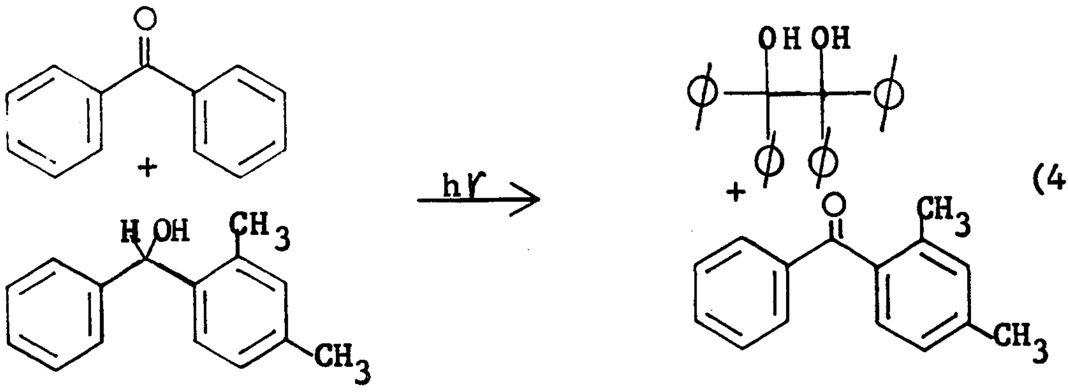
By systematic solvent polarity variations, Franzen[41], Cohen[39], and Backstrom[40] reached the same conclusion about this labile photo-transient (44) it "persisted to higher concentrations in more polar media."[39] When 2-propanol was diluted by benzene, as long as the dilution did not diminish the 2-propanol concentration below that of the benzophenone, the concentration of the light-screening transient complex was diminished and the apparent rate of photoreduction increased (relative to that in undiluted 2-propanol). These experiments illustrate that a similar effect could be operating in the 2-alkylbenzophenones.

Indeed, further evidence for the intermediacy of such specific complexes between the photoreducible ketone and its corresponding ketyl radical, is available from this study.

The irradiation of an equimolar quantity (0.025 M) of benzophenone and 2,4-dimethylbenzhydrol in benzene gave, as the sole pinacolic product, benzpinacol. No "mixed pinacol" in which a benzophenone ketyl radical dimerized with a 2,4-dimethylbenzophenone ketyl radical, was observed. Instead, 2,4-dimethylbenzhydrol served as the hydrogen atom donor to reduce benzophenone to benzpinacol while at the same time being oxidized to 2,4-dimethylbenzophenone. If Franzen's[41] specific ketone-ketyl complex (in this case $Ph_2CO\text{-}PH_2\underset{\bullet}{C}\text{-}OH$) is invoked, then the hydrogen-donor species in this medium, i.e., 2,4-dimethylbenzhydrol, is seen to play the same role as 2-propanol in a normal diarylketone photopinacolization.

If one makes a quantitative comparison of the photoreduction data from the dilution experiments, it is apparent that some factor other than Cohen's "light-absorbing transient" must be involved. If correction is made for the fact that both 2-methylbenzophenone and 2-propanol are being diluted it is noted that the 2-propanol/2-methylbenzophenone mole ratio is being varied from 10/1 in the reaction yielding 33% diol to 12/1 in the reaction producing a 47% conversion. From the results obtained by Cohen[39], it can be noted that such a small relative change had no measurable effect on the benzpinacol production per unit time. It is possible that the solvent concentration effect observed herein can be explained by the greater solubility of pinacolic product in benzene-propanol than in pure 2-propanol. The light-reflecting property of the precipitated diol apparently diminishes the effective rate of pinacolic reduction.

Although diol precipitation may exert a rate-retarding influence on continued pinacol formation, it is without effect on the product outcome. Pure authentic 2,4-dimethylbenzpinacol could be suspended in 2-propanol and exposed for 12 hours without decomposition. Even a homogeneous solution of the diol in 2-propanol-benzene containing traces of the corresponding ketone precursor, i.e. 2,4-dimethylbenzophenone, was essentially photostable for double the normal exposure time (24 hours). The ketone-pinacol mixture was selected in order to approximate the concentrations present at the termination of a normal 12 hour irradiation of 2,4-dimethylbenzophenone with the exception that diol precipitation was avoided by the presence of sufficient benzene to insure homogeneity. At the termination of the irradiation, 77% of pure diol was recovered. Spectral analysis of the oily, semi-solid concentrate from the mother liquors gave evidence of additional diol admixed with ketone. These experiments clearly demonstrate that the diol itself undergoes no extensive photodecomposition under the conditions of irradiation.



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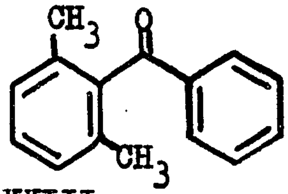
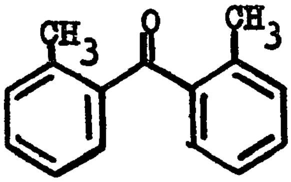
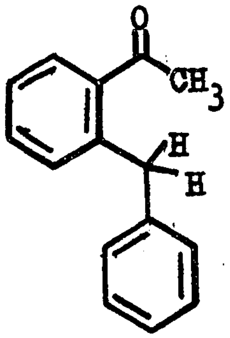
Although benzophenone can be photoreduced by either 2-propanol or benzhydrol[42], similar results were not encountered with an o-alkyl ketone in this work. The irradiation of an equimolar (0.05 M) solution of 2,4-dimethylbenzophenone and 2,4-dimethylbenzhydrol in benzene for double the normal exposure time (24 hours) produced no pinacol. Since the irradiation of benzophenone and 2,4-dimethylbenzhydrol establishes that the hydrol is capable of serving as a hydrogen atom donor, other explanation must be sought for its lack of reactivity with 2,4-dimethylbenzhydrol. Certainly the hydrogen-atom abstracting potential of the photoexcited carbonyl in 2,4-dimethylbenzophenone is greatly diminished by its potential for internal abstraction (photoenolization). In fact, quantum yield measurements show that in a vast excess of 2-propanol, 2,4-dimethylbenzophenone undergoes photopinacolization with a Φ of 0.03.

The reported maximum quantum yield for photoreduction of benzophenone is 2.0. The lack of photoreduction in the equimolar 2,4-dimethylbenzophenone-2,4-dimethylbenzhydrol system is probably a reflection of a "kinetic effect". If it were possible to utilize an excess of 2,4-dimethylbenzhydrol as a solvent then the statistical likelihood of its collision with the small fraction of activated hydrogen-abstracting 2,4-dimethylbenzophenones would be improved and photoreduction should be observed. Solubility difficulties preclude such an experiment (2,4-dimethylbenzhydrol is a solid) and the only conclusion we can draw is that 2,4-dimethylbenzhydrol does not function as a hydrogen donor to 2,4-dimethylbenzophenone under conditions in which it does donate to benzophenone.


XXIII


XXIV

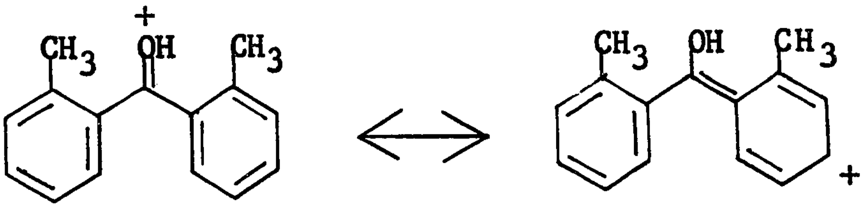

XXV

Since it has been shown that several 2-methyl aryl ketones are photoreduced, the discovery that 2,6-dimethylbenzophenone XXIII, 2-benzylacetophenone XXV and 2,2'-dimethylbenzophenone XXIV are inert to photoreduction is somewhat surprising. Even after prolonged (24 hours) irradiation in de-oxgenated 2-propanol, these ketones could be recovered completely unchanged. Several plausible explanations exist for the non-photopinacolization of these materials.

All three compounds have excellent structural opportunities for internal hydrogen abstraction. In the case of 2,6- and 2,2'-dimethylbenzophenone there are two adjacent ortho-methyl sites for photoenolization. Since inertness toward external hydrogen abstraction from solvent is related to accessibility for internal abstraction by the photoexcited carbonyl, this explanation alone could explain the lack of pinacolic reduction. For 2-benzylacetophenone the methylene proton available for internal abstraction is a highly labile benzylic hydrogen and the potential photoenol would be extensively resonance stabilized. Photoenol results, to be discussed in a subsequent section, rule out this explanation in the case of 2,6-dimethylbenzophenone. No photoenol could be detected by "trapping" or "deuterium exchange" techniques.

Simple steric arguments might be invoked to justify the lack of reactivity in the 2,6-dimethyl case. Maruyama[43] has reported that the ketonic carbonyl of 2,4,6-trimethylacetophenone is highly hindered and indeed is probably non-conjugated with the aryl system. He demonstrated that the two ortho-methyl nmr resonances are shifted some 0.2 to 0.3 ppm toward higher field than the corresponding system with only one ortho-methyl group. Thus, even if 2,6-dimethylbenzophenone did extract hydrogen from 2-propanol the resulting ketyl radical might not be resonance stabilized. Studies on the photoreduction of aliphatic ketones have shown that the process is extremely inefficient and the short lifetime of the ketyl, $R_2\cdot C\text{-}OH$, is cited as a contributing factor[44]. Pinacol formation demands that the self-dimerization of two ketyl radicals constitute the product generating step[4]. Even if the ketyl radical from 2,6-dimethylbenzophenone possessed a normally sufficient lifetime to permit dimerization the steric approach of two such species to bond-forming distance would be unlikely.

An interesting test of the steric-electronic argument is found in the results with 2,2'-dimethylbenzophenone. Here the ketonic carbonyl is apparently planar with the aryl system. NMR studies have been reported[45] on 2,2'-dimethylbenzophenone which show that even in strongly protonic medium there is no hindrance to free rotation about the carbonyl carbon-to-aryl linkage and which imply that the two aryl rings are essentially coplanar with the carbonyl. The authors claim that the protonated ketone experiences considerable



(46)[45]

resonance delocalization by aryl overlap.[45]

If the carbonium ion, shown above, is capable of a planar, resonance-stabilized existence it might be expected that a similar situation exists for the ketyl radical. Thus the lack of photoreduction in such a system cannot logically be attributed to a steric destabilization of the necessary ketyl intermediate. From the observation that photoenol formation, and subsequent trapping by acetylenedicarboxylate, is extremely facile in 2,2'-dimethylbenzophenone it appears that a more plausible explanation for non-reducibility lies in its circumvention by a more favorable internal hydrogen abstraction.

The most unusual example of a ketone which is inert to photopinacol formation is 2-benzylacetophenone. Wettermark has reported[46] that exposure of a variety of o-alkylacetophenones in CH_3OD results in incorporation of the deuterium into the o-alkyl position. A photoenol intermediate was presumed but was not trapped in a Diels-Alder reaction. He also noted that in a slow kinetic process 2,5-dimethylacetophenone exposed in alcoholic medium diminished in concentration. Again pinacol formation was presumed but not established. Other workers[47] have also concluded that Wettermark's statements imply that photoreduction does occur in o-alkylacetophenones. Becker has recently proven the point by isolating diol products from o-alkylacetophenones[48]. None of the workers studied 2-benzylacetophenone.

When a 0.05 M solution of 2-benzylacetophenone in 2-propanol was irradiated for 24 hours a complete recovery of starting material could be effected. Under the same conditions, a greater than 40% conversion to diol would be observed with the photoreducible o-alkyl ketones. It is noteworthy that recent workers have established the importance of intramolecular energy transfer as a key factor in inhibition of photoreductions. Several examples are known of "multi-phenyl" ketones which do not photoreduce: p-phenylbenzophenone[49], o-phenylbenzophenone[49], α-benzylacetophenone[49], p-(1-naphthylmethyl)benzophenone[50], and p-phenylacetophenone[51]. Ermolaev and Terenin performed a detailed comparison of the $\pi^* \longleftarrow n$ absorption spectrum and the phosphorescence emmission spectrum of p-phenylbenzophenone[52]. They concluded that the normal radical abstraction potential of the $\pi^* \longleftarrow n$ state was being diverted into a lower lying, non-radical abstracting $\pi^* \leftarrow \pi$ state characteristic of the aryl chromophoric system. Leermakers[50] demonstrated, by similar phosphorescence spectral analysis, that the absorbing carbonyl chromophore and the emitting aryl chromophore of a given ketone did not have to be in resonance conjugation. This theory has been embraced by other authors as an explanation for the lack of radical-like abstracting character in many other ketones.[53,54]

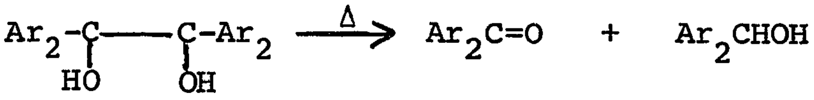
Since a variety of o-methylacetophenones apparently do photoreduce and photoenolize (although the evidence is by no means convincing), it is tempting to justify the anomalous behavior of 2-benzylacetophenone on the basis of the Ermolaev-Terenin theory. We shall discuss in a following section the inertness of 2-benzylacetophenone to photoenolization. Phosphorescence experiments would be required to establish the validity of the argument in this particular case.

In addition to the pinacolic products obtained from the photolysis of the o-methyl ketones, a careful search for monomeric reduction products (benzhydrols) was carried out. Studies on photopinacolization of benzophenone have concluded that reduction to hydrol is an extremely rare situation[4] and when it occurs, it can be attributed to thermal[55] or base-catalyzed cracking[56,57] of the diol. Remarkably small traces of base contamination can catalyze cleavage of pinacols to hydrol-ketone mixtures and the necessary experimental precautions to avoid this problem have been indicated.[58] The exact mechanistic origin of the hydrol is uncertain and some authors claim that, in the presence of base, it is a direct photoproduct[57] while others insist it arises in a non-photolytic step from the diol[56].

Other than utilization of anhydrous, reagent-grade chemicals, no special precautions were taken in this research to avoid traces of base contamination. Therefore, hydrol formation might be anticipated. After removal of the majority of pinacolic product from the photoreduction mixtures, the concentrated mother liquors were examined by infrared spectroscopy. They were found to contain intense hydroxyl absorptions (3250-3550 cm^{-1}) and ketonic absorptions characteristic of the starting methylbenzophenones (carbonyl at 1660 cm^{-1}). The hydroxyl O-H absorptions were of no value in establishing the presence or absence of hydrol because the related absorptions of pinacol occur in the same spectral region. Although, as stated before, pinacols are remarkably insoluble in the irradiation solvent, 2-propanol, they do dissolve in their corresponding benzophenone precursors and hence the mother liquors, rich in ketone, cannot be completely freed from diol.

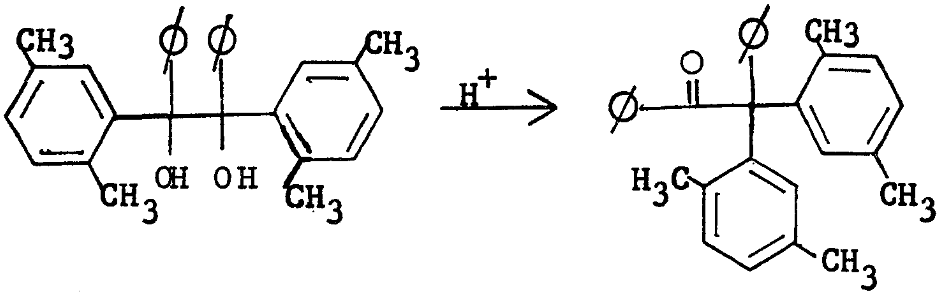
The authentic monohydric alcohols, i.e., 2,4-dimethyl- and 2,5-dimethylbenzhydrol were synthesized by lithium aluminum hydride reduction of the corresponding ketones. These hydrols were used as peak-enhancement standards in the gas chromatographic analysis of oily mother liquors from photoreductions. Although the mother liquors from every photoreduction so examined contained hydrol by vapor chromatographic separation, this method was found to be insufficient to establish the presence of hydrol.

Previous workers have clearly shown that thermal cracking[55] of pinacols produces hydrol-ketone mixtures. Authentic



$$\underset{HO}{Ar_2-C}-\underset{OH}{C-Ar_2} \xrightarrow{\Delta} Ar_2C{=}O \; + \; Ar_2CHOH$$

2,4-dimethyl- and 2,5-dimethylbenzpinacol were found to fragment in the gas chromatograph to ketone-hydrol mixtures. No pinacol escaped the column undecomposed. Alternative methods to establish the presence or absence of mono-reduction products appear necessary. In the infrared spectra of the 2,4-dimethylbenzhydrol and 2,5-dimethylbenzhydrol characteristic bands were observed at 1345 cm^{-1} which were completely lacking in the corresponding pinacols or ketones. Cross[59] points out that these absorptions can be attributed to C-O stretching modes in secondary carbinols. In the concentrated oily residues from photochemical reduction of 2,4-dimethyl- and 2,5-dimethylbenzophenones, no trace of this characteristic secondary alcohol absorption was present.



(47)

In addition, the nmr spectrum of authentic 2,4-dimethylbenzhydrol possessed the characteristic H-C-OH resonance at 5.62 ppm, in CCl_4 vs tetramethylsilane standard. No resonance absorption was found at this position in the photolysis residue from 2,4-dimethylbenzophenone.

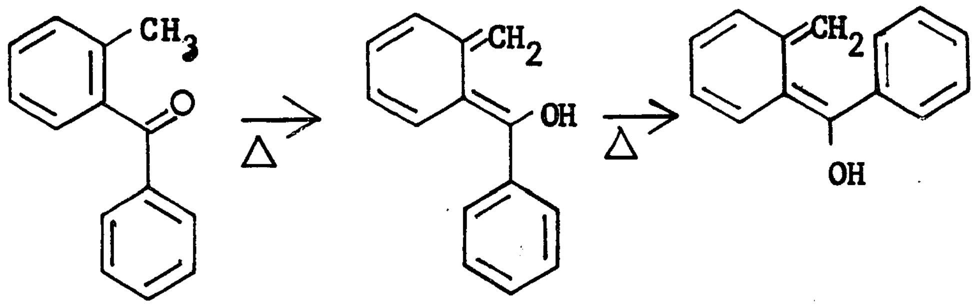
When a pinacolone rearrangement catalyzed by a trace of (p-toluenesulfonic acid) was carried out on the residue from a 2,5-dimethylbenzophenone photolysis, all the hydroxyl absorption that was formerly present in the infrared spectrum vanished. These results indicate that no monohydric reduction occurs during the photolysis of the 2-methylbenzophenones.

Attempted Photo-Elbs Reactions

The reaction which bears his name was discovered by Karl Elbs in 1884[60]. Experimentally it is carried out by heating an ortho-methylbenzophenone to approximately 400°C until the evolution of water ceases. Although in some cases large amounts of carbonized material are obtained the reaction often serves as a convenient synthesis of polycyclic aromatic hydrocarbons. The mechanism has never been fully elucidated but contributions have been made by several authors.

Fieser and Dietz[61] postulated that the ketone is converted to an intermediate 9,10-dihydro-9-anthranol. Earlier workers had demonstrated that 9,10-dihydro-9-anthranol was extremely unstable and dehydrated to anthracene spontaneously in air or with greater rapidity by warming in solution.[62]

Cook[63] elaborated on Fieser's mechanism by suggesting that the enol form of the original ketone was formed in a high energy thermal step and that this enol ring-closed to the dihydroanthranol. Product formation was completed by a tautomerism and dehydration. The mechanism is outlined below.



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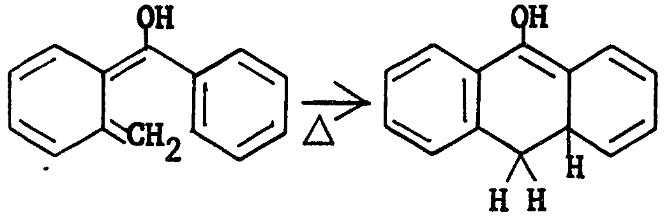

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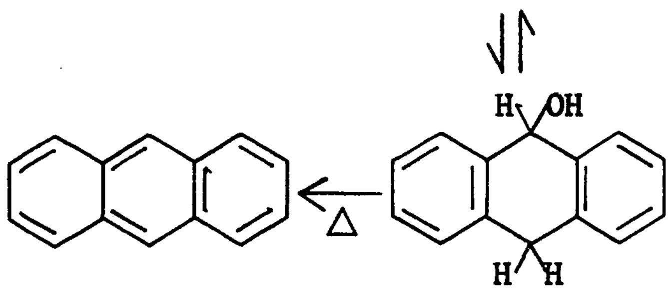
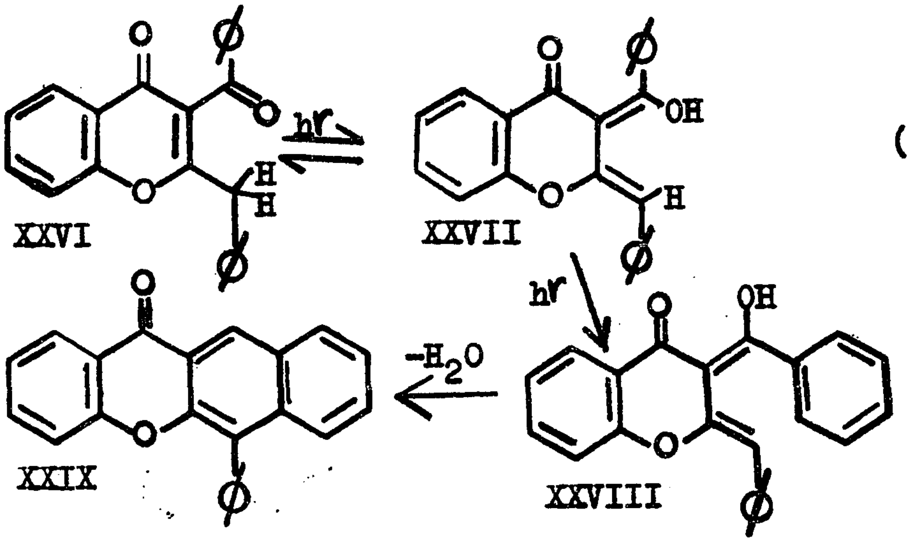


(50)

Since the phenomenon of photo-enol formation in this system has now been firmly established by Pitts (16) and Yang (17), it is plausible that if the enol were photochemically generated under thermally favorable conditions a spontaneous ring-closure might result. An apparatus was constructed in which the photolysis could be carried out in toluene solution in a jacketted cell through which live steam was being passed. Several of the methylbenzophenones - 2,2'-dimethyl-, 2,2'-dimethyl-4-methoxy- and 2,3'4-trimethylbenzophenone were exposed for 15 to 18 hours. The internal solution temperature throughout the photolysis was $90^{\circ}C$. No products were isolated and the reaction mixtures afforded a return of starting material.

The first example of a true photochemical Elbs reaction has recently appeared in print and the comments by the author on the reasons for its success are pertinent here.[64] Ullman claims the isolation of a 3.4% yield of the benzoxanthenone shown below. He was able to demonstrate

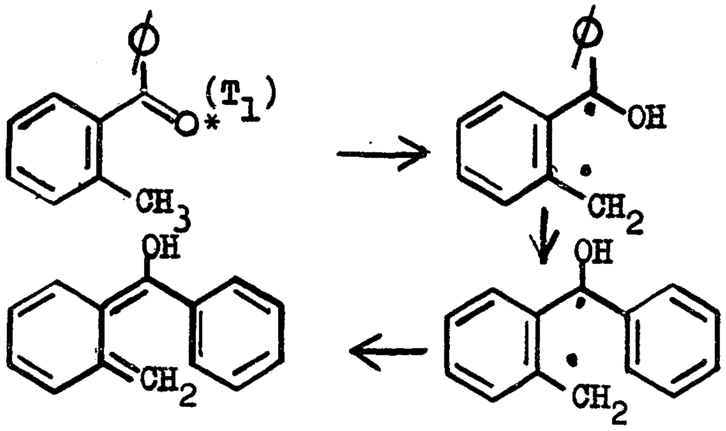


(51)

(52)

by spectral analysis and chelate-forming experiments with nickel acetate that the originally formed enol underwent double bond isomerism of the appropriate olefinic linkage. As he has indicated[65], the isomeric form in which the enol hydroxy is hydrogen bonded to the chromone carbonyl is a necessary species for Elbs-type ring closure. Only in this form is the second aryl ring properly oriented for cycle formation.

It is generally agreed that at the moment of internal hydrogen abstraction the photo-excited carbonyl must be oriented toward the adjacent alkyl seat bearing the proton, i.e., conformation XXVI shown above[64,32]. Ullman argued that it might not be necessary for a double bond isomerism to take place in the fully formed enol, XXVII. The thermal barrier to rotation about a double bond is rather variable, 25 to 65 kcal/mole, but most such conversions of systems like XXVII to XXVIII would be thermally unfavored.[66] Similarly, the kinetics of any photochemical isomerization (either sensitized or non-sensitized) of XXVII to XXVIII would be unlikely to compete with re-ketonization of these species[65]. Thus, since the enol precursor, at the instant of hydrogen atom abstraction, is more probably a



(53)

(54)

diradical, bond rotation might occur at this stage. This point remains unsettled. Nevertheless, Ullman has found long-lived enols of high steady-state concentration only in those cases in which a hydrogen-bonding acceptor (such as the chromone carbonyl) freezes a conformation. There is no reason to believe that the simple methylbenzophenones employed in this study would be capable of generating photoenol in this required ring-closure configuration, in the absence of a hydrogen bond acceptor at carbon #6.

Photoenolization: Intramolecular Hydrogen Abstraction

The deuterium exchange procedure employed to establish the enol as an intermediate by Yang[18] has come into general use by many other workers to demonstrate the existence of these transients.[67] It has been necessary to utilize it on several occasions in this work where normal trapping by the Diels-Alder technique was not feasible. The benzoylpyridine system forms a 1:2 adduct with acetylenedicarboxylate in a dark process and for this reason, the enol's presence was demonstrated by the deuterium exchange method.

Photolysis of 2-o-toluoylpyridine in deuteromethanol-d_1 for 0.5 hours resulted in a 30% decrease in the integrated intensity of the methyl resonance. The hydroxyl resonance from the trace of CH_3OH present in the medium increased by a similar amount. The results of this experiment established that this ketone does undergo intramolecular hydrogen abstraction upon excitation, a fact which "trapping" experiments were unable to prove. It is noteworthy that previous investigators[67] have reported 2-benzoylpyridine to be inert to photo-catalyzed hydrogen abstraction in alcoholic solvents. This example appears to be unique since other six-membered heterocyclic systems photopinacolize normally[68] but five-membered rings are usually inert to dimeric reduction.[54]

Since 2,6-dimethylbenzophenone was shown inert to photoreduction, the most plausible extention would be to evaluate its photoenolization potential. The ketone was sealed in an nmr tube as a 10% solution in deuteromethanol-d_1. Nmr spectra before exposure and after extensive irradiation by the 450 watt Hanovia lamp showed no deuterium incorporation. The methyl resonances of the ketones were unshifted and of calculated intensity relative to the aromatic proton integration. Several check runs of the experiment revealed the same result. Thus it appears that this ketonic system neither photoreduces nor enolizes. Steric inhibition of planarity of the carbonyl in the six-member transition state may inhibit the intramolecular abstraction while lack of planarity of the ketyl radical might equally justify the undetectable intermolecular hydrogen abstraction.

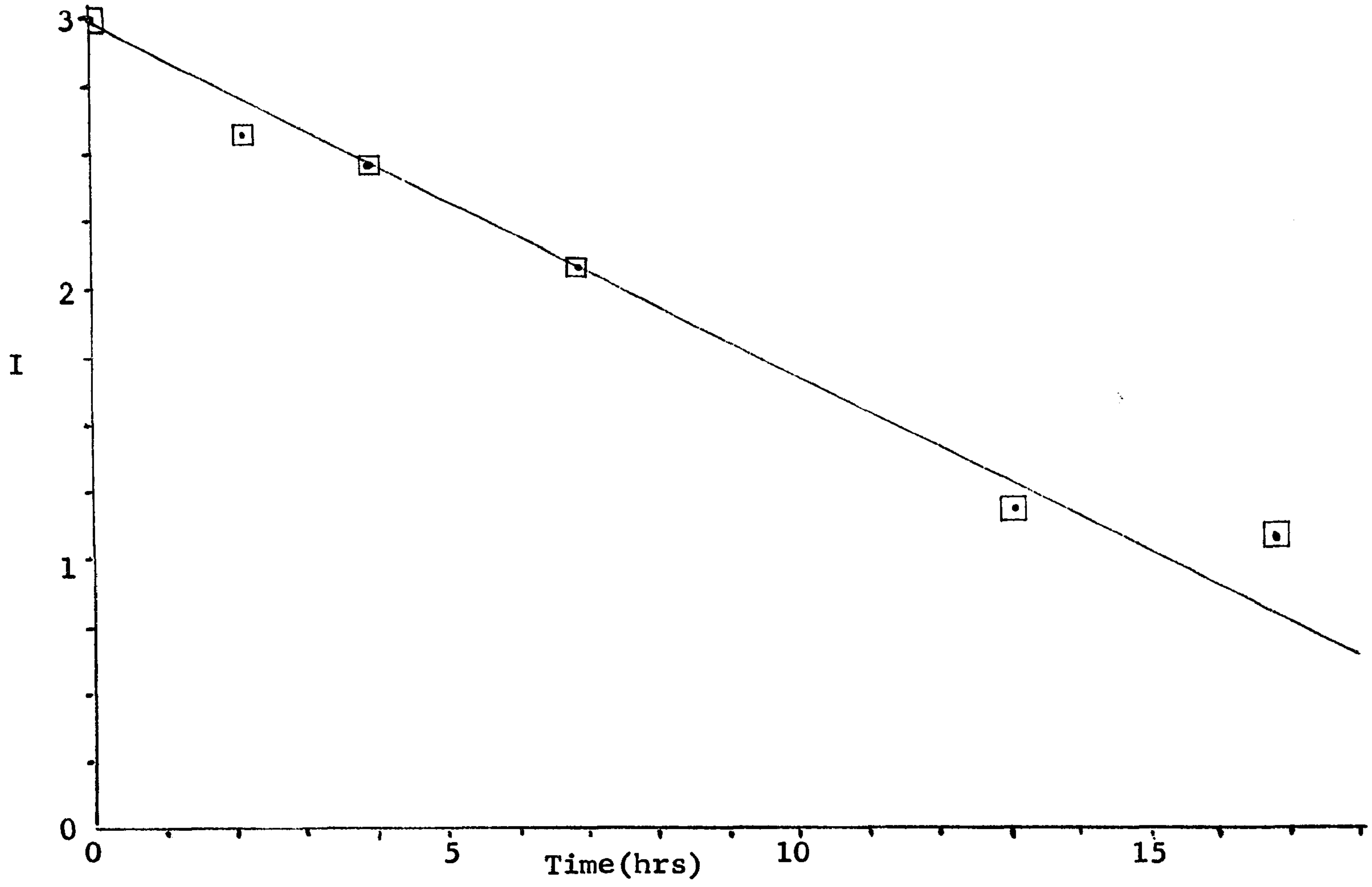
Although it has been demonstrated that 2,4-dimethylbenzophenone[19] photoenolized by trapping the enol in the Diels-Alder reaction, it has not been shown that many enolization events can occur in the same ketone. In fact, it is possible to establish that the deuterium exchange process can exhaustively deuterate the "ortho" methyl function. The experiment (irradiation in CH_3OD) did demonstrate quite convincingly that most of the CH_3- hydrogens were replaced by deuterium. The ortho-methyl resonances in the nmr spectrum diminished from an integrated value of 3.0 to 0.7 protons during the time of observation. Even more startling was the fact that the integrated intensity of the methyl resonance dropped linearly with exposure time (see Figure 1). These observations imply that the excited carbonyl distinguishes between a proton and a deuterion attached on the ortho-methyl position. This result is not inconsistent with the normal primary isotope effect (K_H/K_D ratio of 6.9/1) observed when hydrogen-carbon bonds are cleaved in the rate step of a mechanism.[69] Other workers have not studied the deuterium exhange process beyond the incorporation of D per methyl group.[17]

Dimethyl Acetylenedicarboxylate Method of Enol Trapping

A recent report by Yang[70] has claimed the detection of a photoenol species in the 2-benzylbenzophenone series by analysis of kinetic flash spectral data. Yang, although the originator of the two chemical methods of enol detection (deuterium exchange and Diels-Alder trapping), did not apply either technique to this system. If such a photoenol exists, in any significant steady-state concentration, it should be detectable by the chemical procedures.

FIGURE 1

PROTON INTEGRATION vs HOURS of PHOTOLYSIS



The irradiation of a substituted benzylbenzophenone, 2-(p-methylbenzyl)benzophenone, with dimethyl acetylenedicarboxylate in benzene resulted in complete recovery of unchanged ketone. The experiment was repeated several times under conditions in which 2-methylbenzophenone produced high yields of "trapped" adducts. Similarly, the exposure of 2-benzylacetophenone and dimethyl acetylenedicarboxylate resulted in no trace of the "trapped-enol".

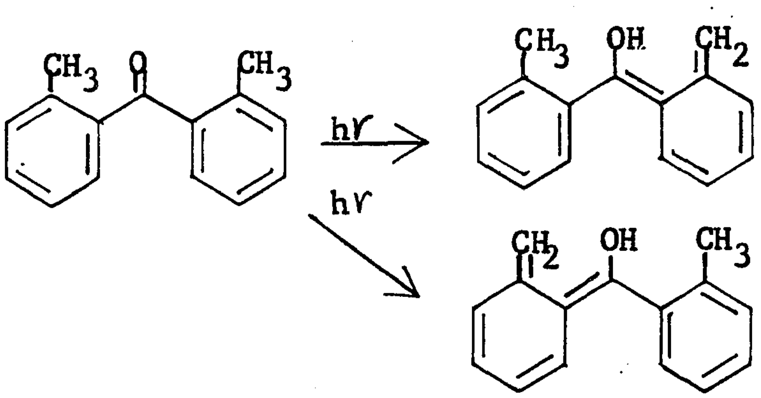
The essence of Yang's flash photolysis study of 2-benzylbenzophenone was the conclusion that a long-lived (rate constant for decay = 9.4×10^{-2} sec^{-1}) transient species was produced. No firm evidence for the enol structure was provided, no "trapping experiments" were performed, and no comparison was made with the flash spectrum of 2-methylbenzophenone known from chemical evidence to form a photoenol.

It is possible that Yang observed the intramolecular charge-transfer complex reported by Porter for benzophenone[71] instead of a photoenol. It is also possible that a benzyl photoenol reketonized at a rate faster than the trapping or deuterium exchange rates. It is apparent, however, that these benzyl ketones constitute a special class for they neither undergo photopinacolization nor detectable photoenolization.

Data from previous work on photoenols has demonstrated that the ortho-alkylbenzophenone system traps efficiently but not quantitatively with dimethyl acetylenedicarboxylate as a dienophile. For example, even such benzophenones as 2,3'-dimethylbenzophenone which yields a 40% conversion to 2,3-dicarbomethoxy-1,4-dihydrol-1-(3-methylphenyl)-1-naphthol when exposed with the acetylenic dienophile for 24 hours, cannot be driven to 100% product. Experimental difficulties in the isolation and purification of the often oily dihydronaphthols preclude intelligent comparisons from system to system.

No accurate quantum yield or kinetic measurements have been performed on the photoenol trapping process by any of the previous researchers. Little or nothing is known about what benzenoid substituents retard or encourage the enol trapping process. Too many experimental variables and isolation difficulties exist to attempt a kinetic study comparing the various possible ortho-methylbenzophenones with each other.

The most meaningful data regarding substituent effects on enolization should be available from an internal comparison. In a molecule like 2,2'-dimethylbenzophenone, two potential but equivalent ortho-methyl groups are available to serve as hydrogen atom donors to the excited carbonyl.



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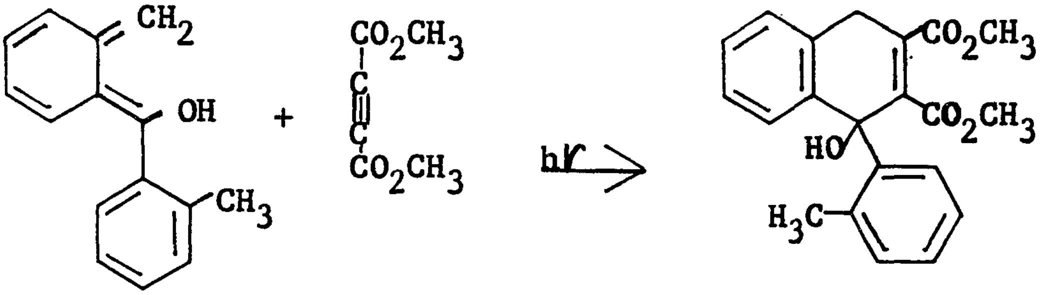
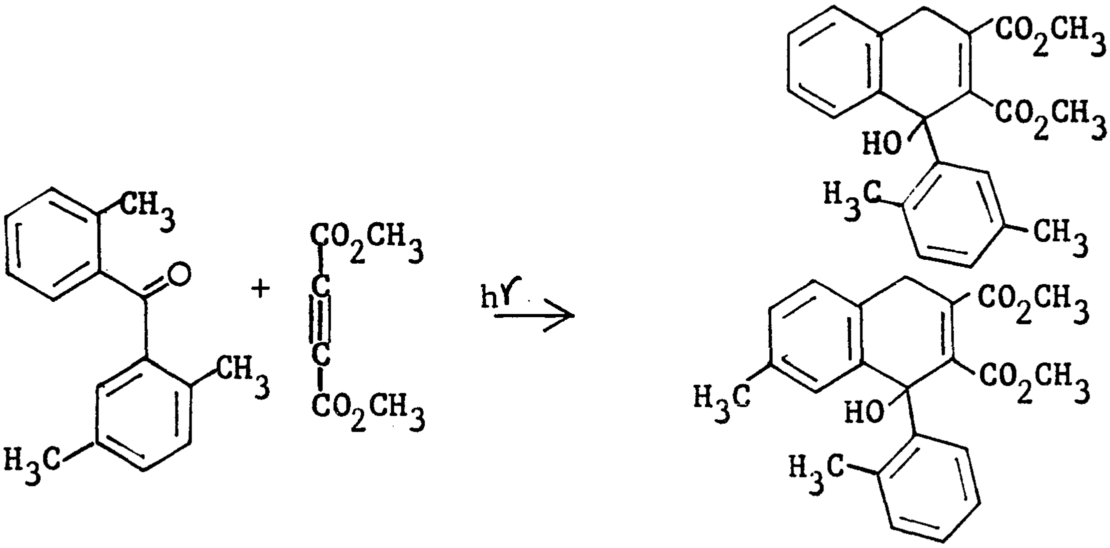
The intermediate dihydronaphthol which would be trapped in this situation would be the prototype of a family of potential trapped enol adducts from other non-symmetrical



(56)

2,2'-dimethylbenzophenones. When the experiment written in equation form above was carried out, a 61% yield of 2,3-dicarbomethoxy-1,4-dihydro-1-(2-methylphenyl)-1-naphthol was recovered and identified by conventional means (combustion and spectral analysis). Dissimilarities in the nmr spectrum of this trapped adduct, compared to those from 2-methyl, 2,4-dimethyl-, and 2,5-dimethylbenzophenone, were quite marked. One of the ester methoxy groups was shifted some 0.21 ppm up field to 3.42 ppm compared to trapped adducts in which the 1-aryl group did not contain an ortho-methyl. The ortho-methyl itself was shifted upfield (to 1.75 ppm) compared to the resonances for the naphthalene ring methyls in trapped adducts of 2,4- and 2,5-dimethylbenzophenone. These shifts may reflect steric changes in the methyl environments which partially remove the CH_3 groups from the deshielding region of the aryl rings.

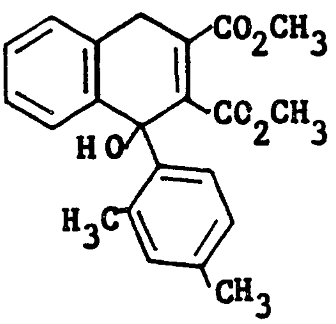
These spectral shift differences were encouraging in that they might indicate that the two different trapped adducts arising from a species such as 2,2'5'-trimethylbenzophenone, might be distinguishable. If the trapped



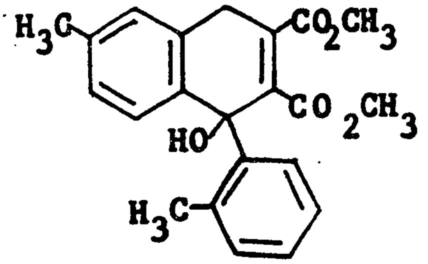
(57)

enols could be distinguished by nmr then conclusions about the relative enolization into the two non-equivalent benzenoid rings might be drawn.

An attempt was made to synthesize the desired 2,2'5'-trimethylbenzophenone by Friedel-Crafts acylation of 2-methylbenzoyl chloride onto p-xylene. Under the reaction conditions selected, the aluminum chloride apparently catalyzed methyl group migration because two inseparable trimethylbenzophenones (VPC) were obtained. The Friedel-Crafts reaction of 2-methylbenzoyl chloride and meta-xylene was somewhat more successful and produced cleanly one product, 2,2'4'-trimethylbenzophenone. This ketone was exposed in the presence of an equimolar quantity of dimethyl acetylenedicarboxylate and the product isolated. Thin layer chromatography showed that it was a mixture of two materials. Elemental analysis confirmed that an isomeric mixture was in hand, but unfortunately the composite nmr was not sufficiently unique to assay the product mixture by this technique.



XXIX



XXX

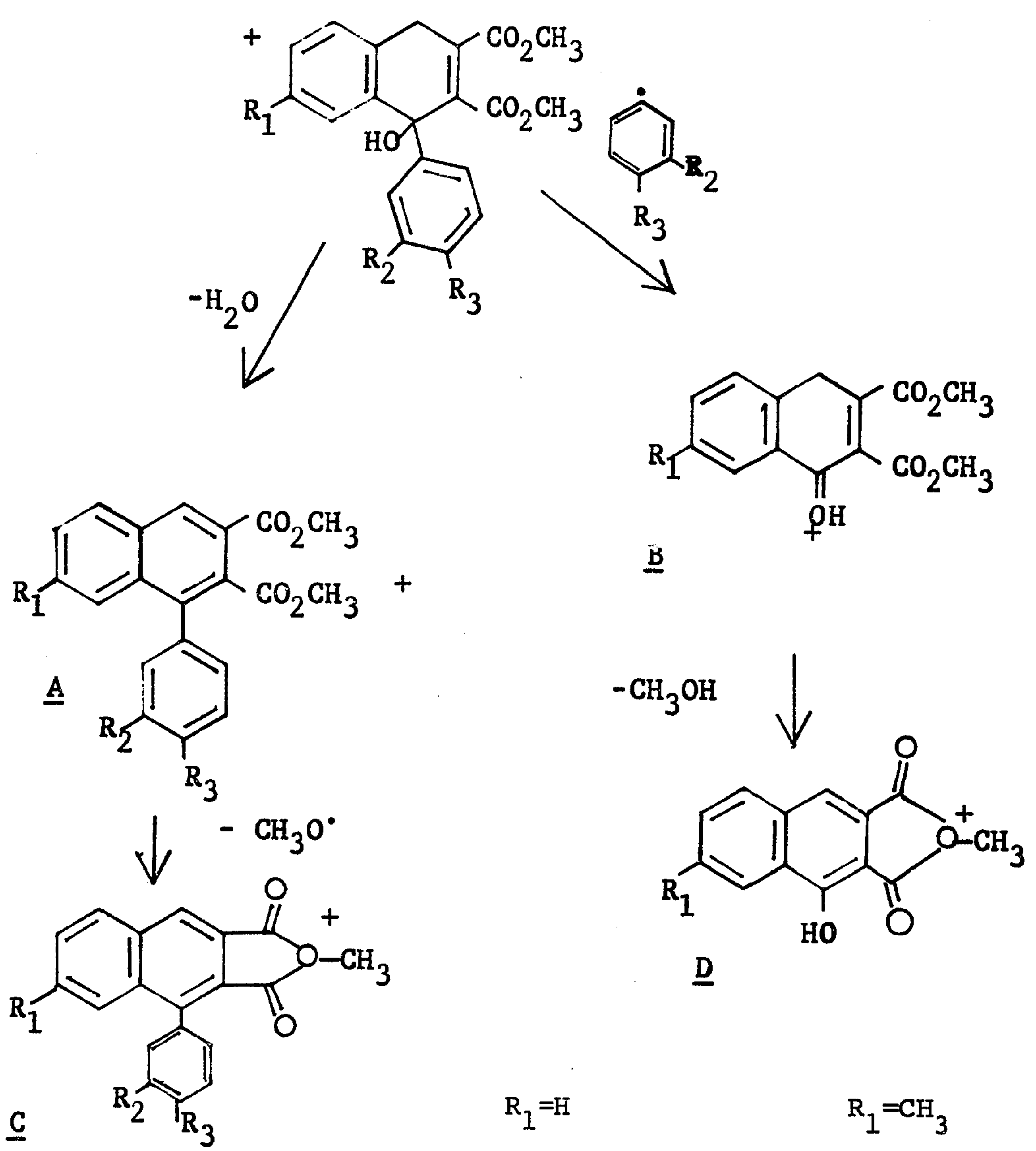
For this reason it was decided to resort to mass spectroscopy as a method for analyzing the components of this mixture. Four pure dihydronaphthols were introduced into the ion chamber of the Perkin-Elmer Hitachi RMU-6E Mass Spectrometer by use of the direct solids inlet port.

Singularly unique cracking patterns were obtained which were analyzed in detail for the high mass fragments. The mass spectra permitted the classification of the trapped photoenol adducts into two families. Class 1, those dihydronaphthols in which the aryl moiety at C_1 does not possess an ortho-methyl, display characteristic peaks at P-18, P-49 (base peak), P-Aryl, and P-(Ar + CH_3OH). Table 3 shows the fragmentation pattern for these high mass units in Class 1 compounds. See Table 3.

If the aryl ring on C_1 of the dihydronaphthol possessed an ortho-methyl, a second type of cracking sequence, Class 2, was observed. Thus the fragmentation of 2,3-dicarbomethoxy-1,4-dihydro-1-(2-methylphenyl)-1-naphthol was distinguished in several ways. Main peaks were found at P-18, P-50, P-91 and P-109. Table 4 illustrates the cracking pattern of Class 2. See Table 4.

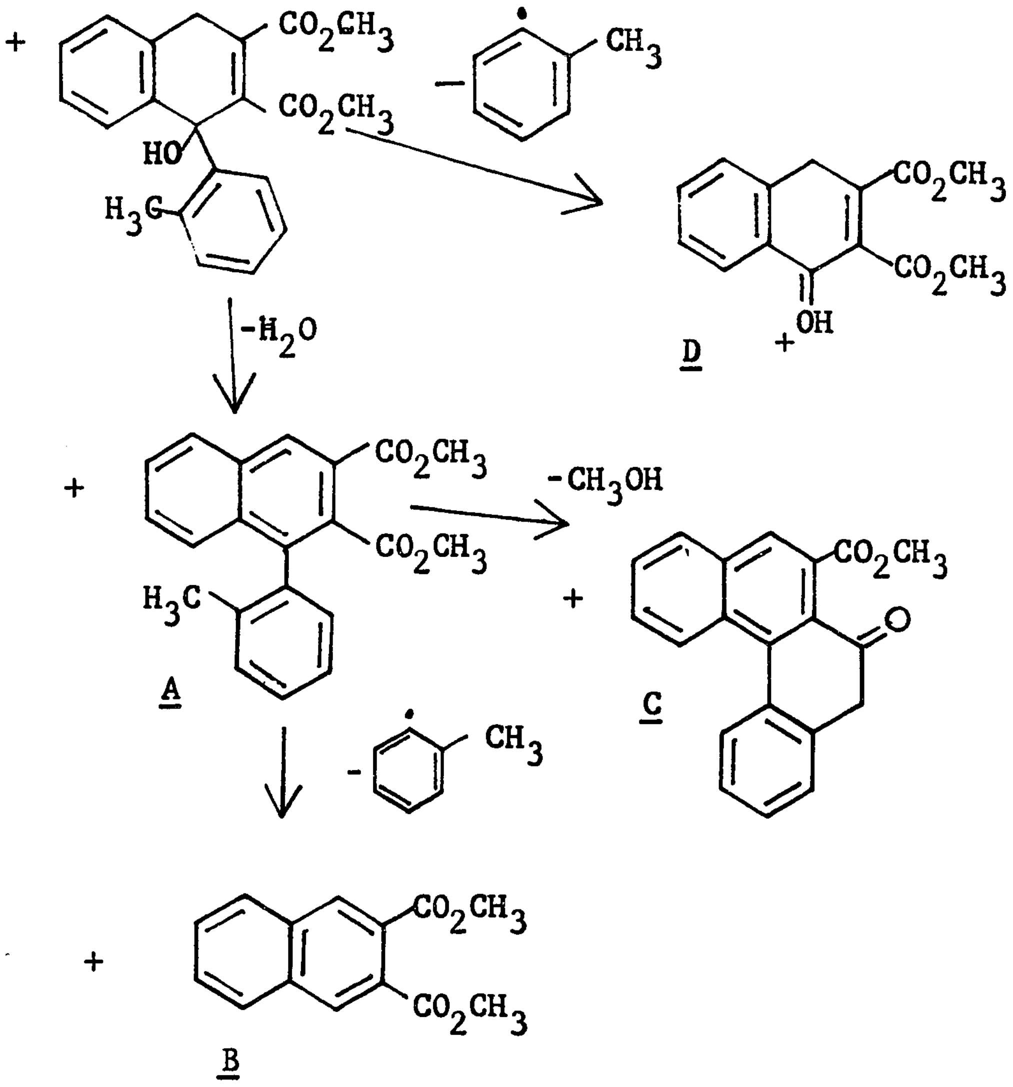
Considering that the base peak is now P-50 (i.e., loss of water + methanol) and not P-49 (water + methoxide) as observed in Class 1, there is already a clear distinction in the two types of naphthols. Furthermore, the direct loss of the aryl ring, P-Ar (or P-91) was a very minor fragment of intensity 5.7%, in this system but the P-109 (i.e., Parent losing aryl and water) is significant. This combination peak represents the only accurately measurable fragment in which the loss of the aryl ring can be monitored and compared

Table 3: Fragmentation Patterns for Class 1



Ion	R_1=R_2=R_3+H		R_1=H R_2=R_3=CH_3		R_1=CH_3 R_2=R_3=H	
	Mass m/e	Intensity	Mass m/e	Intensity	Mass m/e	Intensity
Parent	338		366		352	
A	320	87%	348	100%	334	40%
B	289	100%	317	87%	303	100%
C	261	98%	261	39%	275	57%
D	229	71%	229	54%	243	89%

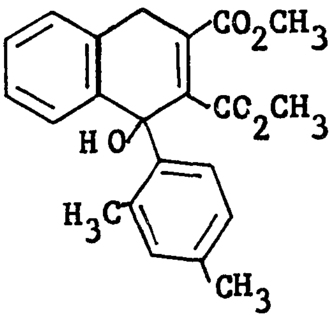
Table 4: Fragmentation Pattern for Class 2



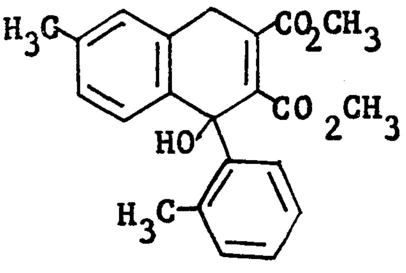
Ion	Mass	Intensity
Parent	352	
A	334	33%
B	243	23%
C	302	100%
D	261	6%

for structures XXIX and XXX which are the two isomeric trapped enols. The integrated P-109 (i.e., loss of water and aryl in structure XXX) and the integrated P-123 (i.e., loss of water and aryl in structure XXIX) were compared to provide an approximate measure of the two components in the dihydronaphthol mixture. The total intensity of these two peaks (using the base peak of P-50 as standard) was 24.5%. The P-123 contributed 19% to this total while the P-109 contributed 81%. Table 5 shows the masses and intensities of the major peaks of this mixture.

The mass spectral analysis of the mixed dihydronaphthols indicates that the enol form XXIX shown below is trapped to the extent of 20% while form XXX comprises the majority



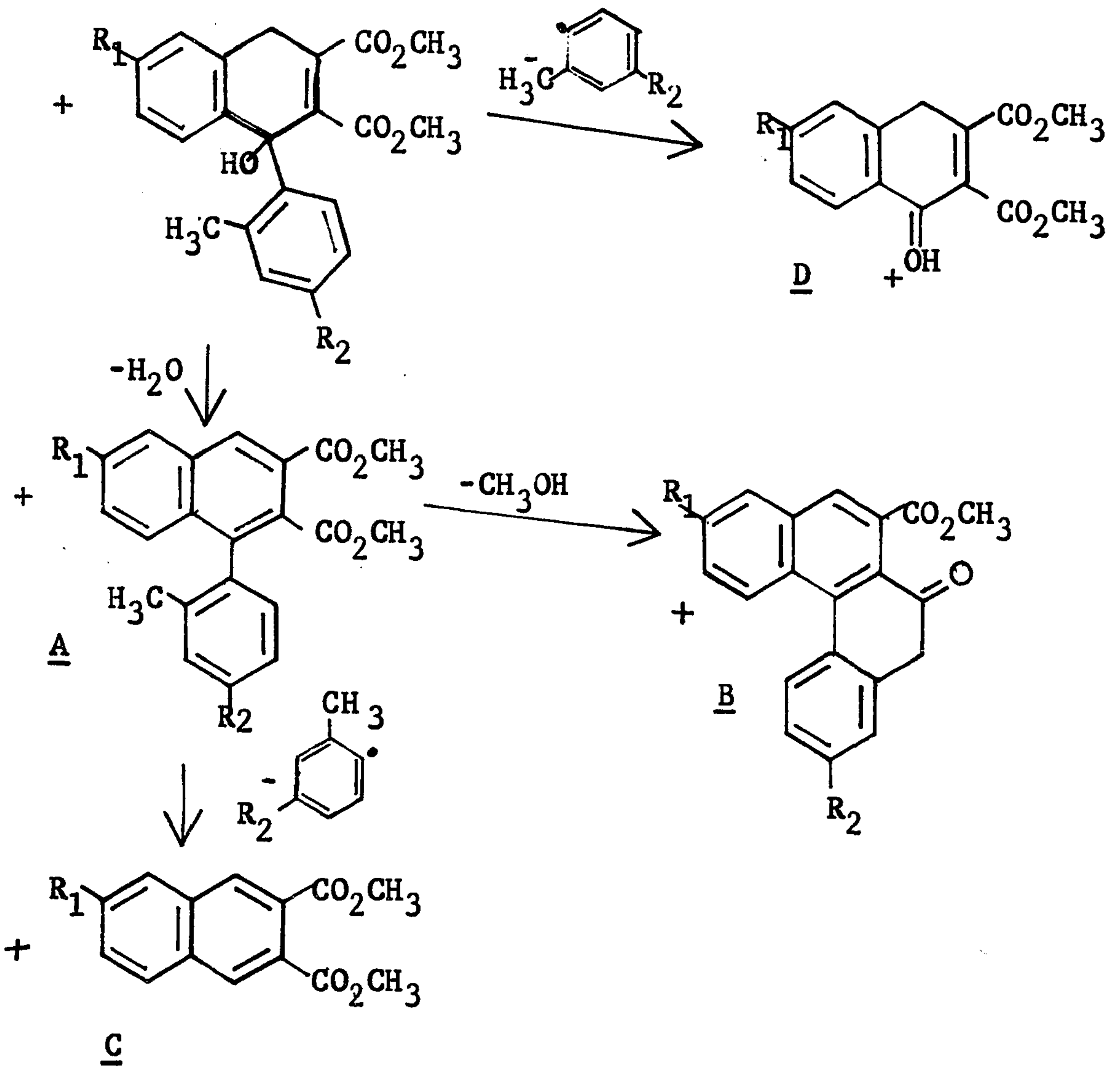
XXIX



XXX

(80%) of the product balance. One possible explanation for the higher percentage of product arising from XXX would be the greater reactivity of dienic systems substituted with electron donor substituents. It has been noted that the reactivity of a diene increases with alkyl substitution[72],

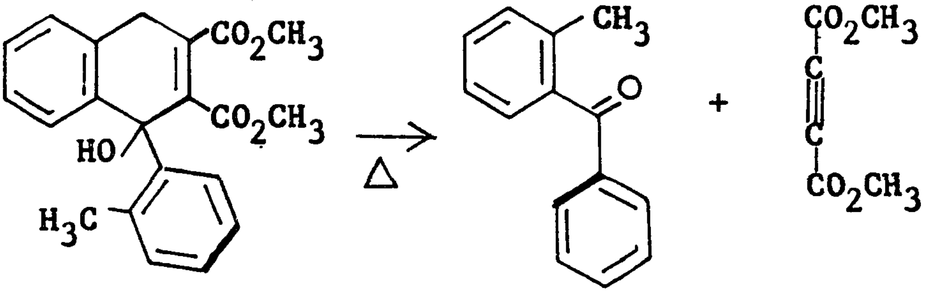
Table 5: Fragmentation for 2,3-Dicarbomethoxy-1,4-dihydro-1-(2,4-dimethylphenyl)-1-naphthol and 2,3-Dicarbomethoxy-1,4-dihydro-6-methyl-(2-methylphenyl)-1-naphthol



	$R_1=CH_3, R_2=H$		$R_1=H, R_2=CH_3$	
Ion	Mass	Intensity	Mass	Intensity
Parent	366		366	
A	348	35%	348	35%
B	316	100%	316	100%
C	257	20%	243	4.6%
D	275	1.7%	261	2.5%

or electron donors in general, as long as this substitution does not contribute to steric interactions in the six-membered transition state. Since enol formation is reversible[19], but dihydronaphthol formation is not, and since no apparent structural basis exists to expect greater enolization into one of the aryl rings than the other, the product explanation should rest in the greater reactivity of one enol compared to the other.

Mixed irradiations of a Diels-Alder photo-adduct (for example one derived from 2-methylbenzophenone and dimethyl acetylenedicarboxylate) in the presence of another benzophenone, 2,2'-dimethylbenzophenone, provided an interesting reflection of the stability of the photo-adducts. In the event that the photo-Diels-Alder reaction displayed the same reversibility often ascribed to the non-photo counterpart, it would be expected that the liberated dimethyl acetylenedicarboxylate would be trapped by the foreign ketone to produce a new photo-dihydronaphthol. The nmr spectra of these adducts are sufficiently characteristic that the reaction progress could be monitored by nmr.



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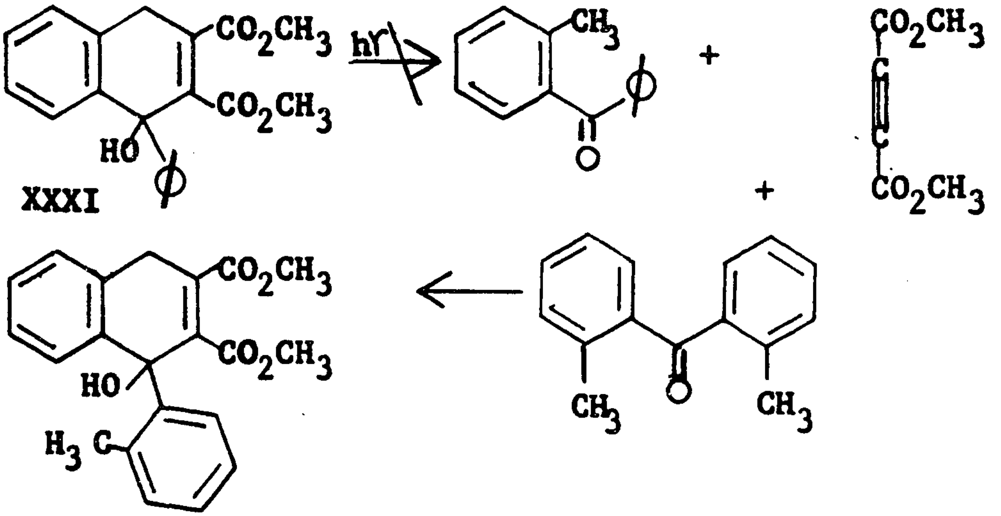
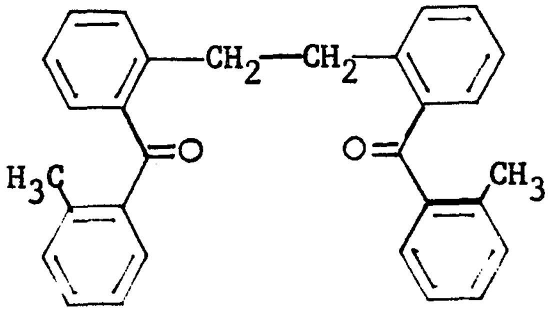
No evidence of photo-Diels-Alder reversal was observed. After more than 70 hours of irradiation in benzene or d_6-benzene solvent, the intial photo-adduct showed no diminution



(59)

in concentration but the added ketone had been depleted to less than 20% of its initial concentration. The photolability of o-alkylketones in benzene has already been commented upon and two primary pathways are open. They are known to be capable of photoreduction by H atom abstraction from benzene[73] or, if traces of phenolic-like -OH materials are present, they can produce coupling products with bibenzyl structures.[33]



Although the nmr peaks of the initial photoadduct XXXI remained at the identical chemical shift position and in indentical intensities both before and after 70 hours of exposure, the o-methyl groups of the ketone, 2,2'-dimethylbenzophenone shifted upfield by 0.35 ppm. This shift corresponds exactly to that observed in converting o-methyl ketones to their corresponding pinacols. Not all of the photolytic transformation of the added ketone could be explained by photoreduction to the pinacol. Integration of the newly created methyl signals revealed that about 50% of the o-methylbenzophenone suffered another photochemical fate. Downfield complex absorptions corresponded to the expected bibenzyl resonances in the o-methyl coupling product. Indeed, as Becker[33] has demonstrated, the bibenzyl-like coupling occurs to the same degree as pinacolic reduction in order to provide a stoichiometric accounting for the rearranged hydrogen atoms.

The major demonstration of two such experiments with different sets of substitutents, in which a photo-adduct was exposed in the presence of a foreign ketone, was the photostability of the Diels-Alder adducts. The photolytic instability of the added o-methyl ketones is not at all surprising and the general work of this thesis documents the multitude of photolysis pathways open to these materials. Subsequent irradiation of 2,2'-dimethylbenzophenone in d_6 benzene without any adduct added revealed no new peaks or diminution of the original peak after 12 hours. Under similar conditions without the presence of adduct, the previously described reaction does not proceed.

Competitive Photoenol-Photoreduction Irradiations

Yang[17] has reported that the quantum yield, Φ , for photoenol trapping, was 0.5 in the ortho-methylbenzophenone system. The quantum yield for bimolecular photoreduction of 2,4-dimethylbenzophenone as measured in this work was approximately 0.03. In a stoichiometric situation where 2,4-dimethylbenzophenone could undergo both photoreduction and photoenol trapping, it would be expected that the enol trapping process would predominate.

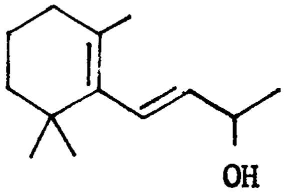
The irradiation of exactly equimolar quantities of 2,4-dimethylbenzophenone, 2-propanol, and dimethyl acetylenedicarboxylate in a benzene medium produced a 78% conversion to 2,3-dicarbomethoxy-1,4-dihydro-6-methyl-1-phenyl-1-naphthol. No trace of pinacolic product was observed in the mother liquors.

If instead of equimolar quantity, the 2-propanol was present in vast excess (as solvent), then the molecular probability of collision of an activated 2,4-dimethylbenzophenone with a hydrogen donor greatly exceeds the probability of collision with the dienophile. In this experiment, the sole photolysis product was a 30% conversion to the pinacol with no trace of the expected naphthol.

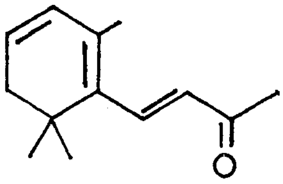
A 0.05 M solution in 2,4-dimethylbenzophenone and dimethyl acetylenedicarboxylate dissolved in 1:1 benzene: 2-propanol produced a mixture of trapped enol and pinacol on 24 hour photolysis. A 13% yield of 2,4-dimethylbenzpinacol and a 17% yield of 2,3-dicarbomethoxy-1,4-dihydro-6-methyl-1-phenyl-1-naphthol were isolated. It was readily apparent that variation of the relative concentrations of dienophile and hydrogen donor, with respect to the methylbenzophenone, can adjust the product composition. It is also apparent that the photoenol trapping was a much more efficient process than photoreduction.

Photo-oxidations of 2-Alkylbenzophenones

Schenck[34] has reported the trapping of certain dienic systems by photoexcited oxygen which had been sensitized by energy transfer from long-wavelength absorbing dyes. Katsumura[74] observed a similar oxidation of β-ionol XXXII and dehydro-β-ionone XXXIII upon exposure in the presence of oxygen. He established that the reaction could take place with or without sensitization of the oxygen.



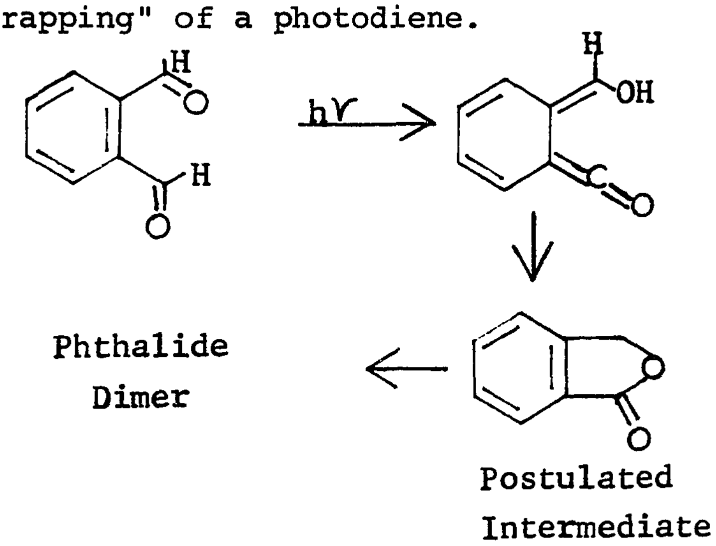
XXXII



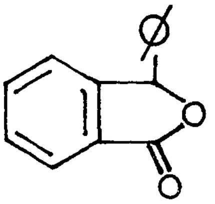
XXXIII

The furan system, whose photooxidation was initially studied by Schenck[34], has been established to form peroxide products merely by standing in air. In all these previous examples, however, the diene was initially present in the medium and was not generated *in situ* as is the case for the photoenolic compounds.

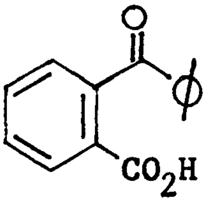
At the inception of this project the literature was devoid of any reports in which a photochemically generated diene of an o-methylbenzophenone was trapped by molecular oxygen. One largely overlooked report by Schonberg[21] in 1955, records the photolysis of o-phthaldehyde into phthalide derived products. As was later indicated by contemporary researchers, this probably represents the "intramolecular trapping" of a photodiene.



The photolysis for 9 hours of 2-methylbenzophenone in benzene solution which was continuously saturated with air led to formation of two unexpected oxidation products. It was anticipated that the anthrene claimed by Ullman as an oxidation product of the enol would be the major component, but nmr, ir, and mass spectral analyses indicated the major isolated product to be 3-phenylphthalide (6.1%).



XXXIV

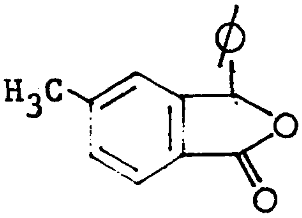


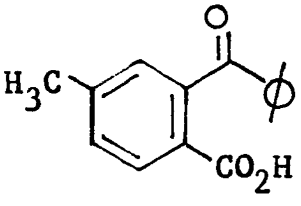
XXXV

The nmr spectrum of this component of the reaction mixture revealed a sharp resonance at 6.41 ppm integrating for a unit proton. All other resonances (relative area = 9H) were found in the aromatic region δ 7.2-8.0 ppm. The mass spectrum revealed a molecular ion at M/e 210 which corresponded to the molecular formula of $C_{14}H_{10}O_2$. The zinc dust-acetic acid reduction of o-benzoylbenzoic acid by a published technique[75] provided an authentic sample of the phthalide. It was identical in all respects to the reaction product.

Extraction of the reaction mixture with sodium bicarbonate solution yielded an acidic compound (5.8%) which was subsequently established as o-benzoylbenzoic acid. The ir spectrum was superimposable on that of an authentic sample.

The generality of these results was confirmed when the irradiation of 2,5-dimethylbenzophenone under the same aerated conditions yielded 5-methyl-3-phenylphthalide and 2-benzoyl-4-methylbenzoic acid. The photoreaction components were readily identified in mixtures by characteristic infrared absorptions which each possessed. For example, the phthalides displayed high frequency carbonyls at 1750 cm^{-1} in the solid state and 1765-1780 cm^{-1} in CCl_4 solution. The unreacted 2-methylbenzophenones were distinguished by the ketonic carbonyl at 1660 cm^{-1} and the intermediate oxidation products, 2-benzoylbenzaldehydes, were characterized by the aldehydic C=O at 1700 cm^{-1}. Once these assignments were made on pure, independently synthesized sample, they served as fingerprints to detect the reaction products in mixtures.


XXXVI

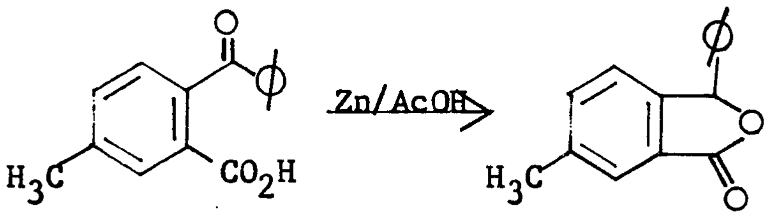

XXXVII

A solution of 2,5-dimethylbenzophenone in benzene was photolyzed in an air stream for 24 hours. Although a resinous material coated the walls of the irradiation vessel a clear supernatant benzene phase was isolated. The concentrated benzene layer was extracted with bicarbonate and an 8% yield of 2-benzoyl-4-methylbenzoic acid was isolated by neutralization. The non-acidic portion was a complex mixture of high boiling carbonyl containing compounds which could not be separated by distillation or gas phase chromatography.

When the experiment was repeated for three hours of aeration-irradiation a 2.5% conversion to acidic product was obtained. The oily residue after removal of acid could be separated into a tacky resinous material which was hexane insoluble and 1.2 g of product whose ir revealed it to be a mixture of the phthalide, benzoylbenzaldehyde, and starting ketone. This portion of the reaction product was exposed in the absence of air and examined spectrally at six hour intervals. After 18 hours, the characteristic aldehydic CO had disappeared and 0.45 g, 12% based on starting ketone, of 5-methyl-3-phenylphthalide were obtained.

It is interesting to note that no phthalide could be isolated by the continuous 24 hour aeration-irradiation of the 2,5-dimethylbenzophenone. The short aeration followed by prolonged non-oxidative irradiation provided the best conversion to phthalide. These results are in keeping with the observations of Schönberg[21] who found that the parent phthalide (from o-phthaldehyde) gave higher molecular weight condensation products when oxidized in air. Brief aeration apparently gives the corresponding intermediate 2-benzoylbenzaldehyde which, as will be shown later, is converted to the phthalide in a non-oxidative irradiation.

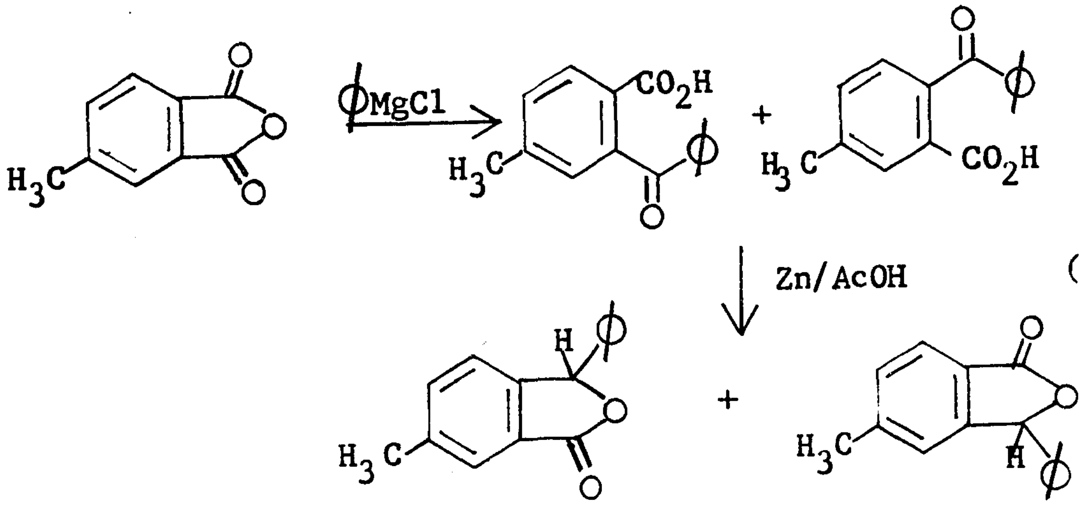
Photolysis in air for 9.5 hours of 2,4-dimethylbenzophenone yielded no phthalide but did provide a conversion to 45% of the 2-benzoyl-5-methylbenzoic acid. Proof of oxidation at the ortho-methyl site was provided when zinc dust reduction converted the product to the corresponding



(61)

3-phenyl-6-methylphthalide.

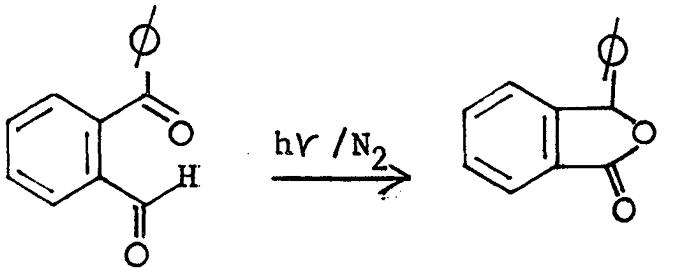
The phthalide products derived from 2,4-dimethyl- and 2,5-dimethylbenzophenone were firmly established in structure by one independent synthesis which gave rise to both components. The phenylmagnesium chloride ring opening of 4-methylphthalic anhydride produced the two isomeric 2-benzoylbenzoic acids.



(62)

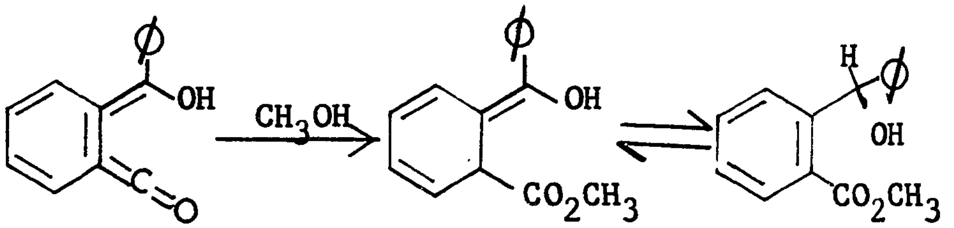
This acid mixture was reduced by the zinc-acetic acid method and gave the isomeric 3-phenyl-5-methylphthalide and 3-phenyl-6-methylphthalides. The phthalide isomers could be laboriously separated on thin layer chromatography with the indication that a simple two component mixture existed. Combustion analysis was in agreement with the expected values and the nmr spectrum of the mixture was superimposable on a composite spectrum of the two phthalides derived from the dimethylated benzophenones.

From photolysis experiments with o-phthaldehyde, Cohen[20] showed that the optimum conditions for generation of phthalide involved exposure in an acetic acid solution containing trace quantities of hydrochloric acid. When 2-benzoylbenzaldehyde, the proposed intermediate in formation of 3-phenylphthalide, was irradiated for 18 hours in acetic acid containing 1% of concentrated hydrochloric acid, a virtually quantitative yield of the 3-phenylphthalide was obtained. Oxygen was rigorously excluded from this photolysis clearly demonstrating that the aldehyde-to-phthaldehyde step was non-oxidative.



(63)

At equivalent concentration and exposure time in methanol solution, the 2-benzoylbenzaldehyde was converted to its phthalide with only 68% efficiency. An appreciable recovery (28%) of the unreacted aldehyde was possible. Since previous workers on the phthalaldehyde photolysis have postulated a ketene intermediate[20], it was of interest to explore the interception of this proposed ketene by alcohol. In the methanol solvent experiment involving 2-benzoylbenzaldehyde, none of the desired methyl 2-hydroxybenzylbenzoate was isolated or detected spectroscopically.



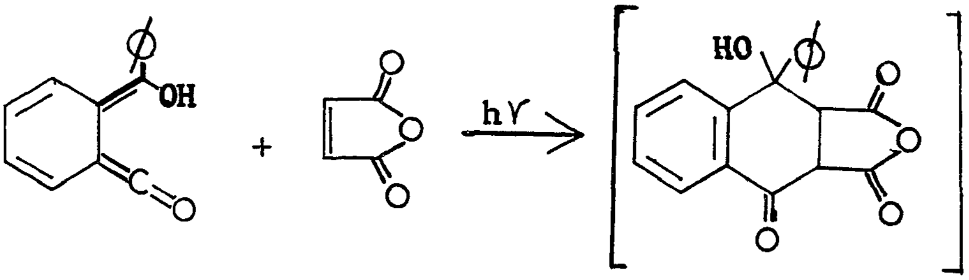
(64)

If this γ-hydroxy ester had been formed it would have added additional support to the proposed ketene transient. However, the failure to find such a hydroxy ester does not rule out the ketene formation. It has been shown that γ-hydroxy esters readily undergo intramolecular esterification to lactones[76] (in this case a phthalide). A similar experiment by Pappas[28] in which he tried to trap the proposed ketene of o-phthalaldehyde with methanol was also unsuccessful.

None of the photochemical runs carried out in the absence of oxygen produced the benzoylbenzoic acids. However, when 2-benzoylbenzaldehyde in benzene was exposed for 18 hours in an oxygen stream it produced 34% of 2-benzoylbenzoic acid and 29% 3-phenylphthalide. The acid thus arises in an oxidative step from the aldehyde.

In order to establish whether the aldehyde-to-acid oxidation was a photochemical or non-photochemical process, the 2-benzoylbenzaldehyde was reacted in a "dark-reaction" with oxygen. Under concentration and time conditions which approximated the photolytic procedure, no trace of 2-benzoylbenzoic acid was obtained. The pure 2-benzoylbenzaldehyde could be recovered unchanged.

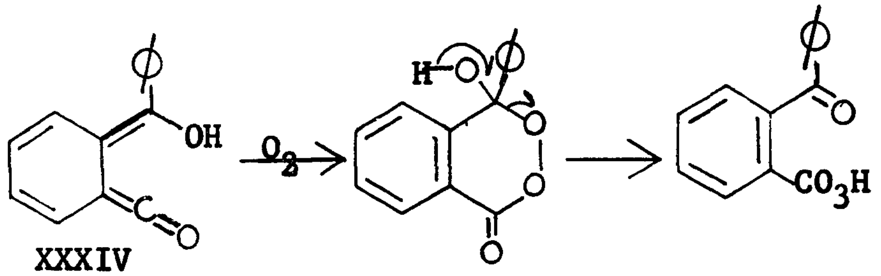
The intermediacy of the ketene in these photooxidation reactions of the 2-methylbenzophenone or 2-benzoylbenzaldehyde being converted to phthalide, rests on firm experimental grounds. One report[20] has appeared stating that the dienic ketene (from o-phthalaldehyde) has been trapped by a dienophile



(65)

although, in fact, another worker disputes this claim[28]. Furthermore, even though the proposed ketene could not be intercepted with alcohols, the very fact that its transformation to phthalide proceeds with greater rapidity in polar or protonic media provides support for its intermediacy. It has been established that hydroxyl additions to ketenes are accelerated by polar solvents or proton donors.[77] Phthalide formation would require an intramolecular -OH to ketene addition.

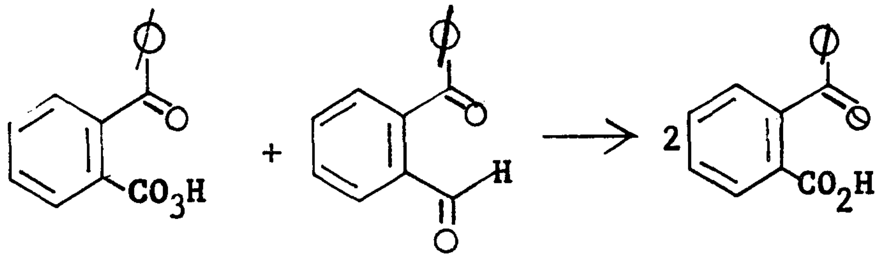
A plausible mechanism which can account for the formation of the acid product would be the oxygen trapping of this ketene enol XXXIV in the same fashion as Schenck[34] has proposed for the formation of cyclic peroxides from dienes.



XXXIV

(66)

Oxidation of another molecule of 2-benzoylbenzaldehyde by this proposed peracid would represent an efficient path for conversion of the initial aldehyde to the benzoylbenzoic acid.[78]



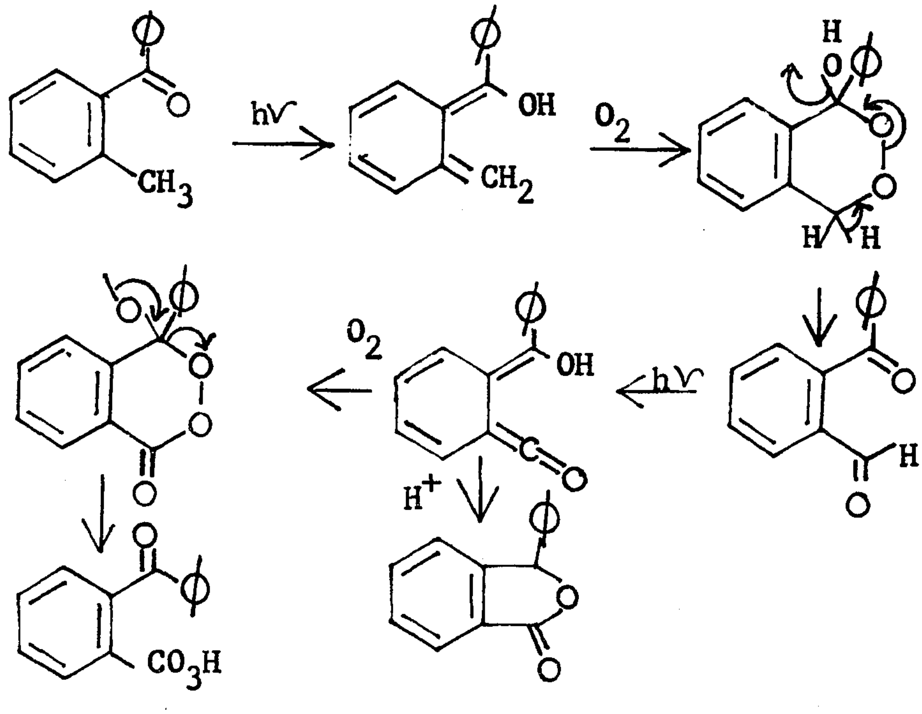
(67)

Although the results of the "dark-reaction" oxidation indicate that non-photolytic oxidation of aldehyde-to-acid was not sufficiently rapid to account for the acid observed in photooxidations, another acid-forming mechanism is possible. It has been established[79] that the direct photooxidation of

$$\mathrm{ArCHO} + \mathrm{O_2} \xrightarrow{h\nu} (\mathrm{ArCO_3H}) \xrightarrow{\mathrm{ArCHO}} 2\mathrm{ArCO_2H} \quad (68)$$

benzaldehyde to benzoic acid can be light promoted. Thus it is not necessary to invoke the ketene enol intermediate as a precursor of the acid.

The ketene enol, however, was also attractive because its presence would also justify the phthalide formation. A cyclic peroxide, similar to that postulated from ketene enol, has been isolated by Yates[27] as a product of the photooxidation of 2,5-dimethylacetophenone. Thus the total mechanism for conversion of 2-methylbenzophenones to phthalides and acids might reasonably involve two enolization and two oxygen-trapping steps as follows.



The intermediate 2-benzoylbenzaldehyde was not isolated from the photolysis of the initial methylbenzophenone but it could be detected spectrally. The fact that this ketoaldehyde, independently synthesized and reintroduced into the reaction mixture, photolyzed to the same products, adds support to the suggested mechanism.

Experimental Section

Melting points were determined in Kimax capillary tubes employing a "Mel-temp apparatus (Laboratory Devices, Box 68, Cambridge, Mass.) and are uncorrected. Boiling points are also uncorrected.

Infrared spectra were determined either between sodium chloride plates as a Nujol mull, neat, or as potassium bromide pellets on a Perkin Elmer 257 spectrophotometer.

Nmr spectra were determined on a Varian A-60 spectrometer with tetramethylsilane as an internal standard. Data were presented in the order δ (multiplicity, number of protons, assignment) using tetramethylsilane as 0.00 ppm δ .

Microanalysis was performed by the late Dr. V. B. Fish of Lehigh University and Dr. G. I. Robertson of Florham Park, New Jersey.

Gas phase chromatography was carried out using a Hewlett Packard 700 Laboratory Chromatograph equipped with a thermal conductivity detector and a Hewlett Parkard Model 240 temperature programmer. The column employed was a six-foot one-eight inch tube packed with Union Carbide W98 substrate on 80-100 mesh Chromasorb S. High purity helium was used as the carrier gas.

Mass spectra were run on a Hitachi-Perkin Elmer RMU-6E double focusing sector mass spectrometer with a direct solid inlet system. All samples were analyzed by placing 1 mg of the sample into a 1 mm ID quartz tube which was introduced into the vacuum train adjacent to the ion source by a vacuum interlock. The temperature of the sample was raised until a sufficient ion current was registered. Peak positions were assigned relative to peaks found in the fragmentation pattern of tungsten hexacarbonyl, perfluorokerosine, and residual air entrapped in the vacuum system.

Apparatus----Irradiation

The photolysis equipment was of three basic types. The Hanovia apparatus was a 450 watt high pressure quartz mercury-vapor lamp which has a virtual continuum of light in the 3000° A range. It was placed in a water cooled immersion well constructed of pyrex.

The outer portion of the well was a 350 ml reaction vessel fitted to the immersion well by a 50/60 standard tapered joint. The reaction vessel was also equipped with two 10/30 standard tapered female joints and a vertical side arm on which to mount a reflux condenser. To carry out air oxidations, the vessel was equipped with a capillary tipped tube which exited through one of the small joints, and a reflux condenser in the side arm which has a gas outlet in the upper joint. A differential in pressure was created over the solution by drawing a vacuum on the gas outlet joint by means of an aspirator.

When the system was sealed after degassing, the capillary tube was not used and the joints were closed with high vacuum grease. The gas outlet joints were connected to a mercury trap.

When the system was flushed with nitrogen before irradiation, the nitrogen was passed through the capillary tube for a period of no less than 15 min, and the gas outlet was connected to the previously mentioned mercury reservoir.

The Rayonet reactor is a Model RPR-100 chamber reactor equipped with sixteen "black light" mercury-vapor lamps. The output of the lamps was 24 watts with approximately 90% of the light in the 3500°A range. The cell employed was a 25 mm ID tube 210 mm long holding 100 ml of liquid which was exposed to the light. Agitation was accomplished by a magnetic stirrer placed in the bottom of the reactor. Cooling was acheived by a fan which forced air through the reactor between the lamps and the cell. At the top of the cell was mounted a 24/40 standard joint which accomodated a reflux condenser in turn connected to a gas outlet tube. The whole system was closed to a degassing apparatus. When the system was utilized to flush the medium with a gas, a glass adapter was employed and an extra coarse sparger was fitted into the cell with the condenser on the side arm portion of the adapter.

The General Electric lamp was a medium pressure quartz mercury-vapor lamp C37-5. The lamp was housed in a specially designed aluminum box which contained a two mirror reflector system. The reaction cell was an 18 mm ID 110 mm long jacketted Pyrex tube with a 24/40 standard tapered joint at the top of the cell. The cell's capacity was 20 ml and it was located at the focal point of one mirror, with the second mirror mounted to the rear of the lamp in order to reflect the light to the first mirror. The distance between the cell and the lamp was 130 mm.

Chemicals used were purchased from commercial sources whenever possible. All chemicals except highest purity grade were purified either by distillation, sublimation or recrystallization. 2,4-Dimethyl- and 2,5-dimethylbenzophenone were gifts from the Tensyn Division of Velsicol Chemical Corp. (Chicago, Ill.) and were redistilled in vacuum. 4-Cyano-3-methylpyridine was donated by Reilly Tar and Chemical Co. (Indianapolis, Indiana) and was used as received. Benzene, which was used in photolysis, was dried over sodium ribbon. 2-Propanol was distilled from magnesium to remove any residual water, but it was later observed that the 2-propanol was sufficiently pure to be used directly from the bottle if purchased as "Reagent Grade". All other solvents were "Reagent Grade" and were used without any further purification.

Preparation of 2-Benzylacetophenone.

This compound was prepared by the method of Bradsher and Webster. The yield was 13%: mp 48-50°C, literature[80] mp 49-50°C.

Preparation of 2-o-Toluoylpyridine

o-Tolylmagnesium bromide was prepared from 37.5 g (0.219 moles) of o-bromotoluene and 5.3 g (0.22 g atoms) of magnesium in 150 ml of dry ethyl ether. The solvent was exchanged for a benzene-ether mixture. This solution was cooled in an ice bath and 15 g (0.14 moles) of 2-cyanopyridine were added. After the addition was complete, the solution was refluxed for 11 hrs. The solution was cooled and poured onto 200 g of ice and 160 g of ammonium chloride. The whole reaction mixture was transferred to a two liter flask and refluxed for several hours. The organic layer was isolated and the solvent was removed in vacuo. The residue was distilled and the imine fraction boiling at 127-28°C at 0.30 torr was retained. This fraction was dissolved in EtOH, treated with excess hydrochloric acid and hydrolyzed to the desired ketone. The product was crystallized from petroleum ether (20-40°C) and 4.7 g of material were collected for a 16.5% yield; mp 68-69°C, literature[81] mp 69-70°C.

Preparation of Deuteriomethanol-d_1

The compound was prepared by the method of Streitweizer, Verbilt and Stang. The yield was quantitative: bp 64-66°C, literature[82] bp 66°C. The CH_3OD was redistilled from sodium to ensure an anhydrous solvent.

Preparation of 3-Methyl-4-benzoylpyridine

The Grignard of 31.4 g (0.20 mole) bromobenzene was prepared in 150 ml of dry ether by the standard method. To this solution a mixture of 23.8 g (0.20 moles) 3-methyl 4-cyanopyridine and 100 ml of dry ether was added dropwise with constant agitation. The resultant mixture was stirred for 24 hrs. and poured over 200 g of ice and 30 g of NH_4Cl. The crude imine was redissolved in ethanol containing 30 ml of 6N HCl, heated for two hours, neutralized with NH_4OH, and then extracted with ether. The ethereal layer was dried and concentrated *in vacuo*. The residue was distilled and yielded 14.5 g (36.7%) of material bp 112°C at 0.3 torr: ir (neat) 1670 cm^{-1} (C = O).

Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N 7.10. Found: C, 78.93; H, 5.89; N, 6.99.

Preparation of 2,2'-Dimethylbenzophenone - Method #1

A solution of 0.22 moles of 2-tolylmagnesium bromide was prepared from 37.5 g (0.22 moles) of 2-bromotoluene, 5.3 g (0.22 moles) of magnesium and 150 cc of dry ether. The solvent was modified by adding 100 ml of toluene and removing 100 ml of ether by distillation. To the Grignard reagent, 16.7 g (0.14 moles) of 2-tolunitrile in 60 ml of toluene was added dropwise, with cooling, and constant stirring. After the addition was complete, the solution was allowed to warm to room temperature. The solution was heated to 80°C and then allowed to remain at reflux for 12 hrs. The cooled reaction mixture was poured into 100 ml of 95% ethanol. This two phase mixture was refluxed for 3 hrs. The mixture was still in two phases after refluxing. Conc. hydrochloric acid (20 ml) was added to the mixture. The mixture was refluxed for two hrs. and cooled. The resultant mixture was extracted with 200 ml ethyl ether. The organic layer was dried over magnesium sulfate, concentrated and the residue was distilled.

The first cut, 2.93 g, was shown by spectral comparison to be 2-tolunitrile: bp 89°C at 0.25 torr. Literature bp 118-120 at 25 torr. The second cut, 19.7 g, was not the expected 2,2'-dimethylbenzophenone (literature[83] mp 62-4°C): bp 115°C at 0.30 torr. The products isolated did not correspond to the known ketone.

Preparation of 2,2'-Dimethylbenzophenone - Method #2

A solution of 2-tolylmagnesium bromide was prepared by dripping 19.5 g (0.114 moles) of 2-bromotoluene into a flask containing 40 ml of ethyl ether and 2.7 g (0.11 moles) of magnesium turnings. The mixture was stirred for one hr after the addition was complete. The Grignard reagent was then transferred to a dropping funnel. Another solution of 18.1 g (0.114 moles) of 2- toluoyl chloride was placed in a 500 ml flask which contained 100 ml of dry ethyl ether. The solution was cooled to -10°C in an acetone ice bath. The Grignard reagent was added dropwise over a period of one-half hr, and the reddish brown reaction mixture poured onto 200 ml of 1N sulfuric acid and 100 g of ice. The organic layer was isolated and washed with a mixture of 200 ml of saturated sodium bicarbonate solution and 50 ml of cold water. The ethereal layer was dried over anhydrous magnesium sulfate. The ether was removed by distillation. A residue of 20.5 g of dark brown oil was mixed with 20 ml of 95% ethanol and chilled. The solution produced light yellow crystals of 2,2'-dimethylbenzophenone. The crystals were collected on a filter and after drying weighed 11.3 g (47%). The ketone was further purified by sublimation. This treatment gave colorless crystals: mp 63-5°C: ir (Nujol Mull) 1665, 1655 sh cm^{-1} ($>C = O$). Literature[83] mp 62°C.

Preparation of 2-Toluoyl chloride

A mixture of 20 g (0.125 moles) of 2-toluic acid, 50 ml of petroleum ether (60-110°C) and 10 ml of dimethylformamide was placed into a 200 ml round bottom flask. A solution of 20 ml (.276 moles) of thionyl chloride in 20 ml of petroleum ether (60-110°C) was added to the acid dropwise with constant stirring. When the addition was complete the solution was heated to reflux and held at that temperature for two hours. The solution was cooled. The dimethylformamide layer was allowed to solidify, and the petroleum ether layer decanted. The hydrocarbon solution was concentrated and used without further purification: ir (neat) 1770 cm^{-1}, ($>C = O$).

Preparation of 2-Methylbenzophenone

To a solution of 29.2 g (0.25 moles) of 2-tolunitrile in 100 ml of dry benzene was added dropwise a solution of phenylmagnesium chloride (0.60 moles) in 250 ml tetrahydrofuran. The resultant mixture was stirred for two hrs. After which time it was heated and solvent was removed by distillation until the overhead temperature reached 81°C. The reaction medium was refluxed for 11 hrs with constant stirring. The solution was then cooled and poured into a beaker containing 200 g of ice and 45 g of ammonium chloride. The hydrolysis mixture was extracted with two 200 ml portions of ether. The organic layer was concentrated and the residue distilled. The imine distillate showed a strong N-H stretch in the infrared, and a weak ketonic carbonyl band at 1660 cm^{-1}. The material was mixed with 50 ml of hydrochloric acid (conc.), 50 ml H_2O and a sufficient amount of ethanol to insure miscibility, and the solution was refluxed for 12 hrs.

The acid phase was neutralized, and then 100 ml of ethyl ether added. The two layers were separated, and the organic phase was washed with 50 ml of saturated sodium bicarbonate. The aqueous layer was extracted with 100 ml ether. The two ethereal layers were combined and dried over magnesium sulfate. The solution was concentrated and distilled to yield 37.24 g (76%) of 2-methylbenzophenone bp 96-100°C at 0.075 torr; ir(neat) 1660 cm^{-1} ($>C = O$), literature[84] bp 175-180°C at 13 torr.

<u>Preparation of 2,3'-Dimethylbenzophenone</u>

A Grignard was prepared in 500 ml of ether from 0.20 moles of o-bromotoluene and an equimolar quantity of magnesium turnings. To this Grignard was added dropwise 17.5 g (0.15 moles) of m-tolunitrile in 25 ml ether. A white-yellow solid began to precipitate during the addition process and this suspended solid was stirred at reflux for one hour. Dry toluene (100 ml) was added and the reaction mixture was distilled until the overhead temperature reached 110°. The contents of the flask were cooled to room temperature and diluted with 25 cc of 6N hydrochloric acid and sufficient ethanol to effect miscibility. This homogeneous solution was refluxed for four hours and then poured into 300 ml of water, extracted well with ether and ethyl acetate, washed with 5% aqueous sodium bicarbonate and dried over magnesium sulfate. Evaporation and vacuum distillation of the resulting oil gave 22.7 g (72%) of product bp 130-133° at .21 torr; literature[85] bp 228-231° at 24 torr.

Preparation of 2,2',5-Trimethylbenzophenone

A mixture of 60.5 ml (0.50 moles) of p-xylene and 37.3 g (0.280 moles) of aluminum chloride was placed 200 ml round bottom flask. The flask was equipped with a dropping funnel and a reflux condenser by means of a glass adapter. The mixture was agitated by a magnetic stirrer.

While the mixture was being stirred continuously, 22.0 g (0.14 moles) of 2-toluoyl chloride was added dropwise over a period of one hr. After the acid was completely added, the solution was stirred for 30 minutes and poured over 150 g of ice and 150 ml of conc. hydrochloric acid. The bright green organic layer was washed with a 10% sodium hydroxide solution. The aqueous layer was extracted with 100 ml of ether. The two organic layers were combined and dried over magnesium sulfate. The sample was concentrated and the residue distilled. The product cut 27.4 g (86%) was a yellow liquid: bp 128-130°C at 0.075 torr: ir(neat) 1660 cm^{-1} ($>C = O$).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.62; H, 7.11.

The product was found by VPC to be a mixture of two trimethylbenzophenone isomers.

Preparation of 2-Methyl-2'-Methoxybenzophenone

A Grignard was prepared from 0.04 moles of magnesium and a like quantity of o-iodoanisole in 20 ml ether. This

Grignard was added dropwise to a solution of 0.04 moles of 2-toluoyl chloride in 20 ml of ether with vigorous stirring and chilling in an ice-salt bath. The reaction medium was stirred for two hours and allowed to warm to room temperature. Hydrolysis with chopped ice and 1N hydrochloric acid, extraction with ethyl acetate, washing with 5% aqueous sodium bicarbonate, drying over $MgSO_4$ and concentration _in vacuo_ yielded an oily organic phase. This oil solidified on scratching and fractional crystallization from either ether or ethyl acetate affected a separation of the less soluble triarylcarbinol from the more soluble ketone. A total of 3.0 g (45%) of o-tolyldi(o-anisyl)carbinol, mp 164-165^{o}, was obtained. The infrared spectrum, in Nujol, displayed an intense O-H absorption at 3530 cm^{-1}.

Anal. Calcd. for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63. Found: C, 78.76; H 6.86. From the mother liquors it was possible to isolate 1.2 g or 13% of 2-methyl-2'-methoxybenzophenone, 74.5-76^{o}C. An intense ketonic carbonyl was evident in the infrared at 1658 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.23. Found: C 79.34; H, 6.45.

Preparation of 2,2',4-Trimethylbenzophenone

A suspension of 37.5 g (0.28 moles) of aluminum chloride in 60 g of meta-xylene was charged to a 200 ml one-neck flask equipped with a dropping funnel, a reflux condenser and a magnetic stirrer. To this vigorously agitated mixture 22 g (0.14 moles) of o-toluoyl chloride were added dropwise over a period of one-half hour. The resultant medium was heated to reflux for an additional one-half hours. The reaction mixture was poured over 100 g of ice and 50 ml of 1N sulfuric acid. This two phase system was heated to reflux for one hour. After cooling the reaction mixture to room temperature, 200 ml of ethyl ether were added and the organic layer was separated. The ethereal layer was washed with 50 ml of 10% sodium hydroxide, 50 ml cold water and dried over magnesium sulfate. The ether was removed in vacuo and the residue distilled. The first cut was identified as meta-xylene. The second cut, 10.1 g: bp 117-131°C at 0.05 torr, was found to be rich in ketone, but there were other significant components. The third cut, 16.1 g (50%): bp 131-133°C at 0.05 torr, was examined by gas chromatography and contained only one component, the ketone: ir(neat) 1660 cm^{-1} ($>C = O$): nmr (CCl_4) δ 2.24 (S,3,CH_3), 2.34 (S,3,CH_3), 2.38 (S,3,CH_3), and 6.75-7.35 ppm (m,7, aromatic protons).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.62; H, 7.11.

Preparation of 4-Hydroxy-2-methylbenzaldehyde

A reaction medium composed of 54 g (0.50 moles) of m-cresol, 200 g (2.5 moles) of 50% sodium hydroxide, 200 g

(1.7 moles) of chloroform and 300 ml of water was charged to a 100 ml three-neck flask. The flask was equipped with a mechanical stirrer, a reflux condenser and a steam inlet tube. The initial reaction was extremely exothermic and had to be moderated by external cooling until the exothermic phase was completed. After the first reaction subsided, the mixture was heated to reflux for two hrs. The deeply colored solution was cooled to room temperature, and sufficient conc. hydrochloric acid was added until the pH was slightly acidic. The reflux condenser was replaced by a still head connected to a Friedrick condenser and steam was passed through the mixture. The distillate was collected until it became clear and then an additional 200 ml of distillate was passed overhead. The 2-hydroxy-4-methyl-benzaldehyde was not isolated from the distillate. The residual mixture was separated while yet hot by decanting the water from the tarry residue. The tarry residue was extracted twice by 500 ml portions of hot water. The aqueous phase was saturated with sodium chloride, and the product was extracted in a 2 liter liquid-liquid extractor by ethyl ether. Concentration of the ethereal layer gave 21.6 g (32%) of 4-hydroxy-2-methyl-benzaldehyde: mp 108-110°C; literature[86] mp 100°C.

Preparation of 4-Methoxy-2-methylbenzaldehyde

A sample of 17 g (0.13 moles) of 4-hydroxy-2-methylbenzaldehyde was dissolved in 10 g of 50% sodium hydroxide and 35 ml of water. The solution was charged to a three-neck 200 ml flask which was equipped with a reflux condenser, a dropping funnel and a thermometer. By means of the dropping funnel 12 ml (.17 moles) of dimethylsulfate were added dropwise. The solution was held at 10°C during the addition. When the addition was complete, the reaction was warmed to reflux for a period of two hours. To the cooled solution 100 ml of water were added, followed by 200 ml of methylene chloride. The whole mixture was shaken together in a 500 ml separatory funnel and the phases separated. The organic layer was washed with water and the product isolated. The aqueous layer was neutralized by adding conc. hydrochloric acid. It was then saturated with sodium chloride and extracted with 200 ml methylene chloride. The organic layer was separated and extracted with saturated sodium bicarbonate solution. Neutralization of the bicarbonate wash netted 0.90 g of a product which was not further purified. The initial methylene chloride wash was dried over anhydrous magnesium sulfate and concentrated to give 9.0 g (48%) of 0-methyl-p-anisaldehyde: ir(neat 1685 cm^{-1} ($>C = 0$). The material was used without further purification.

Preparation of 4-Methoxy-2-methylbenzoic Acid

A mixture of 18.3 g (0.122 moles) of 4-methoxy-2-methylbenzaldehyde, 155 ml of water and 16.4 g (0.155 moles) of sodium carbonate was charged to a 500 ml Erylenmeyer flask.

The contents of the flask were heated on a hot plate. The temperature was maintained between 80°C and 90°C. To the hot two-phase mixture, 41.3 g (0.261 moles) of potassium permanganate were added in 3 g portions. After each addition, the flask was shaken until the purple color disappeared and then additional $KMnO_4$ was added. After the final portion had been added and the color had disappeared, the solution was filtered while yet hot. The filtrate was transferred to a two l beaker and cooled. A white solid which formed in the medium upon acidification, was collected on a filter. The mother liquor was concentrated, and a second crop of crystals was collected. The total amount of 4-methoxy-2-methyl benzoic acid was 16.6 g (82%). The product was used without further purification: mp 170-171°C, literature[87] mp 176°C.

Preparation of 4-Methoxy-2-methylbenzoyl Chloride

A one-neck 200 ml flask was charged with 20 g (0.12 moles) of 4-methoxy-2-methylbenzoic acid, 10 ml (0.084 moles) of dimethylformamide and 40 ml of petroleum ether (60°-110°C). The two-phase system was agitated by a magnetic stirrer and the addition of thionyl chloride was effected by means of a dropping funnel. To the well stirred solution, 16 ml (0.147 moles) of thionyl chloride was added dropwise over a period of one-half hour. The resultant system was heated to reflux for two hours. After the solution cooled, the dimethylformamide layer solidified and the petroleum ether solution was decanted into a 200 ml distilling flask. The petroleum ether was removed in vacuo and 22 g of the acid chlordie were obtained: ir(neat) 1770 cm^{-1} ($\gt C = O$). The chloride solidified upon standing and was used without further purification. The conversion was essentially quantitative.

Preparation of 2,2'-Dimethyl-4-methoxybenzophenone

2-Tolylmagnesium bromide was prepared by reacting 20.0 g (0.117 moles) of o-bromotoluene and 2.8 g (0.12 moles) of magnesium turnings in 80 ml of dry ethyl ether. The Grignard reagent was used immediately after preparation. A solution of 19.7 g (0.106 moles) of 4-methoxy-2-methylbenzoyl chloride and 100 ml of dry ethyl ether was charged to a dry 500 ml one-neck flask. The solution was stirred by means of a magnetic stirrer and the reaction medium was cooled to -10°C before the addition was started. The temperature of the reaction was maintained at -10°C while the Grignard reagent was added dropwise to the solution. After addition was complete, the solution was warmed to room temperature. The mixture was poured onto 100 g of ice and 200 ml of 1 N sulfuric acid. The reaction flask was cleaned with 50 ml of water which were added to the hydrolysis mixture. The layers were separated, the ethereal layer was washed with saturated sodium bicarbonate solution and dried over magnesium sulfate. The ether was removed in vacuo, and the residue was distilled to yield 14.5 g (57%) of analytically pure 2,2'-dimethyl-4-methoxybenzophenone: bp 147°C at 0.075 torr ; ir(neat) 1660 cm^{-1} ($>C = O$); nmr ($CDCl_3$)δ 2.33 (S,3,CH_3), 2.54 (S,3,CH_3), 3.73 (S,3,O-CH_3), 6.55-7.50 ppm (m,7, aromatic protons).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.77; H, 6.85.

Preparation of 3-Phenyl-5-methylphthalide and 3-Phenyl-6-methylphthalide

The technique described by Newman[10] for phenylmagnesium bromide ring opening of 3-methylphthalic anhydride was extended to 4-methylphthalic anhydride. According to this procedure 0.03 moles of phenylmagnesium bromide (Fisher Chemical Co. standardized reagent) were added dropwise to 0.028 moles of 4-methylphthalic anhydride being stirred in 50 ml of 1:1 benzene:ether. After five hours reflux the mixture was hydrolyzed with ice and the pH adjusted to slight acidity with dilute hydrochloric acid. The reaction product was extracted into an ethyl acetate phase, concentrated in vacuo and the gummy semi-solid mixture of isomeric benzoylbenzoic acids was collected on a filter. The acids (approximately 2 grams) were dissolved in 15 ml of glacial acetic acid. Zinc dust (1.0 g) was added and the mixture was refluxed with stirring for 24 hours. The zinc dust was removed by filtration and the acetic acid was concentrated to approximately five ml. The addition of water produced a cloudy emulsion which precipitated a gummy white solid on standing at room temperature for one week. The solid was removed by decantation of the liquid, taken up in benzene, dried with $MgSO_4$, and recovered by evaporation of the solvent to dryness. The material was purified by three recrystallizations from methanol to yield 1.1 g (16%), mp 86-108°. Two poorly resolved spots could be observed on Eastmas Kodak 6060 silica gel thin layer chromatograms with 1:1 benzene:cyclohexane elutant; ir (CCl_4 in matched 0.1 mm cells) 1775 (lactone CO), and 1290 cm^{-1} (-C-O-); nmr ($CDCl_3$) δ 2.35 and 2.39 (s,3,CH_3's), 6.26 (s,1,2-C<u>H</u>), 7.0 to 7.4 (m,7,Ar<u>H</u>), 7.64 (d,J = Hz, $\underline{H}_7$ in 3-phenyl-6-methylphthalide), 7.78 (d, J = 14 Hz, $\underline{H}_7$ in 3-phenyl-5-methylphthalide). Comparison of the integrated methyl signals revealed that the two phthalides were present in nearly equal amounts.

<u>Anal</u>. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.64; H, 5.21.

<u>Preparation of 3-Phenylphthalide</u>

A reaction mixture composed of 10 g (0.44 moles) of 2-benzoylbenzoic acid, 20 g (0.31 moles) of 40 mesh zinc, 80 ml of acetic acid and 20 ml of water was charged to a one-neck 200 ml flask equipped with a reflux condenser. The mixture was agitated by means of a magnetic stirrer. The reaction mixture was heated to reflux for two hours and then filtered while hot. The solution was cooled in an ice bath and the inorganic precipitate ($Zn(OAc)_2$) was discarded. Flooding the acetic acid filtrate with water produced a yellow-white solid which was collected on a filter to yield 5.5 g (57%) of the 3-phenylphthalide: mp 113-115°C. The material was recrystallized from ethanol to a constant mp 116-117°C; literature[75] mp 115°C.

Preparation of 6-Methyl-3-phenylphthalide

6-Methyl-3-phenylphthalide was prepared by the method employed by Ullman[75] for 3-phenylphthalide.

A 25 ml one-neck flask equipped with a reflux condenser was charged with a suspension of 1.0 g (0.0045 moles) of 2-benzoyl-5-methylbenzoic acid and 2.0 g (0.03 moles) 40 mesh zinc beads in 8 ml of glacial acetic acid and 2 ml of water. The solution was refluxed for two hours, cooled and filtered to remove the zinc and other inorganic residues. Flooding of the filtrate with 20 ml of water afforded 0.21 g (21%) of 6-methyl-3-phenylphthalide. The material was recrystallized twice to produce analytically pure 6-methyl-3-phenylphthalide: mp 137-139°C; ir(Nujol mull) 1750 cm^{-1} (C = O); nmr ($CDCl_3$) δ 1.49 (s,3,CH_3), 6.37 (s,1,C-H), 7.05-7.50 (m,7, aromatic protons) and 7.73 (s,1, aromatic proton position 7). The nmr spectrum was identical with that of an authentic sample prepared by Newman's method (vide ante).

Preparation of 3-Methoxy-3-phenylphthalide

A 18 g (0.08 moles) sample of 2-benzoylbenzoic acid was suspended in 100 ml of petroleum ether (60°-110°C) and 10 ml (0.08 moles) of dimethylformamide. The suspension was transferred to a 300 ml one-neck flask which was equipped with a magnetic stirrer, a dropping funnel and a reflux condenser. To this well-stirred suspension, 50 ml (0.69 moles) of thionyl chloride in 100 ml of petroleum ether (60-110°C) was added dropwise over a period of one hour. When the addition was complete, the two-phase system was refluxed for two hours. Cooling of the reaction mixture caused the dimethylformamide layer to solidify and allowed the petroleum ether solution to be decanted away from it. Concentration, in vacuo, of this petroleum ether phase yielded a reddish brown oil which was dissolved in 40 ml (0.99 moles) of methanol and 20 ml (0.25 moles) of pyridine. The reaction mixture was charged to a 200 ml one-neck round bottom flask equipped with a reflux condenser and drying tube. The solution was stirred for 48 hours at room temperature and poured into a 800 ml beaker containing 500 ml of water and 50 ml of hydrochloric acid. Ethyl ether (100 ml) was added to the reaction mixture and the organic layer was separated from the aqueous phase. The organic layer was washed with saturated sodium bicarbonate solution, water and saturated sodium chloride solution and then dried over anhydrous magnesium sulfate. The ether was removed in vacuo to yield 13.5 g (70%) of a light yellow liquid which was identified as the expected pseudo ester by its ir spectrum: ir(neat) 1780, 1770 cm^{-1} (pseudoester C = O).

Preparation of 2-Hydroxymethylbenzhydrol

Ethyl ether was dried over lithium aluminum hydride and distilled into a 300 ml one-neck reaction flask and into a 200 ml dropping funnel. A suspension of 2.5 g (0.065 moles) of lithium aluminum hydride in 100 ml of ethyl ether was charged to the flask fitted with the dropping funnel, a reflux condenser and a magnetic stirrer. A solution composed of 13.5 g (0.056 moles) of 3-methoxy-3-phenylphthalide in 100 ml of ethyl ether was added dropwise over a period of one-half hour to the well-stirred suspension. The reaction was stirred at room temperature for an additional two hours and then poured into 100 g of ice and 200 ml of 1 N sulfuric acid. The ethereal layer was separated, washed with saturated sodium bicarbonate solution, water and saturated sodium chloride solution and then dried over anhydrous magnesium sulfate. The ether was stripped off in vacuo. The residue was 10 g (83%) of o-hydroxymethylbenzhydrol : ir (Nujol mull) 3580 sh, 3350 cm^{-1} (O-H).

Preparation of 2-Benzoylbenzaldehyde

A suspension of 6.55 g (0.0585 moles) of selenium dioxide in 23 ml of acetic acid and 45 ml of xylene was charged to a three-neck flask equipped with an addition funnel, a Dean-Stark trap, a magnetic stirrer an a reflux condenser. The mixture was heated to reflux for 15 min before the addition was begun, in order to remove any water present in the reaction solvent system. To the well-stirred refluxing reaction mixture, 10 g (0.047 moles) of 2-hydroxymethylbenzhydrol, 13 ml of acetic acid and 40 ml of xylene were added dropwise over a period of one hour. The reaction medium was maintained at reflux for 23 hours until 3.4 ml (0.19 moles) of water were collected. The reaction mixture was cooled and filtered to remove the selenium. The filtrate was poured into 500 ml of ice water, and the aqueous layer was adjusted to basicity with NaOH. After an ether extraction of the system, the layers were separated and the aqueous layer was extracted one with 150 ml of ethyl ether. The combined organic layers were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The sample was concentrated and distilled to yield 6.4 g (65%) of light yellow oil: bp 141-147°C at

0.15 torr . The oil was dissolved in petroleum ether (20-40°C) and chilled. White crystals of 2-benzoylbenzaldehyde formed: mp 66-67°C, literature[88] mp 64-67°C.

2'-Methylbenzhydrol

A solution of 1.0 grams (5.1 mmoles) of 2'-methylbenzophenone in 20 cc of anhydrous ether was added dropwise over 15 minutes to a well-stirred suspension of 0.2 grams (5.1 mmoles) of lithium aluminum hydride in 20 cc ether. After the mixture was stirred a room temperature for 3 hours, the excess hydride was filtered off and the ethereal layer hydrolyzed by the dropwise addition of water. The precipitated inorganic hydroxides were removed and washed well with benzene. The combined benzene-ether phase as dried over $MgSO_4$ and concentrated *in vacuo* to produce white microneedles, yield 0.82 grams or 82%, mp 90-91°C, literature[89] mp 91°.

2',5'-Dimethylbenzhydrol

By the above method, 10.0 grams (0.048 moles) of 2,5-dimethylbenzophenone were reduced by addition to 1.82 grams (0.048 moles) of lithium aluminum hydride. White crystals, mp 88-89°, were obtained in 75% yield on concentrating the ether extracts, literature[90] mp 88°.

Preparation of 2,4-Dimethylbenzhydrol

A solution of 2.0 g (0.01 moles) of 2,4-dimethylbenzophenone and 10 ml ether was placed in a 100 ml round bottom flask, which was attached to a ground glass reflux condenser. A suspension consisting of 0.10 g (0.0026 moles) lithium aluminum hydride in 50 ml of ether was added. During the first few minutes the solution bubbled. After the initial reaction subsided, the solution was stirred for several hours. The reaction mixture was poured over a mixture of ice and 150 ml of 1 N sulfuric acid. To the hydrolysis mixture 50 ml of ethyl ether was added and the two layers were separated. The aqueous layer was extracted with 50 ml of ether, and the ethereal layer was extracted with cold water. The two ethereal layers were combined and dried. The organic layers were dried over magnesium sulfate. The solvent was removed _in_ _vacuo_. The yield obtained was 1.34 g (67%) of 2,4-dimethylbenzhydrol: ir (Nujol mull) 3520 free, 3460 bonded cm^{-1} (OH); mp 52-54°. Literature[91] mp 57°.

Preparation of 2,4-Dimethylbenzpinacol

A. Aluminum Amalgam Method

An aluminum mixture of 0.84 g (.003 moles) of mercuric chloride, 2.16 g (.08 moles) of 30 mesh aluminum and 5 ml of dry benzene was placed into a dry three neck 500 ml flask. The two-phase medium was heated with stirring for five minutes. A solution of 5.9 g (.03 moles) of 2,4-dimethylbenzophenone in 100 ml dry benzene and 100 ml dry ether was added to the aluminum amalgam with constant stirring. The mixture was refluxed for three hours, cooled and poured onto ice. The two phases were filtered and the organic layer was isolated, washed with saturated sodium chloride solution, dried and concentrated. The organic material was identified as unreacted ketone.

B. Magnesium Subiodide Method

This compound was prepared by suspending 1.3 g (0.05 moles) magnesium turnings and 12 g (0.05 moles) iodine in 7.5 ml dry benzene and 75 ml dry ether under a nitrogen atmosphere. The mixture was stirred until it became transparent green in color. At this point 9.70 g (0.047 moles) of 2,4-dimethylbenzophenone were added while the mixture was being stirred vigorously. A deep red solution developed. After additional agitation for one hour, the solution was poured onto 200 g ice and 30 g ammonium chloride. The pinacol was extracted into a benzene phase and dried over sodium sulfate. When the solvent was removed 3.0 g (31%) of pinacol were collected on a filter. The pinacol was recrystallized from toluene: mp 169-170°C; ir(KBr pellet) 3570 cm^{-1} (O-H).

Anal. Calcd for $C_{30}H_{30}O_2$: C, 85.27; H, 7.16. Found: C, 85.35; H, 6.95.

Photoreduction of 2,4-Dimethylbenzophenone

Run # 1. A mixture of 1.0 g (0.0048 moles) of 2,4-dimethylbenzophenone and 100 ml of 2-propanol was placed into the reaction vessel of the Rayonet reactor. The solution was degassed and maintained under a nitrogen atmosphere. The sample was irradiated for 12 hrs. and the solid was collected. The total recovered yield was 0.28 g (28%) of pinacol which was recrystallized from toluene to give white crystals: mp 179°C; ir (KBr pellet) 3570 cm^{-1} (OH).

Anal. Calcd for $C_{30}H_{30}O_2$: C, 85.27; H, 7.15. Found: C, 85.42; H, 7.21.

Run # 2. A solution of 1.0 g (0.0048 moles) of 2,4-dimethylbenzophenone and 100 ml 2-propanol was introduced into the reaction vessel of the Rayonet reactor. The sample was degassed and maintained under a nitrogen atmosphere. The sample was irradiated for six hrs, and the precipitated solid was collected on a filter. The filtrate was concentrated to 50 ml and rediluted to 100 ml with 2-propanol. This procedure was employed to eliminate any acetone produced which might compete for absorption of light by the benzophenone. The sample was once again placed in the cell, degassed and sealed under a nitrogen atmosphere. It was irradiated for an additional six hrs. The solid was collected on the same tared filter funnel.

The product was dried in an Abderhalden apparatus, and weighed; 0.45 g (55%). The filtrate was concentrated to 0.40 g and diluted to 25 ml total volume with 2-propanol. This solution was injected into a gas chromatograph and separated into three components. Utilizing the peak enhancement technique the three peaks were identified as 2,4-dimethylbenzophenone, 2,4-dimethylbenzohydrol, and a trace impurity which was present in the initial ketone and which could not be removed by standard methods. Integration of the peak areas revealed that hydrol has formed in 27% yield.

Photoreduction of 2,4-Dimethylbenzophenone by 2,4-Dimethylbenzhydrol

A sample composed of 1.0 g (0.0048 moles) of 2,4-dimethylbenzophenone, 1.0 g (0.0048 moles) of 2,4-dimethylbenzhydrol and 100 ml of dry benzene was placed in the Rayonet reactor and irradiated for 24 hrs. No solid precipitated during this irradiation. The solvent was removed *in vacuo* and a yellow residue, 2.0 g, was recovered. The ir of the residue showed the intense hydrol band along with the intense carbonyl band. No pinacol could be detected by product isolation.

Photoreduction of Benzophenone by 2,4-Dimethylbenzhydrol

A solution of 0.50 g (0.0024 moles) of 2,4-dimethylbenzhydrol, 0.5 g (0.0027 moles) of benzophenone and 100 ml of dry benzene was placed in the reaction vessel of the Rayonet reactor. The sample was degassed and maintained under a nitrogen atmosphere. It was irradiated for 24 hrs. The solution was concentrated and 0.30 g of a pinacol were isolated by flooding with cold 2-propanol and hexane. The residue after removal of all of the solvent was found to weight 0.5 g and was identified by mp and ir as benzpinacol.

Photoreduction of 3-Methyl-4-benzoylpyridine: Preparation of 1,2-Di-(3-methyl-4-pyridyl)-1,2-diphenyl-1,2-ethanediol

A mixture of 5.0 g (0.025 moles) of 3-methyl-4-benzoylpyridine and 325 ml of 2-propanol was placed into the well of a Hanovia 450 watt lamp. The solution was degassed and closed under a nitrogen atmosphere. It was irradiated for 24 hrs. The organic solid was collected on a filter and the mother liquor was evaporated but no additional pinacol was recovered from it. The total amount of pinacol recovered was 0.65 g (13%). It was sublimed to obtain an analytical sample: mp 170-171°C; ir (KBr pellet) 3100 cm^{-1} (OH).

Anal. Calcd for $C_{26}H_{24}N_2O_2$: N, 7.06. Found: N, 7.02.

Photoreduction of 2-Methylbenzophenone: Preparation of 1,2-Di-o-tolyl-1,2-diphenyl-1,2-ethanediol

A mixture of 2.7 g (0.014 moles) of 2-methylbenzophenone and 100 ml of 2-propanol was added to the irradiation cell of the Rayonet reactor. The solution was degassed and sealed under a nitrogen atmosphere. It was irradiated for 20 hrs. Upon completion of the irradiation, a white solid was observed floating in the medium and thus 0.45 g was collected on a filter. The mother liquor was concentrated and an additional 0.45 g of product were collected. The two crops were combined to yield 0.90 g (33%) pinacol and this was recrystallized from toluene to produce a white solid: mp 144-145°C: ir (KBr pellet) 3540 cm^{-1} (OH).

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64. Found: C, 85.27; H, 6.57.

Photoreduction of 2,3',4'-Trimethylbenzophenone: Preparation of 1,2-Di(2-tolyl)-1,2-di(3,4-dimethylphenyl)-1,2-ethanediol.

A mixture composed of 2 g (0.009 moles) of 2,3',4'-trimethylbenzophenone and 80 ml of 2-propanol was placed into the cell of the Rayonet reactor. The solution was degassed and closed in a nitrogen atmosphere. It was irradiated for 10 hrs/ in the reactor. A white solid (0.60 g) was collected on the filter, and the mother liquor yielded another 0.25 g after being concentrated. The total yield of the two crops was 0.85 g (43%). The material was recrystallized several times from toluene to give a white solid: mp 147-148°C: ir (KBr pellet) 355o cm^{-1} (OH).

Anal. Calcd for $C_{32}H_{34}O_2$: C, 85.29; H, 7.61. Found: C, 85.20; H, 7.42.

Photoreduction of 2,5-Dimethylbenzophenone: Preparation of 1,2-Di(2,5-Dimethylphenyl)-1,2-diphenyl-1,2-ethanediol

The reaction well of the Rayonet reactor was filled with a solution of 1.0 g (0.0048 moles) of 2,5-dimethylbenzophenone and 100 ml of 2-propanol. The reaction media was degassed and closed under a nitrogen atmosphere. The sample was irradiated for 15 hrs, and during that time the solution became saturated with white crystals and irradiation was terminated. The media gave up 0.35 g of white solid and the mother liquor produced an additional 0.15 g of white solid. The total yield of pinacol was 0.50 g (50%) and it was recrystallized from toluene to achieve analytical purity: mp 142-143°C: ir (Nujol mull) 3560, 3620 cm^{-1} (OH).

Anal. Calcd for $C_{30}H_{30}O_2$: C 85.27; H 7.15. Found: C 85.25; H 7.43.

Photoreduction of 3-Methyl-4-benzoylpyridine: Preparation of 1,2-Di(3-methyl-4-pyridyl)-1,2-diphenyl-1,2-ethanediol

The reaction vessel of Rayonet reactor was filled with a sample of 1 g (0.005 moles) of 3-methyl-4-benzoylpyridine dissolved in 100 ml of 2-propanol. The solution was degassed and kept under a nitrogen atmosphere during the period of irradiation. The sample was irradiated for 18 hrs. From the reaction a total of 0.40 g (40%) of pinacol was obtained and was purified by sublimation to give a pale yellow solid: mp 170-171^{o}C: ir (KBr pellet) 3100 cm^{-1} (OH).

<u>Anal</u>. Calcd for $C_{26}H_{24}N_{2}O_{2}$: N 7.06. Found: N, 7.06.

<u>Photoreduction 2,6-Dimethylbenzophenone</u>

To the reaction vessel of the Rayonet reactor was added 1.0 g (0.0048 moles) of 2,6-dimethylbenzophenone and 100 ml of 2-propanol. The sample was degassed and sealed under a nitrogen atmosphere. The medium was irradiated for 12 hrs, and did not show signs of pinacolization. The solvent was removed and an ir spectrum of the residue was identical to the spectrum of the authentic starting material.

<u>Photoreduction 2-Benzylacetophenone</u>

The reaction cell of the Rayonet reactor was filled with a 1.0 g (0.0048 moles) sample of 2-benzylacetophenone in 100 ml of 2-propanol. The solution was deoxygenated and closed under a nitrogen atmosphere. The sample was irradiated for 24 hrs and no product was observed produced in the cell. The solvent was removed <u>in vacuo</u> and the starting ketone recovered and then identified by means of an ir spectrum which was identical to one of authentic 2-benzylacetophenone.

Photoreduction of 2-Methylbenzophenone

The reaction vessel of the Rayonet reactor was filled with a solution of 1.0 g (0.005 moles) of 2-methylbenzophenone, 50 ml of benzene and 50 ml of 2-propanol. The solution was degassed and maintained under a nitrogen atmosphere. The sample was irradiated for 20 hrs. The mixture was transferred to a flask, and the solvent removed *in vacuo*. The resultant semi-solid was triturated with 10 ml of 2-propanol. The mixture was chilled over night and the crystalline material was collected on a filter. The total amount of pinacol was 0.47 g (47%). The pinacol was identified by comparing the infrared spectrum and melting point with an authentic sample. The filtrate was concentrated and determined by spectral comparison to be unreacted ketone.

Photoreduction of 2,4-Dimethylbenzophenone

A solution of 0.50 g (0.0024 moles) of 2,4-dimethylbenzophenone, 50 ml of benzene and 50 ml of 2-propanol was placed in the reaction vessel of the Rayonet reactor. The solution was degassed and maintained under a nitrogen atmosphere. The sample was irradiated for 25 hrs. The solvent was removed *in vacuo*, and 10 ml of cold 2-propanol was added. The mixture was cooled overnight, and the crystals were collected on a filter. The dried product was 0.20 g (40%) pinacol. The pinacol was confirmed by melting point and infrared comparison. The filtrated yielded 0.3 g of a yellow residue which was shown to be the unreacted ketone: ir(neat) 1660 cm^{-1} ($>C = O$).

Photostability of 2,4-Dimethylbenzpinacol

A mixture of 0.80 g (0.0019 moles) of 2,4-dimethylbenzophenone, and 50 ml of 2-propanol and 50 ml of dry benzene was placed in the reaction vessel of the Rayonet Reactor. The mixture was degassed and maintained under a nitrogen atmosphere. The sample was irradiated for 23 hrs. The sample was filtered and 0.57 g of 2,4-dimethylbenzpinacol was recovered. The mother liquor was concentrated and the residue was dissolved in 10 ml of 2-propanol. The mixture was chilled and filtered. The solid after drying weighed 0.05 g. The total recovered amount of pinacol was 0.62 g (77%). The pinacol was characterized by it's ir spectrum and mp. The residue, 0.38 g, was dissolved in a small amount of ethanol, and the solution was then analyzed by gas chromatography. The gas chromatograph showed two peaks corresponding to 2,4-dimethylbenzophenone and 2,4-dimethylbenzhydrol. The hydrol was in considerable excess compared to the ketone. The ir of the residue showed both the hydrol OH at 3520 free, 3460 bonded cm^{-1} and the carbonyl at 1660 cm^{-1}. The ketone was present in this experiment so that the reaction medium would be very nearly what it was under photoreduction conditions.

Photoreduction of 2,2'-Dimethylbenzophenone

A reaction media of 0.50 g (0.0025 moles) of 2,2'-dimethylbenzophenone, 50 ml of dry benzene and 50 ml of 2-propanol was charged to the reaction vessel of the Rayonet reactor. The solution was degassed and sealed under a nitrogen atmosphere. The sample was irradiated for 24 hrs, but there was no evidence of solid formation. The reaction was terminated and the solvent was removed in vacuo. The residue was taken up in 10 ml of 2-propanol and chilled, but once again no solid precipitated. The solution was analyzed by gas chromatography with one peak corresponding to 2,2'-dimethylbenzophenone in retention time. Along with the chromatograph, an ir spectrum of the residue showed only the ketonic carbonyl of 2,2'-dimethylbenzophenone and was devoid of any known hydroxyl peaks.

Solubility of 2,4-Dimethylbenpinacol in 2-Propanol

A sample of 0.516 g (0.00125 moles) of 2,4-dimethylbenzpinacol was weighed into a 100 ml volumetric flask. The flask was filled to the 100 ml mark with 2-propanol and a magnetic stirring bar was placed in the flask. The two phase system was stirred for 16 hrs. The undissolved pinacol was collected on a medium fritted glass filter. The solution was charged to a tared 150 ml flask, and placed in an air stream. When the solvent has evaporated completely, the flask and its contents were placed in a

60°C vacuum oven for 12 hrs. The flask was weighed and found to contain 0.0228 g of diol. Thus the solubility of the pinacol in 2-propanol is 0.228 g per liter.

Photostability of 2,4-Dimethylbenzopinacol

The reaction cell of the Rayonet reactor was charged with a suspension of 0.60 g (0.0014 moles) of 2,4-dimethylbenzopinacol in 100 ml of 2-propanol. The suspension was degassed and irradiated for 12 hrs. The solid pinacol was recovered by filtration, the filtrate was concentrated to an oily residue, and diluted to 10 ml volume with 2-propanol. The chilled mixture was filtered through the same filter which held the previously collected pinacol. The pinacol was removed from the filter and placed in a tared sample bottle, dried net weight 0.55 g. The final filtrate was analyzed by gas chromatography, but no ketone or hydrol peaks were observed at the lowest possible attenuation.

Photoinduced Elbs Reaction of 2,2'-Dimethyl-4-methoxybenzophenone

A sample of 3.0 g (0.013 moles) of 2,2'-dimethyl-4-methoxybenzophenone and 25 ml of toluene was charged to the jacketed cell of the General Electric lamp. The sample was heated by passing steam through the outer jacket. The sample was irradiated for 15 hrs. The reaction was terminated, and the solvent was removed *in vacuo*. Examination of the residue by infrared spectroscopy revealed only the characteristic bands of the starting ketone.

Photoenolization of 2,4-Dimethylbenzophenone

A solution of 0.5 ml of 2,4-dimethylbenzophenone in 1.0 ml of deutromethanol-d_1 was placed in an nmr tube and sealed. A spectrum of the sample was determined and the sample was irradiated in a water jacketed cell by a G.E. medium pressure lamp. The sample was removed at intervals and the nmr spectra determined. The results of the experiment are summarized in Table 5a. Spectra were observed at 2.5, 4, 7, 13, 17.5, and 42.5 hrs. Crystals of the pinacol were present in the reaction medium after 17.5 hrs.

Table 5a* Deuterium Exchange Reaction of 2,4-Dimethylbenzophenone

Hrs of Irradiation	4-Ch_3	2-CH_3**		Aromatic Protons	
0	2.42	2.39	(6)	7.16-7.92	(8)
2.5	2.42	2.39	(5.5)	7.16-7.92	(8)
4	2.42	2.39	(5.3)	7.16-7.92	(8)
7	2.42	2.39	(5.1)	7.16-7.92	(8)
13	2.42	2.39	(4.3)	7.16-7.92	(8)
17.5	2.42	2.39	(4.3)	7.16-7.92	(8)
42.5	2.42	2.39	(3.7)	7.16-7.92	(8)

* The methyl group of deuteromethanol-d_1 was taken as 3.40 ppm and other resonances are calibrated against this value.

** The methyl group at 2.39 was the peak that was diminishing and broading during the irradiation.

Exploratory Enolizations in other Ortho-Alkyl Ketones

2,6-Dimethylbenzophenone - NMR Method: A solution of approximately 0.2 g of 2,6-dimethylbenzophenone dissolved in 2 ml of 1:1 CH_3OD: hexadeuteriobenzene was prepared in a Pyrex nmr tube. The nmr spectrum of the sample was determined before irradiation and also after 45 minutes exposure at 7 inches from the 450 Watt Hanovia lamp. No spectral changes were observed.

2-o-Toluoylpyridine - Trapping Method: Attempts to utilize the dimethyl acetylenedicarboxylate trapping method as outlined above were thwarted by a vigorous "dark-reaction' which occurred on mixing the reagents. It has been reported that acetylene esters do undergo spontaneous self-condensation across the 1,2-bond of pyridine or quinoline systems.

2-o-toluoylpyridine - NMR Method: A sample prepared as described for 2,6-dimethylbenzophenone was spectrally scanned before exposure and then after exposure for 30 minutes. The integral for the methyl resonance at 2.33 ppm diminished by approximately 30% and the barely detectable O-H absorption at 4.47 ppm for the CH_3OH contaminant in CH_3OD increased considerably.

2,6-Dimethylacetophenone - Trapping Method: The reaction vessel in the Rayonet was charged with 2.0 g (0.013 moles) 2,5-dimethylacetophenone, 2.0 g (0.014 moles) dimethyl acetylenedicarboxylate and 100 ml of dry benzene. After degassing and sealing under nitrogen, the mixture was irradiated for 19 hours. The solvent was removed _in vacuo_ and spectral examination of the recovered material displayed no evidence of reaction.

2-Benzylacetophenone - Trapping Method: A solution of 0.210 g (0.950 mmoles) of 2-benzylacetophenone and 0.142 g (1.00 mmoles) dimethyl acetylenedicarboxylate in 10 ml of benzene was degassed and sealed under nitrogen. Irradiation for 24 hours at 110 mm from the General Electric lamp gave no evidence of reaction product upon spectral examination of the recovered material. Irradiation was continued for an additional 67 hours, solvent removed _in_ vacuo, and the recovered material examined by nmr spectrometry. No changes, compared to initial starting materials, could be detected. The 2-benzylacetophenone was recovered.

2-Benzyl-4'-Methylbenzophenone - Trapping Method: The exposure of an equimolar (0.47 mmoles) quantity of 2-benzyl-4'-methylbenzophenone and dimethyl acetylenedicarboxylate in 9.0 ml of benzene for 24 hours gave no evidence of photoreaction. The nmr spectrum of the recovered material displayed the expected 4.13 methylene resonance, the 2.00 methyl absorption and the methyl ester absorption at 3.15 ppm, all characterisitc of the mixed starting materials.

Photoreaction of 2,2'-Dimethylbenzophenone at 90°C

A sample composed of 0.25 g (0.0012 moles) of 2,2'-dimethylbenzophenone and 20 ml of toluene was charged to the jacketed cell of the medium pressure General Electric lamp. The sample was degassed and retained in a nitrogen atmosphere. The jacket was heated by passing steam through it. The sample was irradiated for 18 hrs. After the irradiation was complete, the sample was an intense yellow, but upon concentration and cooling no solid product was observed. The residue was taken up into a 2 ml volume of 95% ethanol and a trace amount, less than 0.05 g, of solid was isolated. The quantity was insufficient to characterize. The ethanol was removed by distillation and the ir of the residue was consistent with an authenic sample spectrum of 2,2'-dimethylbenzophenone.

Photoenolization of 2,2'-Dimethylbenzophenone

A solution composed of 1.0 g (0.0048 moles) of 2,2'-dimethylbenzophenone, 0.65 g (0.0048 moles) of dimethyl acetylenedicarboxylate and 100 ml of dry benzene was introduced into the reaction cell of the Rayonet reactor. The sample was degassed and sealed under nitrogen. The sample was irradiated for a period of 38 hrs. The solvent was removed and the residue was taken up in cyclohexane. After chilling, 0.62 g of adduct was recovered and a second crop of 0.38 g was later recovered from mother liquors. The reaction netted a total of 1.0 g (61%) reaction product. The material was recrystallized several times from cyclohexane to yield analytically pure (2 3-dicarbomethoxyl-1-(2-tolyl)-1, 4-dihydro-1-naphthol: mp 123-125°C; ir (Nujol mull) 3520 cm^{-1} (OH), 1745 cm^{-1}, 1705 cm^{-1} (ester C = O); nmr ($CDCl_3$) δ 1.75(s,3,CH_3), 3.42 (s,3,O-CH_3), 3.79 (s,3,O-CH_3), 3.95 (s,2,CH_2), 4.14-4.17 (s,1,OH) and 6.92-7.34 ppm (m, 8, aromatic protons)

Anal. Calcd for $C_{21}H_{20}O_5$: C, 72.58; H, 5.79. Found: C, 72.38; H. 5.59.

Photoenolization of 2,3'-Dimethylbenzophenone Illustrated by Trapping with Dimethyl Acetylenedicarboxylate

The well of the Hanovia 450 watt lamp was charged with 4.0 g (0.019 moles) of 2,3'-dimethylbenzophenone and 2.17 g (0.019 moles) of dimethyl acetylenedicarboxylate in 350 ml of dry benzene. The solution was flushed with nitrogen for 15 min and irradiated for 24 hrs. The benzene was removed *in vacuo*. The light yellow residue was dissolved in cyclohexane, The solution was chilled, and the adduct oiled out. The solvent was removed and the residue was taken up in a minimum amount of toluene. Flooding of the solution with hexane, afforded 0.25 g of 2,3-dicarbomethoxy-1,4-dihydro-1-(3-methylphenyl)-1-naphthol: mp 96-98°C. The filtrate yielded an additional 3.4 g of 2,3-dicarbomethoxy-1,4-dihydro-1-(3-methylphenyl)-1-naphthol.

The total yield was 3.6 g (39%) of product: mp 96-98°C; ir (Nujol mull) 3460 cm^{-1} (OH), 1740 cm^{-1}, 1700 cm^{-1} (C = O).

Anal. Calcd for $C_{21}H_{20}O_5$: C. 71.58; H. 5.72. Found: C, 71.37; H, 5.64.

Photoenolization of 2,2',4-Trimethylbenzophenone by Trapping Reaction with Dimethyl Acetylenedicarboxylate

The well of an Hanovia lamp was charged with 3.0 g (0.013 moles) of 2,2',4-trimethylbenzophenone, 2.05 g (0.014 moles) of dimethyl acetylenedicarboxylate and 350 ml of dry benzene. The reaction mixture was degassed, sealed under nitrogen and irradiated for sixteen hrs. The solvent was removed in vacuo, and the residue was taken up in cyclohexane and chilled. The solvent was decanted from the gummy residue. After several treatments of this nature a light yellow solid formed. It was recrystallized twice from cyclohexene to yield a material which had a melting range 105-112° and which separated into two components on tlc 70% benzene, 30% methanol/silica gel plate . However the sample analysed as expected and the material was presumably an isomeric mixture of 2,3-dicarbomethoxy-1,4-dihydro-1-(2-tolyl)-6-methyl-1-naphthol and 2,3-dicarbomethoxy-1,4-dihydro-1-(2,4-xylyl)-1-naphthol. This conclusion was supported by the ir and nmr spectra: ir (Nujol mull) 3460 cm^{-1} (OH), 1730 cm^{-1}, 1700 cm^{-1} (ester C = O); nmr ($CDCl_3$) δ 1.70 (s, 3, CH_3), 2.30 (S. 3, CH_3), 3.45

(S, 3, OCH_3), 3.82 (S, OCH_3), 3.93 (S, CH_2), 3.87 (very broad, OH), and 6.8-8.0 (m, 7, aromatic protons).

Anal. Calcd for $C_{22}H_{22}O_5$: C, 72.11; H, 6.05. Found: C, 72.09; H. 5.87.

Competitive Reactions

Competitive reaction of 2,4-dimethylbenzophenone

Run # 1: A solution composed of 1.0 g (0.0048 moles) of 2,4-dimethylbenzophenone, 0.67 g (0.0047 moles) of dimethyl acetylenedicarboxylate, 1.0 g (0.0167 moles) of 2-propanol and 100 ml of dry benzene was placed in the cell of the Rayonet reactor, degassed and maintained under a nitrogen atmosphere. It was irradiated for 17 hrs. After the irradiation the sample was concentrated and the resulting solid residue dissolved in cyclohexane. This treatment yielded 1.3 g (78%) of 2,3-dimethyl-6-methyl-1,4-dihydrol-1-naphthol-2,3-dicarboxylate. There was no pinacol isolated. The naphthol was identified by spectral comparison to an authentic sample previously prepared: ir (KBr pellet) 3440 cm^{-1} (OH), 1730 cm^{-1} and 1700 cm^{-1} (C = O).

Run # 2: A solution composed of 1.0 g (0.0048 moles) of 2,4-dimethylbenzophenone, 0.67 g (0.0047 moles) of dimethyl acetylenedicarboxylate, 50 ml of 2-propanol and 50 ml of benzene was placed in the reaction vessel of the Rayonet, degassed and maintained in a nitrogen atmosphere.

After ten hrs of irradiation the solution was filled with suspended crystals of the pinacol and the reaction was terminated. The solvent was removed in vacuo, and a small amount of cold 2-propanol was added. The crystals that formed were collected and dried. They were compared with authentic samples of the known pinacol. The total recovered amount of pinacol was 0.12 g (12%). The filtrate was concentrated and flooded with cyclohexane. The oily residue was heated until it formed a solution and was refrigerated overnight. The crystals were collected, dried and weighed. They represented 0.28 g (17%) of the expected naphthol and were identified by comparison of its infrared with that of an authentic sample.

Run # 3: A solution composed of 1.0 g (0.0048 moles) of 2,4-dimethylbenzophenone, 50 ml of 2-propanol and 50 ml of benzene was placed in the reaction vessel of the Rayonet reactor, degassed and maintained under a nitrogen atmosphere. The sample was irradiated for ten hrs after which time the sample contained large amounts of precipitated pinacol. These crystals were collected and dried to give 0.45 g and the mother liquor yielded an additional 0.05 g of pinacol. The total amount of pinacol was 0.50 g (50%). The residue, 0.30 g of a yellow oil, was composed mainly of the starting ketone: ir (neat) 1660 cm^{-1} (C = O).

Run # 4: A solution composed of 2.0 g (0.011 moles) benzophenone, 1.5 g (0.011 moles) of dimethyl acetylenedicarboxylate and 100 ml of 2-propanol was charged to the reaction vessel of the Rayonet reactor, degassed and held under a nitrogen atmosphere. The solution was irradiated for 24 hrs at which time exposure was terminated and the pinacol isolated on a tared filter funnel. The product was dried and weighed 1.85 g (92%). The filtrate was concentrated and 0.65 g of an adduct of the isopropyl ketyl radical and dimethyl acetylenedicarboxylate was isolated. The oily residue was not purified any further: ir (neat) 3500 cm^{-1} (OH), 1760 sh, 1740 cm^{-1} (C = O). The nmr spectrum of this compound was extremely complex and could not be consistant with any one proposed structure.

Photooxidation of 2,4-Dimethylbenzpinacol

A mixture of 1.0 g (0.0027 moles) of 2,4-dimethylbenzpinacol and 100 ml of dry benzene was placed in the reaction cell of the Rayonet reactor. The sample was degassed and kept under a nitrogen atmosphere. It was irradiated for 24 hrs. The pinacol was collected on a filter and dried. The white solid was 0.60 g (60%) recovered pinacol. The pinacol was identified by comparison of the ir and mp. The liquid products were not isolated.

Photooxidations of 2-Alkylbenzophenones

Photooxidation of 2-Methylbenzophenone

The Hanovia lamp reaction well was modified in order that air could be drawn through the reaction mixture. This system was charged with 4.0 g (0.01 moles) of 2-methylbenzophenone and 350 ml of benzene. The sample was irradiated for 9.5 hrs while air was being passed through it. The walls of the reaction vessel became coated with a yellow solid and a yellow solid was suspended in the solution. This material, (0.10 g) was recovered from the solution and reaction vessel. The filtrate was concentrated *in vacuo* to yield an oily residue. An infrared spectrum of the residue showed several broad bands in the carbonyl range and a broad band in the hydroxyl range. The residue was redissolved in ethyl ether and a yellow solid precipitated from the mixture. The small amount of solid was collected on a filter. The melting point was determined to be in the 250-270°C range. The ethereal filtrate was extracted with 50 ml of saturated sodium bicarbonate solution, water and a saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The bicarbonate wash was acidified and the product was collected to yield 0.50 g (5.8%) 2-benzoylbenzoic acid: mp 121-126°C, literature[92] mp 128°C.

The filtrate was concentrated *in vacuo* and distilled.

The recorded cut of the distillation yielded 0.25 g (6.1%) of a light yellow solid. The material was found to be 3-phenylphthalide: mp 113-116°C. A mix melting point with authentic 3-phenylphthalide showed no depression of the melting point. The 3-phenylphthalide showed a parent ion at 214 m/e in the mass spectrum bombardment: ir (Nujol mull) 1750 cm^{-1} (C = O); nmr ($CDCl_3$) δ 6.41 (S, 1, C-H) and 7.18-8.05 ppm (m, 9, aromatic protons).

The ir spectrum of the residue displayed a band at 1700 cm^{-1} which was characteristic of the aldehyde carbonyl in 2-benzoylbenzaldehyde.

Photooxidation of 2,4-Dimethylbenzophenone

A solution of 4.0 g (0.019 moles) of 2,4-dimethylbenzophenone in 350 ml of benzene was charged to the Hanovia lamp, which had been arranged to allow air to pass through the sample. The sample was irradiated for 9.5 hrs. Under these conditions a light yellow solid was deposited on the walls of the reaction vessel and suspended in the reaction medium. The solution was removed from the well and extracted with saturated sodium bicarbonate solution, water and saturated sodium chloride solution. The benzene layer was concentrated in vacuo and the residue was dissolved in a 1:1 mixture of benzene and 95% ethanol. The ethanol/benzene mixture removed in vacuo. This procedure was repeated several times to remove trace amounts of water. The residue was dissolved in ethyl ether and a trace of solid precipitated which was collected on a filter. The solid had a very high melting range, approximately 265°C, and was not characterized further. The residue was distilled, but no distinct sharp-boiling fraction resulted. Each cut showed the multiple carbonyl bands shown in the crude residue's infrared spectrum. The bicarbonate wash was acidified and a yellow-white product, 2.1 g (45%), was recrystallized several times from water yielding analytically pure 2-benzoyl-5-methylbenzoic acid: mp 149-150°C; ir(Nujol mull) 1680 cm^{-1} 1690 cm^{-1} (C = O): nmr ($CDCl_3$) δ 2.46 (S, 3, CH_3), 7.18-8.05 (m, 9, aromatic proton) and 10.60-10.81 ppm (S 1, OH).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.72; H, 5.20.

Photooxidation of 2,5-Dimethylbenzophenone

A solution of 4.0 g (0.019 moles) of 2,5-dimethylbenzophenone and 350 ml of benzene was charged to the Hanovia lamp that had been arranged to allow air to pass through the reaction vessel. The sample was irradiated for 24 hrs. The walls of the vessel were completely covered with a yellow solid and the solution contained similar suspended solid. The solution was filtered, and the filtrate was extracted by a saturated sodium bicarbonate solution, water and a saturated sodium chloride solution. The benzene was removed in vacuo and the residue was dissolved in a 1:1 mixture of benzene and 95% ethanol. The benzene/ethanol mixture was removed in vacuo and this sequence was repeated several times. The residue, 1.2 g showed the characteristic multiple carbonyl bands in its infrared spectrum at 1670 and 1690 cm^{-1} (C = O). The residue was not separated. The bicarbonate wash was acidified and the solid which formed was collected on a filter. The light tan solid, 0.35 g (7.6%) was recrystallized several times from toluene to yield analytically pure 2-benzoyl-4-methylbenzoic acid: mp 145-147°C; ir (Nujol mull), nmr ($COCl_3$) δ 2.45 (S, 3, CH_3), 7.18-8.05 (m, 9, aromatic protons) and 10.58 ppm (S, 1, OH).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H. 5.03. Found: C, 75.25; H. 5.11.

Air Oxidation of 2,4-Dimethylbenzophenone Under "Dark" Conditions

A solution of 2.0 g (0.0095 moles) of 2,4-dimethyl benzophenone was dissolved in 200 ml of benzene. The solution was charged to a three-neck flask equipped with an air inlet tube, a magnetic stirrer, and a reflux condenser. A vacuum was drawn through the condenser causing air to be drawn through the air inlet tube. The solution was protected from light by wrapping it in aluminum foil, and the air was passed through the well-stirred solution for

24 hours. After the reaction period, the solvent was removed in vacuum, and the residue, 2.0 g (100%) was identified as 2,4-dimethylbenzophenone by comparison with a sample of the authentic ketone.

Photooxidation of 2,5-Dimethylbenzophenone

A 4.0 g (0.019 mole) sample of freshly distilled 2,5-dimethylbenzophenone in 375 ml of dry benzene was charged to the well of the Hanovia lamp which had been arranged for passing air through the medium. The sample was irradiated three hrs while air continuously saturated the solution. Extraction of the mixture with 100 ml of 10% sodium hydroxide solution and 100 ml of cold water followed. The residue was concentrated *in vacuo* and a 1:1 mixture of benzene and 95% ethanol was added to the residue and removed *in vacuo*. The last procedure was repeated several times. The residue weighed 3.9 g: ir (neat) 1770 cm^{-1} (C = O), 1700 cm^{-1} (C = O), 1660 cm^{-1} (C = O). The material was redissolved in toluene and flooded with hexane to yield 0.5 g of a polymeric material of undefined mp. The toluene and hexane were removed and the residue was taken up in carbon tetrachloride. The solution was allowed to stand for 12 hrs after which time a fluffy yellow precipitate was found. Collection of the crystals afforded 0.20 g of 5-methyl-3-phenylphthalide: mp 126-132°C. The filtrate was concentrated, redissolved in 100 ml of dry benzene, transferred to the cell of the Rayonet reactor, degassed and irradiated for six hrs. Evaporating the solvent and redissolving the residue in 10 ml of carbon tetrachloride afforded and additional 0.10 g of 5-methyl-3-phenylphthalide. An ir of the residue revealed a band at 1700 cm^{-1} which is characteristic of the 2-benzoylbenzaldehyde's formyl group. The sample was dissolved in 100 ml of dry benzene, transferred to the cell of the Rayonet reactor, degassed and irradiated for an additional six hrs. Evaporation of the solvent and redissolving of the residue in 10 ml carbon tetrachloride precipitated an additional 0.15 g of 5-methyl-3-phenylphthalide. The combined total weight of phthalide was 0.45 g (12%). The material was recrystallized several times from carbon tetrachloride to yield analytically pure 5-methyl-3-phenylphthalide: mp 135-137°C; ir (Nujol mull) 1750 cm^{-1} (C = O): nmr ($CDCl_3$) δ 2.42 (S, 3, CH_3), 6.30 (S, 1, C-H), 7.25-7.37 (m, 7, aromatic proton and 7.80 ppm (d, 1, J = 7Hr, aromatic proton position 7).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.05; H, 5.24.

Photocycloaddition Reaction of 2-Benzoylbenzaldehyde

A 1.0 g (0.0048 moles) sample of 2-benzoylbenzaldehyde was dissolved in 100 ml of benzene and charged to the reaction vessel of the Rayonet reactor. The sample was deoxgenated and sealed under a nitrogen atmosphere. The sample was irradiated for 18 hrs, removed from the cell, and the solvent was evaporated. The residue was triturated with a small amount of 95% ethanol and 3-phenylphthalide precipitated from the solution as yellow crystals 0.20 g (20%): ir (Nujol mull) 1770 cm^{-1} (C = O); nmr ($CDCl_3$) 6.39 (S, 1, C-H) and 7.18-8.05 (m, 9, aromatic protons).

Photostability of 2-Methylbenzophenone and 2,3-Dicarbomethoxy-1,4-dihydro-1-(2-tolyl)-1-naphthol

A solution of 0.0389 g (0.198 mmoles) of 2-methylbenzophenone, 0.0308 g (0.087 mmoles) of 2,3-dicarbomethoxy-1,4-dihydro-1-(2-tolyl)-1-naphthol and 1 ml of benzene was placed in an nmr tube. The sample was chilled in a dry ice - chloroform bath and sealed while partially submerged. The tube was checked for leaks. The nmr spectrum was determined, and the sample was irradiated. At short intervals, the sample was removed from the cell of the General Electric lamp and its nmr spectrum determined. Table 6 tabulates the data obtained.

Photostability of 2,2'-Dimethylbenzophenone and 2,3-Dicarbomethoxy-1,4-dihydro-1-phenyl-1-naphthol

A sample of 0.0420 g (0.200 mmoles) of 2,2'-dimethylbenzophenone, 0.0460 g (0.136 mmoles) of 2,3-dicarbomethoxy-1,4-dihydro-1-phenyl-1-naphthol and 1 ml of benzene was pipetted into a nmr tube, and the tube was sealed while

Table 6**

Photolysis of 2-Methylbenzophenone in the Presences of 2,3-Dicarbomethoxy-1,4-dihydro-1-(2-tolyl)-1-naphthol in Benzene

	Adduct				Ketone	
Hours of Irradiation	4-methylene	2-carbomethoxy	3-carbomethoxy	2'-methyl	methyl*	new peaks
0	3.68 3.76 (2)	3.42(3)	3.18(3)	1.88(3)	2.30(7.2)	
22.5	3.68 3.76 (2)	3.42(3)	3.18(3)	1.88(3)	2.30(5.6)	3.50 3.58 1.2 2.08 (0.4)
47	3.68 3.76 (2)	3.42(3)	3.18(3)	1.88(3)	2.30(3.0)	3.50 3.58 1.9 2.08 (1.0)
72	3.68 3.78 (2)	3.42(3)	3.18(3)	1.88(3)	2.30(2.7)	3.50 3.58 1.7 2.08 (3.0)

* The methyl peak of the ketone was taken as 2.30 ppm. The value was taken from a spectrum of the ketone in carbon tetrachloride with tetramethylsilane as the internal standard.

** The data were reported as δ ppm and (integrated value of methyl esters).

the contents were being cooled in a dry ice - chloroform bath. The tube was checked for leaks and the nmr spectrum was determined. The sample was irradiated in the cell of the General Electric lamp. At short intervals the nmr data of the sample were determined. The nmr data are tabulated in Table 7.

Photostability of 2,2'-Dimethylbenzophenone and 2,3-Dimethyl-1,4-dihydro-1-phenyl-1-naphthol

A nmr sample composed of 0.0319 g (0.152 m moles) of 2,2'-dimethylbenzophenone, 0.0350 m moles) of 2,3-dimethyl-1,4-dihydro-1-phenyl-1-naphthol and 0.6 ml of hexadeutero-benzene was placed in a nmr tube. The tube was sealed, as described above. The nmr spectrum was determined, and the sample was irradiated in the cell of the General Electric lamp. The nmr spectra at different time intervals are tabulated in Table 8.

Photostability of 2,2'-Dimethylbenzophenone

A sample of 0.139 g (0.66 m moles) of 2,2'-dimethylbenzophenone and 1.0 ml of hexadeutrobenzene was pipetted into an nmr tube, sealed as described above and irradiated for 12 hrs. The nmr spectrum of the material was unchanged and additional exposure for five hrs also affected no evidence of reaction.

Table 7**

Photolysis of 2,2'-Dimethylbenzophenone in the presences of 2,3-Dicarbomethoxy-1,4-dihydro-1-phenyl-1-naphthol in Benzene.

	Adduct			Ketone	
Hours of Irradiation	2 carbomethoxy	3-carbomethoxy	4-methylene	Methyl*	Unknown peaks from ketone
4.0	3.40(3)	3.28(3)	3.63(2)	2.44(8.7)	
22.5	3.40(3)	3.28(3)	3.63(2)	2.44(4.5)	2.12,2.04(1.2)
47.5	3.40(3)	3.28(3)	3.63(2)	2.44(2.7)	2.12,2.04(1.6) 2.47,2.52(1)
72 hours	3.40(3)	3.28(3)	3.63(2)	2.44(1.9)	2.12,2.04(3.0) 2.47,2.52(1.2)

* The methyl peak position was taken as 2.44 ppm. The value was taken from a spectrum in carbon tetrachloride as tetramethylsilane as a standard.

** The data was reported δ and (integrated value compared to the methyl esters value).

Table 8**

Photolysis of 2,2'-Dimethylbenzophenone in the Presence of 2,3-dicarbomethoxy-1,4-dihydro-1-phenyl-1-naphthol in Hexadeuterobenzene

	Adduct			Ketone	
Hours of Irradiation	2-carbomethoxy	3-carbomethoxy	4-methylene	methyl*	unknown peaks
0	3.40(3)	3.31(3)	3.63(2)	2.44(8)	
13	3.40(3)	3.31(3)	3.63(2.6)	2.44(2.1)	1.92(1.2) 2.13(0.8)
41	3.40(3)	3.31(3)	3.63(2)	2.44(1.5)	1.92(3.0) 6.49(0.9) 6.05(2.1)
70	3.40(3)	3.31(3)	3.63(2.3)	2.44(0.7)	1.92(3.3) 6.49(1.2) 6.05(2.3)

* The methyls of the ketone were taken as 2.44 ppm. This value was taken from the ketones spectrum in carbon tetrachloride.

** Data were presented as δ ppm and (integrated intensity compared to the methyl esters).

Irradiation of 2-benzoylbenzaldehyde in Glacial Acetic Acid (Oxygen-Free).

To a solution of 0.80 g of 2-benzoylbenzaldehyde in 100 ml of glacial acetic acid was added 1 ml of concentrated hydrochloric acid. The solution was purged for 20 min with de-oxygenated nitrogen gas passed through an O_2 absorbing medium consisting of sodium anthraquinone-β-sulfonate and sodium hydrosulfite. Irradiation with the Rayonet apparatus at 3500 Å was carried out for 18.5 hours. Filtration of the reaction solution removed a small quantity of yellow polymeric material. Evaporation in vacuo produced a completely crystalline mass whose ir spectrum was virtually superimposable on that of 3-phenylphthalide. No evidence for unreacted starting material (aldehydic C-O in ir) was found. The solid was recrystallized from CCl_4 and returned 0.50 g(63%) of pure 3-phenylphthalide, mp 116-117°. Ir spectrum and melting point matched that of authentic material. The mother liquors from the recrystallization were examined by vapor phase chromatography and found to consist wholly of 3-phenylphthalide.

Irradiation of 2-benzoylbenzaldehyde in Methanol (Oxygen-Free)

A solution of 0.80 g of 2-benzoylbenzaldehyde in 100 ml of reagent grade anhydrous methanol was purged for 20 min by the de-oxygenated nitrogen stream. Irradiation for 18 hours produced a trace of yellow amorphous solid which was filtered off. The filtrate was evaporated in the cold and the crystalline residue taken up in ether. Slow evaporation precipitated 0.33 g, 41%, of the phthalide and the resulting ethereal mother liquors were extracted with aqueous sodium bicarbonate. The ether phase was concentrated to 0.32 g of oily material and was analyzed by vapor phase chromatography which revealed the presence of 28% (0.09 g) of unreated 2-benzoylbenzaldehyde, 65% (0.21 g) of 3-phenylphthalide, and 7% (0.02 g) of an unknown component. The phthalide and the 2-benzoylbenzaldehyde in these ethereal mother liquors were identified by peak enhancement with authentic materials. The total conversion to phthalide, based on initial quantity of starting 2-benzoylbenzaldehyde, was 68%.

The bicarbonate wash was neutralized with aqueous hydrochloric acid and extracted with ether. A microscopic quantity, less than 0.09 g, of material was isolated which possessed no spectral similarities to o-benzoylbenzoic acid (ir spectrum lacked the characteristic OH and C=O absorptions).

Irradiation of 2-Benzoylbenzaldehyde in Benzene (Oxygen Flushed)

A solution of 0.60 g of 2-benzoylbenzaldehyde in 100 ml of benzene was presaturated with oxygen gas for 20 min and then exposed for 18 hours in a continuously flowing oxygen stream. After evaporation of the solvent the residue was dissolved in ether and filtered from a small quantity of amorphous solid. The ether solution was washed with aqueous sodium bicarbonate, dried, and concentrated to produce 0.24 g of a semi-solid mixture. Vapor phase chromatography showed this to be a mixture of 70% (0.17 g) of 3-phenylphthalide and 30% (0.07 g) of an unidentified compound. From the sodium bicarbonate layer, by HCl neutralization and extraction with ether, were isolated 0.22 g of authentic (ir mp) o-benzoylbenzoic acid. Thus the irradiation produced 34% of o-benzoylbenzoic acid and 29% of 3-phenylphthalide.

"Dark-Reaction" Oxidation of 2-Benzoylbenzaldehyde

A solution of 0.30 g of the 2-benzoylbenzaldehyde, ml of benzene was continuously flushed with oxygen gas for 18 hours. The temperature of this "dark-reaction" was maintained at 40° in order to approximate the 37-40° temperatures which are developed in the Rayonet reaction chamber. After concentration of the benzene phase, the oily material was taken up in ether and washed with aqueous sodium bicarbonate. The ethereal phase, after separation from the bicarbonate extract, was dried and concentrated in vacuo to 0.26 g of a solid whose ir spectrum was superimposable on authentic 2-benzoylbenzaldehyde. The bicarbonate extract was neutralized with aqueous hydrochloric acid and extracted with ether. A trace material, too negligible to characterize, was isolated.

BIBLIOGRAPHY

1. G. Ciamician and P. Silber, Ber., 33, 2911 (1900), 34, 1530 (1901).
2. A. Schonberg and A. Mustafa, Chem. Rev., 40, 181 (1947).
3. A. Schonberg, "Praparative Organishe Photochmie," Springer - Verland Publishers, Berlin, 1958, pp. 109-116.
4. J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald and R. B. Martin, J. Amer. Chem. Soc., 81, 1068 (1959).
5. W. M. Moore, G. S. Hammond and R. P. Foss, ibid., 83, 2789 (1961).
6. W. M. Moore and M. D. Ketchum, J. Phys. Chem., 68, 214 (1964).
7. G. Porter and P. Suppan, Pure Appl. Chem., 9, 499 (1964).
8. S. G. Cohen, D. A. Laufer and W. F. Sherman, J. Amer. Chem. Soc., 86, 3060 (1964).
9. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, 1966, p. 308.
10. J. G. Calvert and J. N. Pitts, Jr., ibid., p. 300.
11. H. E. Zimmerman and D. I. Schuster, J. Amer. Chem. Soc., 84, 4527 (1962).
12. W. G. Herkstroefer, A. A. Lanamola and G. S. Hammond, ibid., 86, 4537 (1964).
13. A. Beckett and G. Porter, Trans. Faraday Soc., 59, 2038 (1963).
14. A. Beckett and G. Porter, ibid., 59, 2051 (1963).
15. L. H. Piette, J. H. Sharp, T. Kuwana and J. N. Pitts, Jr., J. Chem. Phys., 36, 3094 (1962).
16. J. N. Pitts, Jr. and R. M. Martin, Abstract 27B, Report to the American Chemical Society, Petroleum Research Fund (1959).

17. N. C. Yang and C. Rivas, J. Amer. Chem. Soc., 83, 2213 (1961).

18. R. Nerdel and W. Brodowski, Ber., 101, 139 (1968).

19. M. Pfau, N. D. Heindel and T. F. Lemke, C. R. Acad. Sc., Paris, 261, 1017 (1965).

20. K. F. Cohen, J. T. Pinhey and R. J. Smith, Tetrahedron Let., 1968, 4729.

21. A. Schonberg and A. Mustafa, J. Amer. Chem. Soc., 77, 5755 (1955).

22. S. Kagan, Tetrahedron Let., 1966, 6097.

23. H. A. Staab and J. Ipakschi, ibid., 1966, 583.

24. H. A. Staab and J. Ipakschi, Angew. Chem., 78, 308 (1966).

25. H. A. Staab and J. Ipakschi, Ber., 101, 1457 (1968).

26. R. F. C. Brown and R. K. Solly, Tetrahedron Let., 1966, 169.

27. P. Yates and L. Kilmurry, J. Amer. Chem. Soc., 88, 1564 (1966).

28. S. P. Pappas and J. E. Blackwell, Jr., Tetrahedron Let., 1968, 3337.

29. P. Yates, A. C. Mackay and F. X. Garneau, ibid., 1968, 5389.

30. C. Rivas and E. Pago, J. Org. Che., 32, 2981 (1967).

31. W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., "Advances in Photochemistry", Interscience Publishers, New York, 1968, p. 301.

32. E. F. Ullman and K. R. Huffman, Tetrahedron Let., 1965, 1863.

33. H. D. Becker, J. Org. Chem., 32, 2140 (1967).

34. K. Gollnick and G. O. Schenck, Pure and Appl. Chem., 9, 507 (1964).

35. A. Schonberg, Ann., 518, 299 (1935).

36. H. Kautsky, Biochem. Z., 291, 271 (1937).

37. C. S. Foote and S. Wexley, J. Amer. Chem. Soc., 86, 3879 (1964).

38. J. N. Pitts, Jr., H. W. Johnson, Jr. and T. Kawana, J. Phys. Chem., 66, 2456 (1962).

39. S. B. Cohen and R. J. Baumgraten, J. Amer. Chem. Soc., 89, 3471 (1967).

40. H. L. J. Backstrom, K. L. Appelgren and R. J. V. Niklasson, Acta. Chem. Scand., 19, 1555 (1965).

41. V. Frenzen, Ann., 633, 1 (1960).

42. K. R. Kopecky, G. S. Hammond and P. A. Leermarkers, Jr., J. Amer. Chem. Soc., 84, 1015 (1962).

43. K. Maruyama, Bull. Chem. Soc. Japan, 39, 2772 (1966).

44. A. Schonberg, "Preparative Organishe Photochemie", Springer-Verlag, Berlin, 1958, p. 109-116.

45. R. Van der Linde, J. W. Dornseiffer, J. V. Veenland and T. J. de Boer, Tetrahedron Let., 1968, 525.

46. B. Wettermark, Photochem. Photobiol., 4, 621 (1965).

47. T. Matsuura and Y. Kitaura, Tetrahedron Let., 1967, 3309.

48. H. D. Becker, J. Org. Chem., 32, 2115 (1967).

49. F. Bergman and Y. Hirshberg, J. Amer. Chem. Soc., 65, 1429 (1943).

50. P. A. Leermarkers, G. Byers, A. Lamola and G. S. Hammond, ibid., 85, 2670 (1963).

51. N. D. Heindel, Ph.D. Thesis, 1963, University of Delaware.

52. V. Ermolaev and A. Terenin, J. Chim. Phys., 1958, 698.

53. R. D. Rauh, T. R. Evans and A. Leermarkers, J. Amer. Chem. Soc., 90, 6897 (1968).

54. N. D. Heindel, J. Hetero. Chem., 3, 379 (1966).

55. D. Neckers and D. Colenbrauder, Tetrahedron Let., 1968, 5045.

56. W. E. Bachmann, J. Amer. Chem. Soc., 55, 391 (1933).

57. S. G. Cohen and W. V. Sherman, ibid., 85, 1642 (1963).

58. W. E. Bachmann, "Organic Synthesis", Coll. Vol. II, John Wiley, New York, 1943, p. 71.

59. A. D. Cross, "Practical Infra-red Spectroscopy", Butterworths, London, 1964, p. 67.

60. K. Elbs and H. Larsen, Ber., 17, 2847 (1884).

61. L. F. Fieser and E. M. Dietz, ibid., 62, 1827 (1929).

62. V. Perger, J. prakt. Chem., [2] 23, 139 (1881).

63. J. W. Cook, J. Chem. Soc., 1931, 487.

64. W. A. Henderson and E. F. Ullman, J. Amer. Chem. Soc., 87, 5424 (1965).

65. K. R. Huffman, M. Loy and E. F. Ullman, ibid., 87, 5417 (1965).

66. S. W. Benson, "Foundation of Chemical Kinetics", McGraw-Hill Co., 1960, p. 254-256.

67. W. L. Bence, C. A. Burckhardt and W. L. Yost, J. Org. Chem., 27, 2865 (1962).

68. N. D. Heindel and E. W. Sarver, Proc. W. Va. Acad. Sci., 38 2118 (1966).

69. E. M. Kosower, "Physical Organic Chemistry", John Wiley and Sons, New York, 1968, p. 24.

70. E. F. Zwicker, L. I. Grossweiner and N. C. Yang, J. Amer. Chem. Soc., 85, 2671 (1963).

71. G. Porter and P. Suppan, Proc. Chem. Soc., 1964, 191.

72. H. L. Holmes, "Organic Reactions", Vol. IV, R. Adams, ed. John Wiley and Sons, New York, 1948, p. 89.

73. N. D. Heindel and E. W. Sarver, Tetrahedron Let., 1968, 3579.

74. S. Isoe, S. BeHyeon, H. Ichikawa, S. Katsumura and T. Sakan, ibid., 1968, 5562.

75. F. Ullman, Ann. 291, 23 (1896).

76. W. A. Bonner, J. Amer. Chem. Soc., 85, 441 (1963).

77. G. Quadbeck, "Newer Methods of Preparative Organic Chemistry", Vol. 2, W. Foerst, ed., Academic Press, New York, 1963, p. 135.

78. H. L. J. Backstrom, Z. physk. Chem., B25, 99 (1934).

79. A. Ingles and H. W. Melville, Roy. Proc. Soc. (London), A218, 175 (1953).

80. C. K. Bradsher and S. Webster, J. Amer. Chem. Soc., 79, 393 (1957).

81. G. M. Badger and R. Pettit, J. Chem. Soc., 1953, 2774.

82. A. Streitwieser, Jr., L. Verbilt, and P. Stang, J. Org. Chem., 29, 3706 (1964).

83. L. C. Craig, J. Amer. Chem. Soc., 56, 231 (1934).

84. M. S. Kharash, W. Nudenberg and S. Archer, ibid., 65, 495 (1943).

85. M. S. Newman, ibid., 63, 1537 (1941).

86. H. H. Hodgson and T. A. Jerkinson, J. Chem. Soc., 1929, 469.

87. L. Gatterman, J. prakt. Chem. [2] 59, 572 (1899).

88. W. Metlesics, T. Arton, M. Chaykovsky, V. Toome and L. H. Sternbach, J. Org. Chem., 33, 2875 (1968).

89. R. Montagne and V. Charante, Rec. Trav. Chim., 31, 347 (1912).

90. K. Elbs, J. prakt. Chem., [2] 35, 475 (1887).

91. K. Elbs, ibid., [2] 35 472 (1887).

92. C. R. Rubidge and N. C. Qua, J. Amer. Chem. Soc., 36, 732 (1914).

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