Photooxidation Of Some 2-methylbenzophenones.

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PHOTOOXIDATION OF SOME 2-METHYLBENZOPHENONES

by

James Molnar

A DISSERTATION
Presented to the Graduate Faculty
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in Candidacy for the Degree of
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CERTIFICATE OF PRESENTATION

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.

James Molnar

James Molnar

CERTIFICATE OF APPROVAL

This thesis is approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Dec. 7, 1970
Date

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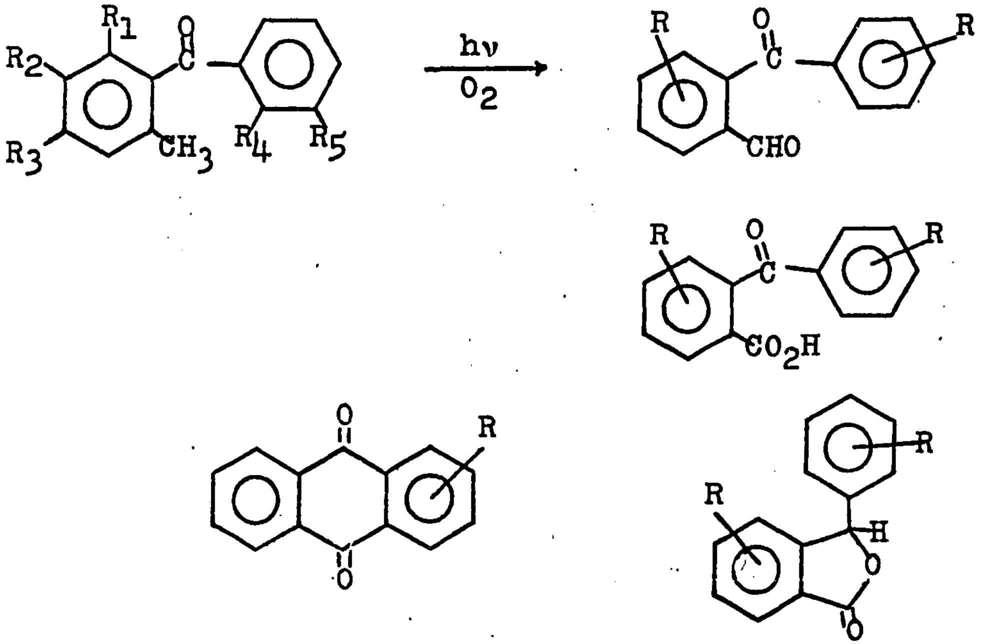
ABSTRACT

The irradiation in the presence of oxygen of 2-methylbenzophenones has been shown to lead to 2-formylbenzophenones, 2-benzoylbenzoic acids, 3-phenylphthalides, and anthraquinones. The generality of this photooxidation reaction has been demonstrated with six different 2-methylbenzophenones in benzene and in acetic acid media.



a. $R_1 = R_2 = R_3 = R_4 = R_5 = H$
b. $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = CH_3$
c. $R_1 = R_3 = R_4 = R_5 = H$, $R_2 = CH_3$
d. $R_1 = R_2 = R_3 = R_4 = H$, $R_5 = CH_3$
e. $R_2 = R_3 = R_4 = R_5 = H$, $R_1 = CH_3$
f. $R_1 = R_2 = R_3 = R_5 = H$, $R_4 = CH_3$

A mechanistic rationalization for the production of the 2-formylbenzophenones, 2-benzoylbenzoic acids, and 3-phenylphthalides has been postulated to first involve trapping of

the photo-produced enol of the original ketone by molecular oxygen and transformation of this adduct into the 2-formylbenzophenone. Photoenolization of this ketoaldehyde followed by an intramolecular cycloaddition of the resultant enol species has been suggested to explain the formation of the 3-phenylphthalides. Oxygen trapping of this enol species has been proposed as the mode of production of the 2-benzoylbenzoic acids.

The hitherto unreported formation of anthraquinones has been shown to result from a Photo-Elbs cyclization with subsequent oxidation and to require two activating wavelengths of incident light for production from the starting ketones. An attractive mechanistic pathway for anthraquinone formation can be postulated which involves anthrone as an intermediate. Independent experiments have verified the facile conversion of anthrone to anthraquinone under the same ambient conditions prevailing during the photooxidation of the initial 2-methylbenzophenones.

When the ketone photooxidations were carried out in acetic acid media, the 2-formylbenzophenones, 2-benzoylbenzoic acids, and 3-phenylphthalides were produced, but no anthraquinones were formed. This lack of quinone formation was explained by a very low steady state concentration of the photoenol species of the original ketone in this media.

The photooxidations of 2,2'- and 2,6-dimethylbenzophenone have been found to proceed readily although these materials have previously been found to be inert in photopinacolization experiments. In the case of 2,2'-dimethylbenzophenone, the concurrent photooxidation of the two methyl groups was ascertained by the isolation of the cyclic anhydride of 2,2'-dicarboxybenzophenone as a photolysis product.

A significant yield of a phthalide dimer compound has been isolated from a photooxidation experiment on 2-methylbenzophenone and its formation has been shown to be dependent on the wavelength of the incident light. This dimer was also shown to be identical to the dimeric product obtained on irradiation of 2-formylbenzophenone under an inert nitrogen atmosphere. Some mechanistic implications of these results have been put forth.

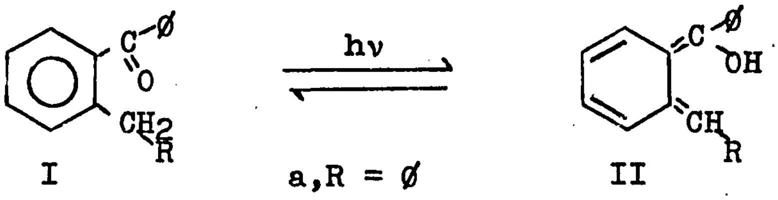
INTRODUCTION AND HISTORICAL

A. Photoenolization: Intramolecular Hydrogen Abstraction

The photoreduction of benzophenone to benzpinacol was first reported by Ciamician and Silber in 1900[1]. Since this initial discovery the synthetic utility and mechanistic aspects of the photopinacolization of alkyl aryl and diaryl ketones have been well investigated[2a,3,4a]. The literature on the photopinacolization reaction of benzophenones has been reviewed by Turro[5].

It has been amply demonstrated that substitution at the ortho position to the carbonyl group in benzophenones has a very pronounced effect on the reactivity in the photopinacolization reaction[2a,4a,5]. Pitts found that pinacol formation was completely inhibited in all cases where the substituent had a fairly labile hydrogen atom directly attached to a group in the ortho position[6]. Thus, the quantum yield of pinacol formation was observed to be 0.00 for 2-hydroxy-, 2-amino-, 2,4-dihydroxy-, and 2-monomethylamino-benzophenone. However, he also found that 2-methoxybenzophenone and 2-benzoylbenzoic acid were photoreduced in good yields[7]. The presence of an ortho hydrogen atom was blamed for inhibiting the photoreduction reaction.

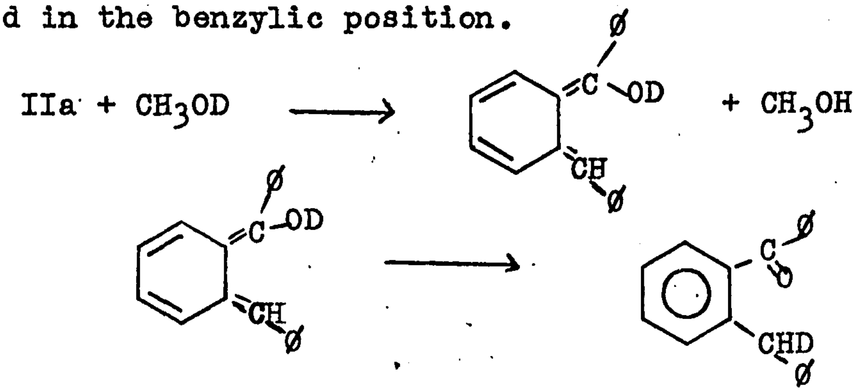
Yang found that photochemical pinacol reduction was completely suppressed in the cases of 2-methylbenzophenone and 2-benzylbenzophenone[8]. Instead, the o-alkylbenzophenone I underwent a photoactivated intramolecular hydrogen transfer to give the corresponding enol II. Thus the intermolecular hydrogen atom abstraction from solvent by the excited ketone required for photopinacolization[5] was circumvented by an intramolecular hydrogen atom abstraction process. Yang has termed this quenching process "photoenolization".



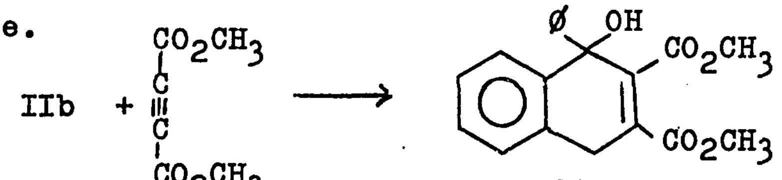
I II

a,R = ø
b,R = H

The photochemical enolization was demonstrated by two different experiments. When a solution of 2-benzylbenzophenone in CH_3OD was irradiated, the recovered ketone was found to contain 1.04-1.09 atoms of deuterium per molecule. N.m.r. spectrometry showed that all deuterium was incorporated in the benzylic position.



The photoenol of 2-methylbenzophenone was found to react in a Diels-Alder fashion with the dienophile dimethyl acetylenedicarboxylate.



III

The quantum yield of this "trapping" reaction was estimated at >0.5.

Yang and co-workers later showed by flash spectroscopy that the $n\rightarrow\pi^*$ triplet state of the 2-benzylbenzophenone was the reactive intermediate in this photoenolization reaction[9]

A similar photoenolization process was then postulated to be responsible for the lack of photopinacolization observed with the 2-hydroxy- and 2-amino-benzophenones[10,11].

The deuterium exchange method developed by Yang[8] for detecting the phenomenon of photoenolization has, along with other mechanistic studies, been applied to phenyl pyridyl ketones[12]; α,β-unsaturated ketones[13]; substituted 2-methylbenzophenones and alkyl aryl ketones[14a,15]; α-diketones[16,17]; o-phthalaldehyde[18]; derivatives of 2-benzyl-3-benzoylchromones and 2-benzyl-3-benzoyl-4-quinolones[19]; alkyl substituted acetophenones[20]; and other polyaromatic ketones[19].

The synthetic generality of Yang's[8] photoenol "trapping" procedure has been demonstrated in a variety of 2-methylbenzophenones[14b,21].

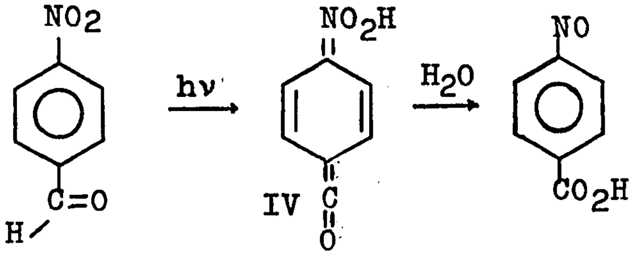
Maleic anhydride was successfully used as a dienophilic trapping agent for the photoenol of 2-methylbenzophenones[22]. An 80% yield of the expected Diels-Alder adduct was isolated. This same dienophile was used by Cohen to trap a photoenol from o-phthalaldehyde[23]. Ullman has trapped the photoenol from 2-benzyl-3-benzoylchromone with tetracyanoethylene[24].

Beckett and Porter have investigated the reasons for the low photochemical reactivity of some alkyl substituted and hydroxy-benzophenones using quantum yields, absorption spectra, luminescence characteristics, and flash photolysis[25].

The quantum yield of photoreduction for both 2-methyl and 2-ethylbenzophenone was ten times lower than that of 4-methyl and 2-t-butyl-benzophenone. The low photochemical reactivity of the 2-methyl and 2-ethyl compounds was attributed exclusively to reversible tautomerization, i.e., photoenolization. That steric hindrance of the carbonyl group by an ortho substituent with consequent suppression of the intermolecular hydrogen atom abstraction step necessary for photoreduction was not the reason for this low reactivity was indicated by the relatively high quantum yield of photoreduction observed for 2-t-butylbenzophenone (Φ disappearance of ketone = 0.5).

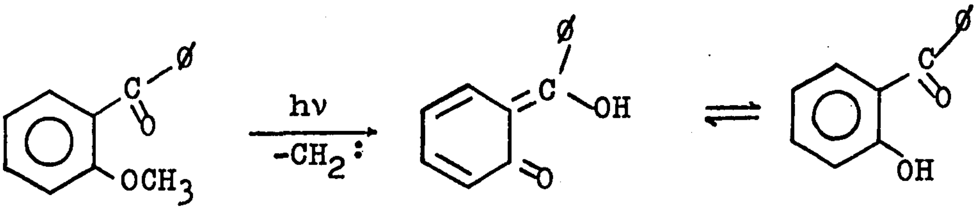
Mass spectral studies of ketones which are capable of enol-keto tautomerism have shown that the excited enol- and keto-molecules exhibit different fragmentation patterns and that the observed mass spectrum of such an enolizable ketone can be interpreted as coming from a mixture of the two different tautomers[26]. Numerous acylic 1,3-diketones[26,27,28] have been studied in this manner and investigations on substituted benzophenones[29,15] have also been reported.

The photochromic behavior of a large variety of organic systems has been interpreted in the light of reversible photoenolization processes[30,19]. For example, the photochromic properties of ortho-nitrobenzyl derivatives have been shown to be due to a reversible photoinduced hydrogen abstraction[31,32,33]. The well known photoisomerization of o-nitrobenzaldehyde to o-nitrosobenzoic acid has been postulated to proceed via a similar enolic intermediate[2b]. Recently the enolic structure IV has been suggested as a transient in the related photoisomerization of p-nitrobenzaldehyde to p-nitrosobenzoic acid[34].



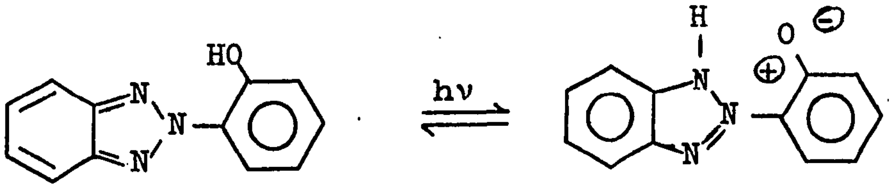
This reaction was much less efficient than the analogous reaction of o-nitrobenzaldehyde.

The photochemical demethylation of some 2-methoxybenzophenones has been reported[35]. A photoinduced hydrogen abstraction was proposed as a mechanistic pathway.



Intramolecular hydrogen abstraction and other photochemical atom abstractions have been treated by Neckers[4b].

The photochemical stability of the 2-hydroxybenzophenones has resulted in their use as ultraviolet absorbers for polymers[36]. All the presently known effective benzophenone stabilizers possess a 2-hydroxy substituent. Derivatives of 2-(2'-hydroxyaryl)benzotriazole V are also used as photostabilizers and the mechanism of their protection is believed to be an analogous photoenolization[36].



V

B. Photooxygenation of Olefins and Dienes

Photooxygenation is a reaction in which a substrate A in the presence of molecular oxygen and light is converted into the addition product AO_2[37]. The reaction may be a direct process where light is absorbed by A or O_2 or the process may be indirect, i.e., photosensitized, where light is absorbed by a photosensitizer and not directly by A or O_2[37].

Photooxygenation reactions have been arbitrarily but conveniently classified into two different processes according to the type of intermediates involved in these reactions. When free radicals and electronically excited molecules are involved, the reaction is designated as a type I process. Reactions in which only electronically excited molecules occur as intermediates are classified as type II processes[37,38,39].

Extensive research has been carried out on photooxygenation reactions and several excellent reviews have appeared. Type I and type II direct and indirect processes have been discussed with emphasis on mechanisms[40]. Type II photosensitized oxygenation reactions have been reviewed by Gollnick[37,41a]. Type II direct reactions of polycyclic aromatics are summarized by Bowen[42]. Direct photooxygenation reactions are also treated by Hochstrasser and Porter[43].

For the preparative aspects of type II direct and indirect photooxygenations of dienes, the reviews by Gollnick and Schenck[44] and Arbuzov[45] should be consulted.

Type I processes involve free radicals and chain reactions. Quantum yields are usually greater than unity and inversely proportional to the square root of the light intensity[40]. Quantum yields for type II photooxygenation reactions are not greater than unity and independent of the absorbed light intensity[40].

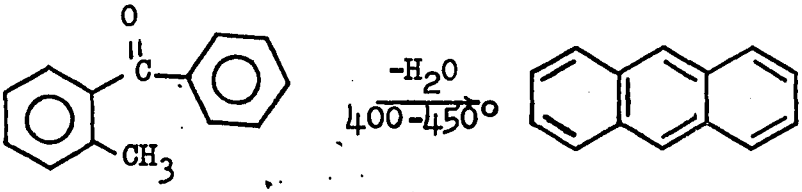
Regarding type II processes, the primary species which is activated could be either molecular oxygen or the substrate. Thus an oxygen-activation mechanism and an acceptor or substrate-activation mechanism are possible. In each of these possible mechanisms a complex of the primary excited species (A or O_2) could also be involved[37]. In the type II photooxygenation reactions of polycyclic aromatics, aryl substituted carbo- and heterocyclic pentadienes, cyclic 1,3-dienes, furans, and olefins, the oxygen-activation mechanism has been found to be operative[37].

The oxygen-activation mechanism is further complicated by the state of the "activated oxygen" involved. The ground state of molecular oxygen is a triplet and is designated $^3\Sigma$[41b]. There are two electronically excited singlet states of oxygen located 22.5 kcal and 37.5 kcal above the ground state. The lower state is designated $^1\Delta$ and the higher one is referred to as $^1\Sigma$. The role of each excited singlet state in oxygenation reactions has not yet been fully elucidated and these two excited states are referred to as singlet oxygen[41b]. Various aspects including reactions of singlet molecular oxygen have been extensively treated in several excellent reviews[41a-e,46,47,48].

In the oxygen-activation mechanism, Schenck[39] proposes that triplet oxygen is involved whereas Foote[48] has accumulated a considerable body of experimental evidence for the participation of singlet oxygen. Foote has found that the chemistry of chemically generated singlet oxygen is identical with that of the reactive intermediate in the photosensitized oxygenation of olefins and dienes[48].

C. Elbs Reaction

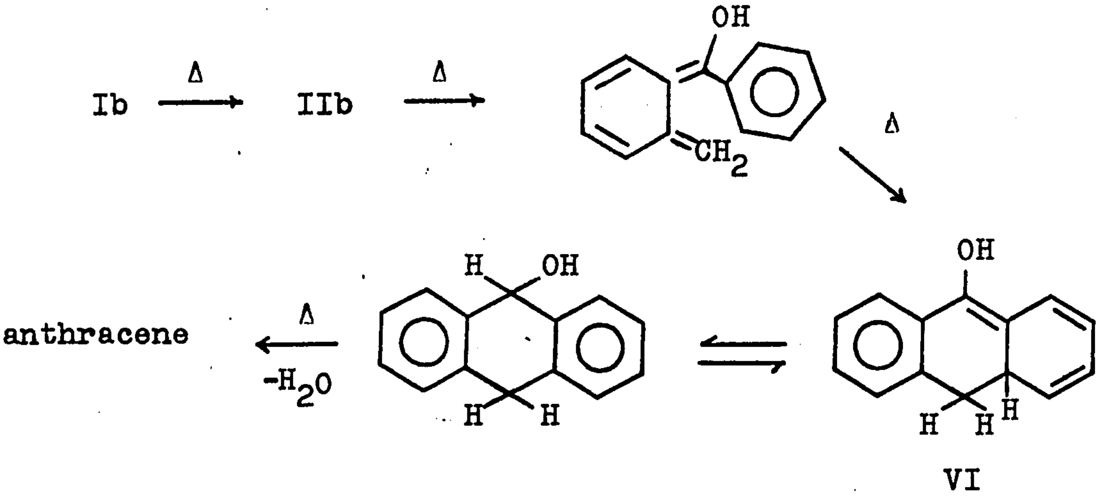
Diaryl ketones containing an ortho methyl or methylene substituent can be cyclized on pyrolysis to afford generally low yields of the corresponding anthracene derivative.



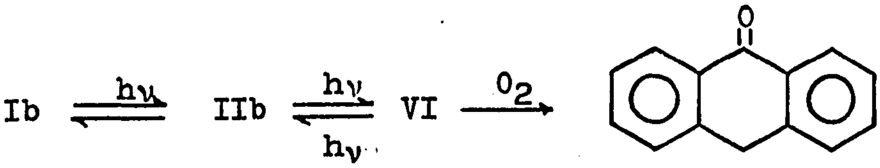
This reaction has been called a "cyclodehydration process" since water is lost and a new ring is formed. Elbs discovered the reaction in 1884 and was first to investigate its generality and synthetic uses[49]. The reaction has been reviewed by Fieser[50].

The general experimental procedure is to heat the ketone without catalyst or solvent at the reflux temperature or at a temperature between 400 and 450° until the evolution of water ceases. Considerable carbonization usually occurs, but the reaction can be used to prepare polycyclic aromatic hydrocarbons not available by other known methods.

The mechanism of this high-temperature pyrolysis has never been fully elucidated. Early workers had suggested that 9,10-dihydro-9-anthranol VI was an intermediate in the reaction[51,52,53]. The formation of this dihydroanthranol was believed to arise by tautomerization of the original ketone to an enolic form which then underwent internal ring closure and a subsequent tautomerism. Hydrocarbon product formation was completed by dehydration. This process is shown below.



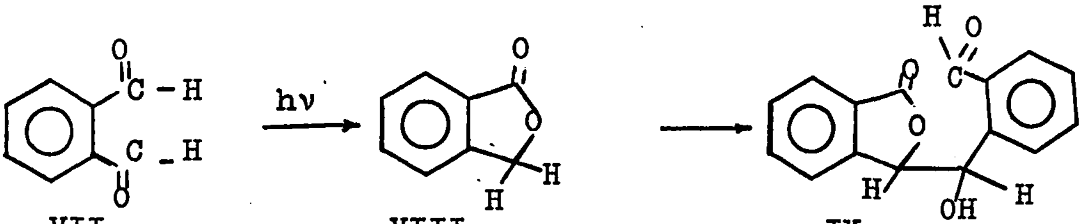
Flash irradiation studies of 2-methylbenzophenone by Ullman have demonstrated that the cycloaddition compound VI can be generated (but not isolated) in a reversible photochemical process, and this work constitutes the first example of a photochemical Elbs reaction[54]. The following sequence of reactions was proposed.



When the previously irradiated solution was exposed to oxygen, it was possible to isolate about a 1% yield of anthrone. Ullman has also uncovered similar photochemical Elbs reactions during irradiation of 2-benzyl- and 2-benzhydryl-3-benzoylchromones[55].

D. Photocyclodimerization - Phthalide Formation

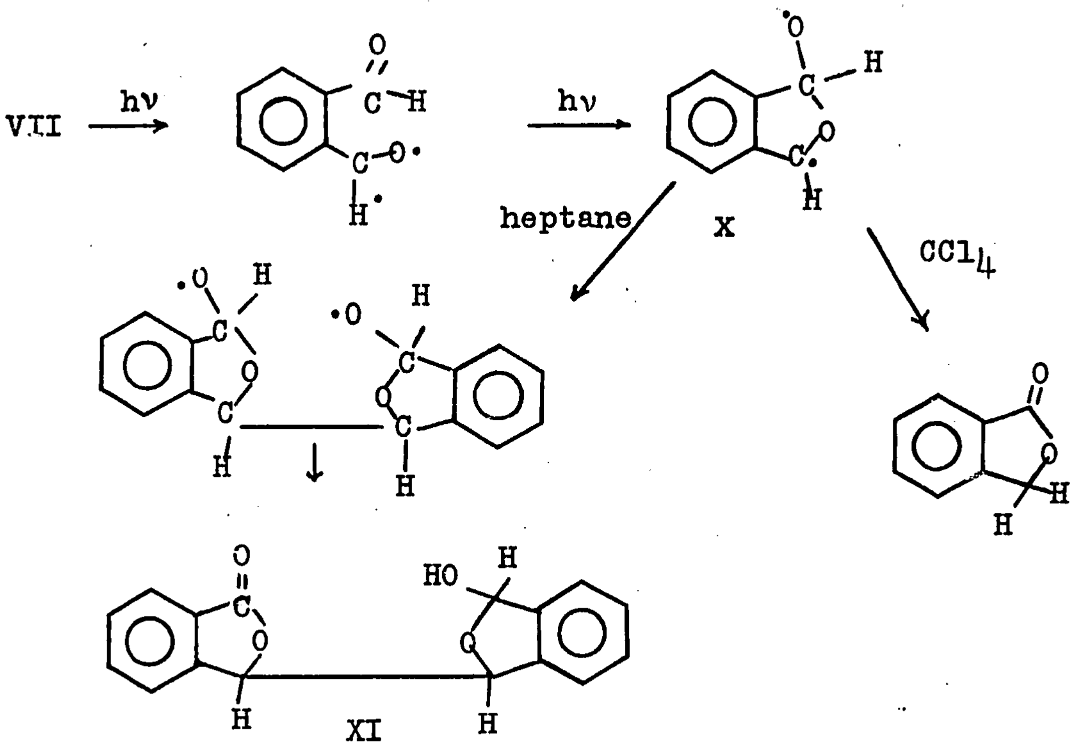
A photodimer, believed to be structure IX, was isolated by Schönberg and Mustafa from an irradiation of ortho-phthalaldehyde[56].



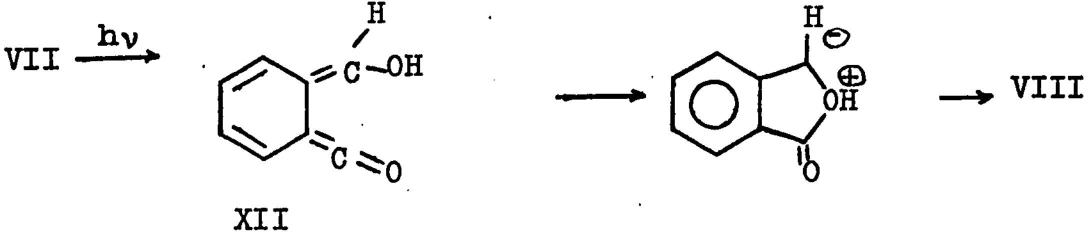
VII VIII IX

Phthalide VIII was proposed as an intermediate but was not isolated.

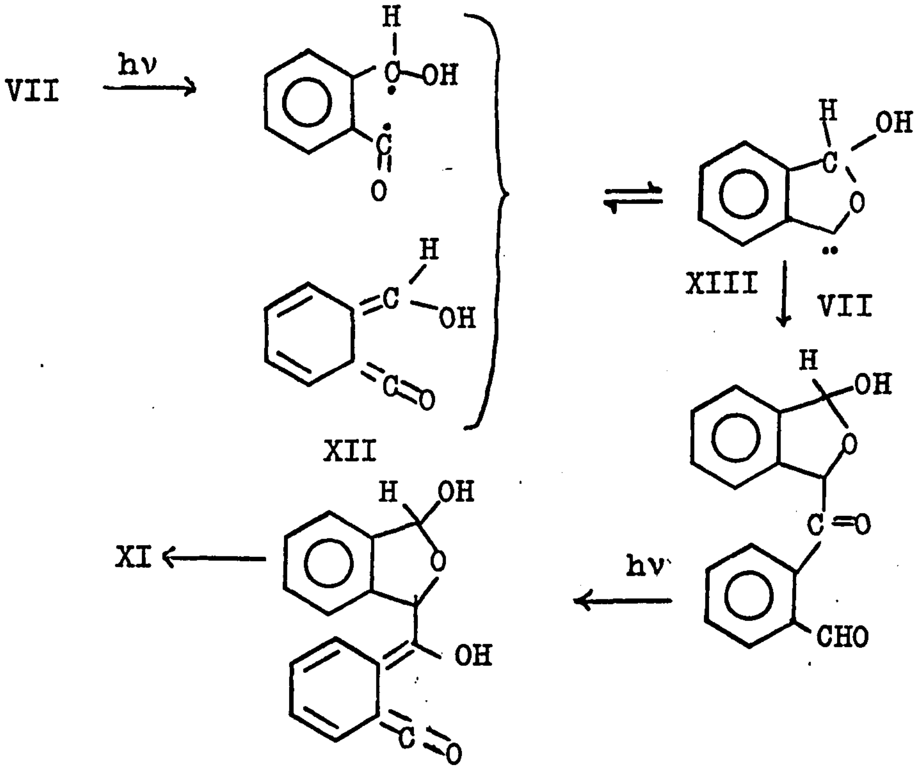
The reaction was reexamined by Kagan who obtained the same dimeric substance but for which he proposed the structure XI on the basis of spectroscopic data[57]. Phthalide VIII was isolated from another photolysis of ortho-phthalaldehyde in carbon tetrachloride. A possible mechanism to explain these solvent dependent results was presented:



Further investigations into phthalide VIII formation were conducted by Pappas and Blackwell[18]. Their results from photolyses of ortho-phthalaldehyde in deuterated solvents were interpreted on the basis of an ionic intramolecular ring closure of an initial photogenerated ketene XII and the data were taken to indicate the absence of any radical mechanism. This pathway is depicted below:



Cohen and his co-workers[23] have found that the dimerization of ortho-phthalaldehyde is stereospecific. Photoenolization of the aldehyde to give the ketene XII which then undergoes cyclization to the carbene XIII has been proposed. Insertion of the carbene XIII into an aldehydic C-H of VII and subsequent photoenolization and ring closure of the adduct would account for the formation of the dimer XI.



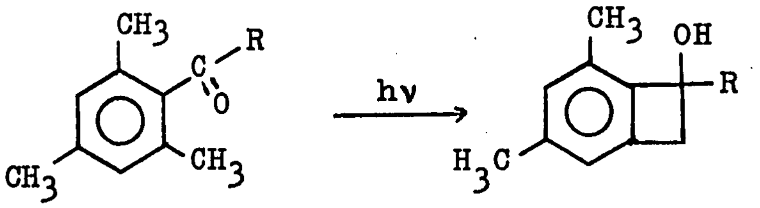
The ketene intermediate was trapped in a Diels-Alder reaction with maleic anhydride.

A related dilactone compound has been obtained from irradiation of 1-methylanthraquinone in the presence of oxygen[58]. This work will be discussed later during the treatment of the photooxidation of 2,6-dimethylbenzophenone.

E. Cyclobutanol Formation

The formation of cyclobutanols from ketones bearing γ-hydrogen atoms is a well known photochemical reaction[59,60].

The first example of cyclobutanol formation from alkyl o-methylphenyl ketones was reported by Matsuura and Kitaura[61,15].



Photolysis of some 1-(o-alkylphenyl)propane-1,2-diones has been shown to lead to hydroxycyclopentenone derivatives[62]. It was proposed that initial hydrogen abstraction leads to a triplet biradical which photocyclizes to a cyclobutanol transient and does not give a photoenol intermediate. Ring expansion of the cyclobutanol then gives the observed products.

A similar reaction was described for 2-hydroxy-4,6-di-t-butylbenzophenone[63].

RESULTS AND DISCUSSION

The sensitized photooxygenation of alicyclic, aromatic, and heterocyclic homoannular 1,3-dienes to give cyclic peroxides is a well documented reaction and has been extensively studied (see Introduction). The cyclic peroxide products can be viewed as structurally analogous to the 1,4-cycloaddition adducts formed with dienophiles in the Diels-Alder reaction. The same homoannular 1,3-dienes undergo the Diels-Alder reaction with a variety of dienophiles. By this analogy, the photooxygenation of the 1,3-diene systems can be regarded as a photoinduced Diels-Alder reaction in which molecular oxygen acts as a dienophile[45].

The photooxidation of 2-methylbenzophenones reported in this study is believed to proceed via a photochemical Diels-Alder type reaction in which molecular oxygen acts as a dienophile. However, the 1,3-diene system is not initially present in the reaction but is formed *in situ* by photochemical means. The 1,3-diene system is the photoenol of the starting ketone.

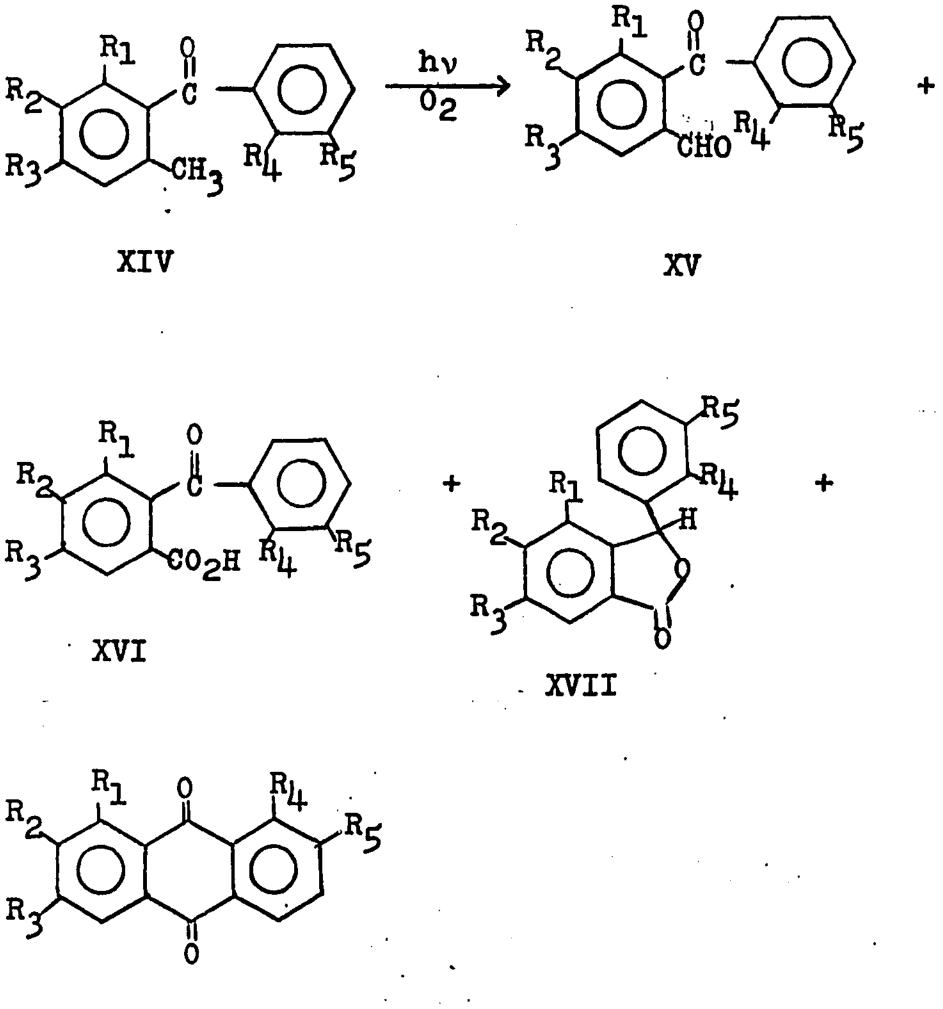
The photooxidation of 2-methylbenzophenones was first reported by Sarver[14c,64]. The irradiation of a benzene solution of 2-methylbenzophenone which was continuously saturated with air led to the formation of 3-phenylphthalide and 2-benzoylbenzoic acid. The acid formation represents the oxidation of the 2-methyl group to a carboxyl function while phthalide formation represents this mode in addition to concomitant reduction of the ketonic carbonyl to the hydroxyl state. Two additional examples of this reaction were obtained. An irradiation-aeration of 2,5-dimethylbenzophenone under the same conditions gave 5-methyl-3-phenylphthalide and 2-benzoyl-4-methylbenzoic acid while 2,4-dimethylbenzophenone yielded 2-benzoyl-5-methylbenzoic acid. In this latter case no corresponding phthalide was isolated but its presence in the photolysis mixture was inferred from spectral evidence. All photoreaction products were found to be identical with authentic samples prepared by literature methods.

In the present study the generality of this photooxidation reaction has been demonstrated with six different 2-methylbenzophenones in benzene and in glacial acetic acid media. In addition a more detailed qualitative and quantitative product analysis has been accomplished which has provided further insight into the reaction mechanism.

Yields of oxidation products resulting from the photolysis-aerations of six 2-methylbenzophenones (Scheme 1) are reported in Tables 1-3. A benzene or glacial acetic acid solution of the ketone was irradiated in a flowing air stream. The two different light sources used were a broad-spectrum medium pressure quartz mercury-vapor lamp (Hanovia 450W) and a Rayonet reactor equipped with 350 nm lamps. All irradiations were performed in Pyrex glassware.

Scheme 1

Photooxidation of 2-Methylbenzophenones



XIV XV XVI XVII XVIII

2-Methylbenzophenones, XIV

2-methyl- $R_1 = R_2 = R_3 = R_4 = R_5 = H$

2,4-dimethyl- $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = CH_3$

2,5-dimethyl- $R_1 = R_3 = R_4 = R_5 = H$, $R_2 = CH_3$

2,3'-dimethyl-$R_1 = R_2 = R_3 = R_4 = H$, $R_5 = CH_3$

2,6-dimethyl- $R_2 = R_3 = R_4 = R_5 = H$, $R_1 = CH_3$

2,2'-dimethyl-$R_1 = R_2 = R_3 = R_5 = H$, $R_4 = CH_3$

Table 1

PHOTOOXIDATION OF 2-METHYLBENZOPHENONES AT 350 nm (RAYONET)

Ketone XIV Irradiated	Initial Ketone Concentr. M	Solvent	Soln. Vol. ml	Reaction Time hr.	Product Distribution, % Yield*				Recovered Ketone XIV %
					XV %	XVI %	XVII %	XVIII %	
2-methyl	0.073	benzene	350	30	**40	13	24	absent	1
2-methyl	0.19	glacial acetic acid	130	24	7	1	2	absent	90
2,4-dimethyl	0.082	benzene	350	67	⊛ **12	43	24	absent	7
2,4-dimethyl	0.068	benzene	350	72	16	45	17	absent	6
2,4-dimethyl	0.095	benzene	350	114	8	35	30	absent	6
2,4-dimethyl	0.15	glacial acetic acid	160	24	8	5	9	absent	76
2,5-dimethyl	0.068	benzene	350	30	⊛ **41	12	36	absent	5
2,5-dimethyl	0.15	glacial acetic acid	160	24	12	3	9	absent	72

*Based on starting ketone and calculated from glpc peak areas. Yield of acid (XVI) calculated from weight of acid isolated.

⊛ Product mixture was later extracted with $NaHSO_3$ solution and reanalyzed by glpc - see Experimental section.

**Product mixture was later subjected to an extended irradiation under nitrogen - see Experimental section.

Table 2

PHOTOOXIDATION OF 2-METHYLBENZOPHENONES IN BENZENE WITH THE HANOVIA LAMP***

Ketone XIV Irradiated	Initial Ketone Concentr. M	Soln. Vol. ml	Product Distribution, % Yield*					Recovered Ketone XIV
			XV %	XVI %	XVII %	XVIII %	Other⊕ %	%
2-methyl	0.087	220	⊛ 8	18	23	30		2
2,4-dimethyl	0.082	350	8	21	23	31		12
2,5-dimethyl	0.082	350	15	12	19	41		8
2,3'-dimethyl	0.068	430	⊛ 11	10	43	22		4
2,3'-dimethyl	0.077	220	9	7	34	16		15
2,6-dimethyl	0.087	200	⊛ 6	none found	17	none found	8(++)	62
2,2'-dimethyl	0.077	220	⊛ 7	7**	45	none found	9*	3

***All photolyses of 24-hour duration.

*Based on starting ketone and calculated from glpc peak areas. Yield of acids (XVI) calculated from weight of acid isolated.

**Assumed to be 2-(2-methylbenzoyl)benzoic acid.

⊕Other products found: (++) = 1-anthraquinone carboxylic acid; *anhydride of benzophenone-2,2'-dicarboxylic acid XXV.

⊛ Product mixture was later extracted with NaHSO$_3$ solution and reanalyzed by glpc - see Experimental section.

Table 3

PHOTOOXIDATION OF 2-METHYLBENZOPHENONES IN GLACIAL ACETIC ACID WITH THE HANOVIA LAMP

Ketone XIV Irradiated	Initial Ketone Concentr. M	Soln. Vol. ml	Reaction Time hr.	Product Distribution, % Yield*					Recovered Ketone XIV %
				XV %	XVI %	XVII %	XVIII %	Other** %	
2-methyl	0.072	350	24	4	30	51	absent		5
2,5-dimethyl	0.068	350	24	3	36	52	absent		6
2,4-dimethyl	0.082	350	24	2	32	37	absent		24
2,3'-dimethyl	0.068	430	24	2	9	21	absent		62
2,6-dimethyl	0.082	350	24	3	11***	13	none found		73
2,6-dimethyl	0.082	230	48	1	29***	26	none found		40
2,6-dimethyl	0.077	430	144	8	1***	79	none found		absent
2,2'-dimethyl	0.068	430	24	5	6***	30	none found	trace*	54

*Based on starting ketone and calculated from glpc peak areas. Yield of acid (XVI) calculated from weight of acid isolated.

**Other products found: *anhydride of benzophenone-2,2'-dicarboxylic acid XXV.

***Assumed to be the expected 2-benzoylbenzoic acid.

The standard analytical procedure for all photo-reaction mixtures first involved removal of the reaction solvent followed by dissolution of the residue in benzene or toluene. The mixture was then thoroughly extracted with sodium bicarbonate solution and the acidic reaction products were precipitated on acidification of the aqueous layer and identified. Products in the organic phase were analyzed by gas phase chromatography using authentic materials prepared by literature methods for peak enhancement whenever possible.

The phthalides and the 2-benzoylbenzoic acids derived from 2-methyl-, 2,4-dimethyl-, and 2,5-dimethylbenzophenone have previously been reported[14c,64] except for the phthalide from 2,4-dimethylbenzophenone. Other hitherto unreported major products from these materials are the 2-benzoylbenzaldehydes and the anthraquinones.

Identification of 2-Formylbenzophenones and 3-Phenylphthalides

A very marked qualitative similarity was apparent among the gas phase chromatographic analyses of the irradiation-aeration product mixtures from all six 2-methylbenzophenones. The gas chromatogram of each photolysis product mixture displayed three major peaks whose ratio of retention times was approximately 1:2:2:5. The peak of the shortest retention time was unequivocally demonstrated for all six ketones studied to be due to the unreacted starting 2-methylbenzophenone by peak enhancement gas chromatography.

The component producing the middle peak was positively ascertained in only one case, namely that of 2-methylbenzophenone. This peak was enhanced by the addition of authentic

2-formylbenzophenone to the photolysis product mixture. When the analysis was carried out with a gas chromatograph whose outlet was connected to the inlet of a mass spectrometer[65], the middle peak gave the expected molecular ion of 2-formylbenzophenone at m/e 210 in the mass spectrum. This mass spectrum was identical to that of authentic 2-formylbenzophenone. Therefore this case represents the first positive evidence for the intermediacy of 2-formylbenzophenones in the photooxidation reaction of 2-methylbenzophenones. Sarver[14c,64] had postulated the intermediacy of these keto-aldehydes from infrared spectral evidence and allied experiments, but had never isolated any of these intermediates from a photooxidation reaction. Sarver claimed that the aldehydic carbonyl absorption at 1700 cm^{-1} in the infrared spectrum of 2-formylbenzophenone served as a fingerprint to detect this component in reaction product mixtures. However, in the present study this was found not to be a generally reliable method since in only a few photoproduct mixtures was a clear-cut absorption at 1700 cm^{-1} in the infrared spectrum noted. This infrared method, however, worked well with the phthalide products which displayed intense absorptions at 1750 - 1770 cm^{-1}.

Authentic samples of the other five 2-formylbenzophenones were not available and the intermediacy of these materials in the photooxidation reaction could not be directly ascertained by peak enhancement. However, a considerable body of evidence has been accumulated based on related experiments and mechanistic logic which tends to support the assignment of this middle peak in the gas chromatograms to the 2-formylbenzophenones. This evidence will now be discussed.

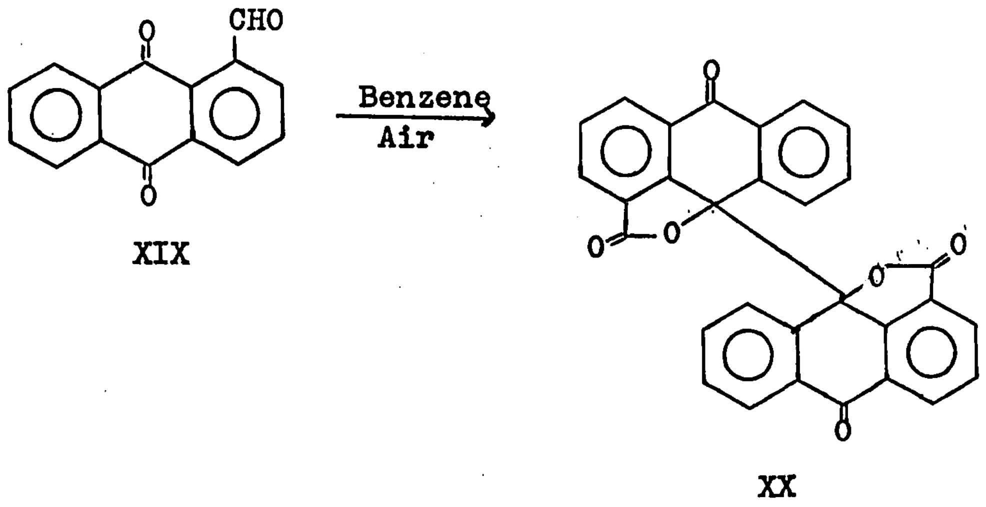
An irradiation-aeration product mixture from 2,4-dimethylbenzophenone was analyzed by gas chromatography-mass spectrometry[65] as per the case of 2-methylbenzophenone treated earlier. A molecular ion at m/e 224 appeared in the mass spectrum of the middle peak in the gas chromatogram which is correct for the expected 2-formyl-4-methylbenzophenone. The mass spectrum is similar to that of 2-formylbenzophenone and is consistent with the ketoaldehyde structure[66]. Peaks were observed at 209 (loss of CH_3), 195 (loss of CHO), 147 (loss of phenyl), 119 (loss of benzoyl), and 105 (loss of aryl, C_8H_7O).

A well known qualitative organic analysis procedure for the identification of aldehydes is the formation of crystalline bisulfite addition compounds[67,68]. Most aldehydes, alkyl methyl ketones, and cyclic ketones react with sodium bisulfite solution to furnish these derivatives. Aromatic ketones and especially benzophenones do not yield addition compounds. Therefore it would seem to be possible to selectively remove the 2-formylbenzophenone from the photolysis product mixture by treatment with a sodium bisulfite solution. The chromatographic peak due to the 2-formylbenzopheonone should have disappeared or at least diminished in relative intensity after this treatment.

In order to test this hypothesis, the sodium bisulfite derivation reaction was first tried on a solution of pure 2-formylbenzophenone. Gas chromatographic analysis of the solution before and after bisulfite treatment showed that the 2-formylbenzophenone concentration was substantially reduced. A photolysis product mixture from 2-methylbenzophenone was now subjected to the same treatment with sodium bisulfite. Gas chromatographic analysis of the product mixture before and after bisulfite treatment again showed that the 2-formylbenzophenone concentration was substantially reduced. The 3-phenylphthalide and 2-methylbenzophenone components were apparently not affected.

The bisulfite treatment was applied to the product mixture obtained from the photolysis-aeration reaction of each of the other five 2-methylbenzophenones studied. For each ketone reaction product gas chromatographic analysis showed that the middle peak had disappeared or at least had been measurably diminished after the bisulfite extraction treatment. By analogy with the 2-methylbenzophenone case these results then affirm the assignment of the middle peak in the gas chromatograms to the respective 2-formylbenzophenones. As has been previously indicated, ample precedent exists to expect these aldehydes to be photo-labile.

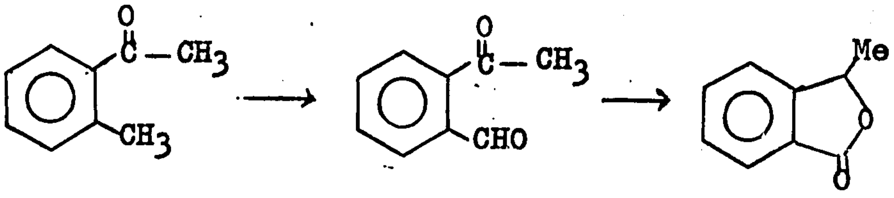
The photolysis of o-phthalaldehyde has been reported to give rise to phthalide[57,18,23]. 1-Formylanthraquinone XIX has been found to yield the related phthalide compound XX on irradiation[58] and in the same work 1-methylanthraquinone



XIX

XX

on photooxidation also gave compound XX via 1-formylanthraquinone as an intermediate. In addition, the photooxidation of 2-methylacetophenone XXI to 3-methylphthalide XXIII was reported[58] to proceed via the intermediate 2-formylacetophenone XXII.



XXI XXII XXIII

The intermedicacy of 2-formylbenzopheone in the photolysis-aeration of 2-methylbenzophenone to yield 3-phenylphthalide is therefore suggested from these reports. This led Sarver[14c,64] to irradiate a solution of 2-formylbenzophenone in a nitrogen atmosphere. A quantitative yield of 3-phenylphthalide was obtained and this aldehyde to phthalide conversion was demonstrated to be non-oxidative since oxygen was carefully excluded from this photolysis. In the presence of oxygen, 2-benzoylbenzoic acid was produced in addition to the 3-phenylphthalide. The conversion to 2-benzoylbenzoic acid was found to be a light induced process since aeration of 2-formylbenzophenone in the dark gave none of this acid. Further experiments by Sarver[14c] and in the present study have conclusively shown that photolysis of 2-formylbenzophenone under conditions identical to those present during the photooxidation of the parent ketone gives rise to the same products, namely 3-phenylphthalide and 2-benzoylbenzoic acid, which were obtained from the photooxidation of 2-methylbenzophenone. As has already been discussed, 2-formylbenzophenone has been identified as a product in the photooxidation of 2-methylbenzophenone. Thus these results firmly indicate that the phthalide product found in the ketone photooxidation arises from the 2-formylbenzophenone intermediate via a photoinduced non-oxidative pathway.

An experiment was undertaken to provide some information about the relative rates of formation of the 2-formylbenzophenone and 3-phenylphthalide during the photooxidation of 2-methylbenzophenone. A glacial acetic acid solution of the ketone was photolyzed in a flowing air stream for 17 hours. Small aliquot samples of the solution were removed every half hour and were analyzed by gas phase chromatography. After less than one hour had elapsed, 2-formylbenzophenone and 3-phenylphthalide products were evident. The ketoaldehyde persisted as the major product during the first five hours of the reaction after which time the phthalide became and remained as the major product for the duration of the photolysis. The 3-phenylphthalide concentration increased throughout the photolysis, but the concentration of the ketoaldehyde appeared to have achieved a steady state value after about five hours of reaction. A large excess of starting ketone was present throughout the photolysis. That a steady state rather than a constantly increasing concentration of ketoaldehyde was observed would seem to indicate that the ketoaldehyde is being consumed by further chemical reactions, i.e. phthalide and o-benzoylbenzoic acid formation, at a rate comparable to its formation.

The photooxidation of 2,5-dimethylbenzophenone in glacial acetic acid and in benzene solvent was followed by the same method as was applied to 2-methylbenzophenone above. The results obtained were very similar to those of 2-methylbenzophenone. Products were detected in about one-half hour of reaction time. The phthalide concentration increased throughout the course of the reaction, but the aldehyde concentration reached a steady state value after approximately five hours in glacial acetic acid and three hours in benzene. The concentrations of the phthalide and aldehyde were roughly equivalent after nine hours of reaction in benzene and five hours in glacial acetic acid.

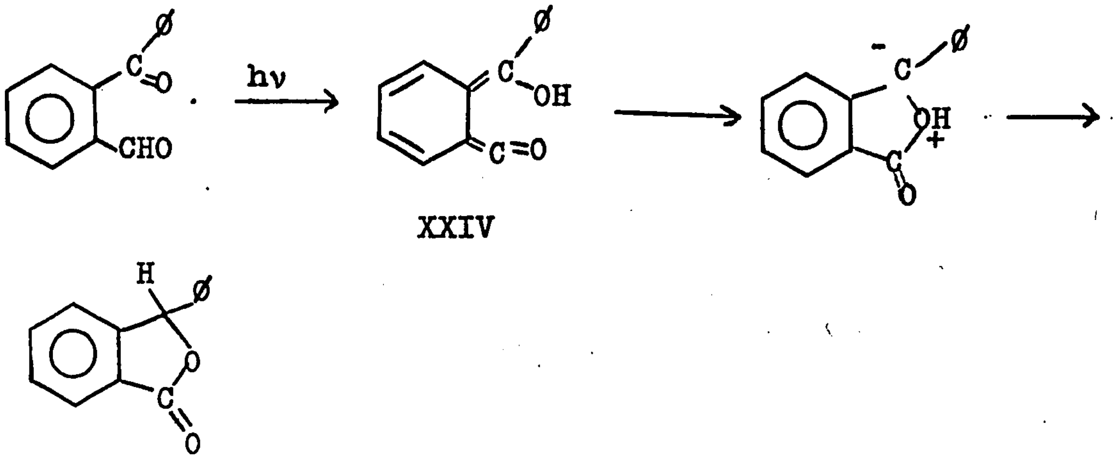
The photooxidation of 2,6-dimethylbenzophenone in glacial acetic acid was also monitored for 21 hours by periodically removing aliquot samples. Again the concentration of the phthalide product showed a progressive increase throughout the course of the photolysis. The aldehyde again exhibited a steady state behavior, this state having been achieved after about seven hours of reaction. The slower rate of disappearance of this ketone was also evident. The appearance of products and the disappearance of ketone occurred more slowly than in the identical 2-methyl- and 2,5-dimethylbenzophenone photolyses. Tables 2 and 3 also show that a considerable quantity of ketone was recovered from the photooxidations.

Further confirming experiments concerning the keto-aldehyde to phthalide conversion were conducted with 2-methyl-, 2,4-, and 2,5-dimethylbenzophenone. A benzene solution of 2-methylbenzophenone was irradiated in a flowing air stream for 30 hours at 350 nm. The product mixture composition of this reaction is reported in Table 1. Separate portions of this product mixture were photolyzed (350 nm) under a nitrogen atmosphere in benzene and in acetic acid-1% hydrochloric acid solution. The two product mixtures were analyzed by gas chromatography. The ratio of 3-phenylphthalide to 2-formylbenzophenone in the product mixture from the photolysis in benzene was 2 to 1 which is just the reverse of the value of this ratio reported in Table 1. The product mixture from the photolysis in acetic acid-1% hydrochloric acid contained no 2-formylbenzophenone, only 3-phenylphthalide. These findings are in agreement with observations made by Cohen[23] and Sarver[14c-d]. Cohen[23] found that the generation of phthalide from o-phthalaldehyde was most efficient in acetic acid solution containing 1% hydrochloric acid. Using the same solvent system Sarver[14c-d] obtained a quantitative yield of 3-phenylphthalide from 2-formylbenzophenone while at equivalent conditions in benzene only a 20% yield of the phthalide product was produced. In methanol the yield was 68%[14d].

Aliquot samples of the photooxidation product mixture from 2,5- and from 2,4-dimethylbenzophenone were also further irradiated under nitrogen in benzene and in acetic acid containing 1% hydrochloric acid. After such extended irradiations of each product mixture in benzene the aldehyde concentration was greatly diminished while in acetic acid-1% hydrochloric acid media it was now undetectable. By analogy with the observed behavior in the 2-methylbenzophenone example these results again strongly support the assignment of the middle gas chromatographic peak to the respective 2-formylbenzophenones.

Enhanced conversions to the phthalide products in glacial acetic acid are also evident under conditions of oxygen saturation. As shown in Tables 2 and 3, the Hanovia photolyses in glacial acetic acid produced lower aldehyde XV yields and accompanying greater phthalide XVII yields than those in benzene.

The conclusion can thus be reached that aldehyde formed in the oxygen-saturated irradiation is converted to phthalide in oxygen-free irradiations. Furthermore, this aldehyde to phthalide conversion is facilitated in polar protonic solvents. An explanation for this behavior can be made by postulating the intermediacy of the photogenerated ketene XXIV which suffers an intramolecular -OH addition in its conversion to the phthalide.



Hydroxyl additions to ketenes are known to be accelerated by polar solvents or proton donors[69].

The intermediacy of the ketene XXIV is also supported by the flash photolysis work of Tchir[70]. Photolysis of degassed ethanol solutions of 2-formylbenzophenone on the laser apparatus[71] produced two absorptions. A decay was observed at 580 nm and a growth at 450 nm and both were of about the same time scale. However, quantitative measurements could not be made, for the absorptions were too weak and the lifetimes too short. On a conventional flash photolysis apparatus, a transient which absorbed between 340 and 470 nm was observed in ethanol (peak at 410 nm) and in cyclohexane (peak at 395 nm). Its lifetime in ethanol was 210 μs and this decreased to 200 μs when oxygen was admitted. In cyclohexane the lifetime was ca. 65 ms and this decreased to about 700 μs when oxygen was admitted. The decaying species at 580 nm was believed to be the triplet or a biradical of the aldehyde and appeared to be the precursor of the transient absorbing at 340-470 nm. The observed lifetime differences between the two solvents tend to support the assignment of the transient to the ketene XXIV. The lifetime of the ketene would be expected to be shorter in ethanol since the intramolecular -OH to ketene addition required for phthalide formation should occur more rapidly in this solvent than in the less polar cyclohexane. The sensitivity toward oxygen is consistent with the observed photoreactivity of 2-formylbenzophenone in the presence of air which leads to the formation of 2-benzoylbenzoic acid (this work). The possible role of the ketene in 2-benzoylbenzoic acid formation is treated later when the overall mechanism for the photooxidation of 2-methylbenzophenones is discussed.

The ketene transient XXIV is not without precedent. Cohen[23] has trapped an analogous photoproduced dienic ketene of o-phthalaldehyde with the dienophile maleic anhydride.

Several attempts to trap the ketene XXIV with dimethyl acetylenedicarboxylate were made in the present study, but were unsuccessful.

The third peak, which possesses the longest retention time, in the gas chromatograms of the photooxidation reaction product mixtures of the 2-methylbenzophenones has been attributed to the respective 3-phenylphthalide products.

This has been unequivocally verified in the four cases of 2-methyl-, 2,5-, 2,6-, and 2,2'-dimethylbenzophenone by gas phase chromatography using authentic samples of the 3-phenylphthalides for peak enhancement. By analogy with these four known examples the third gas chromatographic peak in the case of 2,3'-dimethylbenzophenone has been assigned to 3-(3-methylphenyl)phthalide and to 6-methyl-3-phenylphthalide in the case of 2,4-dimethylbenzophenone. Attempts were made to prepare these latter two phthalides photochemically, but authentic samples could not be secured.

A solution of 2,3'-dimethylbenzophenone in a glacial acetic acid-2% hydrochloric acid media was photolyzed in a flowing air stream for 96 hours in an attempt to drive the aldehyde to phthalide conversion to completion. Gas chromatographic analysis of the product mixture indicated the presence of substantial aldehyde accompanying the phthalide. Similar results were obtained with 2,4-dimethylbenzophenone. No complete conversion to phthalide was possible.

Sarver[14c] was unable to isolate the phthalide product from the irradiation-aeration of 2,4-dimethylbenzophenone. However the presence of this material in the photolysis product mixture was strongly suggested by the observation of the intense 1770 cm^{-1} absorption in the infrared spectrum since the other two authentic phthalides studied displayed carbonyls at 1770 cm^{-1} (neat photolysis mixture).

In the present study this phthalide has also defied all isolation attempts, but more definite evidence for its existence has been gathered. All photolysis mixtures of 2,4-dimethylbenzophenone, especially those from runs made in glacial acetic acid, displayed the expected characteristic high frequency carbonyl at 1760 cm^{-1} (neat) in the infrared spectrum. The mechanistic logic and experimental results gleaned from the investigations on the aldehyde to phthalide conversion reaction (see previous discussion) can also be used as an argument in favor of the photochemical production of this phthalide, i.e. an analogy can be made with the 2-methylbenzophenone case.

An acetic acid-1% hydrochloric acid solution of 2,4-dimethylbenzophenone was irradiated in a flowing air stream for 24 hours in the hope of achieving a good conversion to the phthalide. The product was a semisolid mass whose infrared spectrum contained an intense 1770 cm^{-1} absorption. Gas chromatography indicated two major components, one of which was residual 2,4-dimethylbenzophenone. By analogy with the gas chromatography analyses of the other 2-methylbenzophenones whose phthalides are known, the second component was assigned as 6-methyl-3-phenylphthalide. Trituration of the product mixture and repeated crystallizations of the resultant solid gave a white solid which had an intense 1760 cm^{-1} absorption in the infrared spectrum. This infrared spectrum, moreover, was very similar to that of authentic 5-methyl-3-phenylphthalide. Gas chromatography demonstrated the purity of this component which was identified as 6-methyl-3-phenylphthalide. However, during the repeated crystallizations, the melting point of the sample gradually increased and the compound seemed to undergo further reaction, defying isolation as an analytical sample.

Two unreported phthalides have been prepared by the photolysis-aeration of a glacial acetic acid solution of the corresponding ketone. A solution of 2,6-dimethylbenzophenone was irradiated in the presence of air for 24 hours. Elemental, nmr, ir, and mass spectral analyses indicated the isolated solid product to be 4-methyl-3-phenyl-phthalide. The molecular ion appeared at m/e 224 in the mass spectrum which corresponded correctly to the molecular formula of $C_{15}H_{12}O_2$. Gas chromatography showed that this phthalide was produced in a 13% yield. Similarly 3-(2-methylphenyl)-phthalide was found to be an oxidation product of 2,2'-dimethylbenzophenone. Elemental, nmr, ir, and mass spectral analyses were consistent with the assigned structure. The mass spectrum showed the expected molecular ion at m/e 224. The yield was found to be 30% by gas chromatography. Peak enhancement gas chromatography using authentic samples of these phthalides was then used to identify these materials in product mixtures from other photolyses.

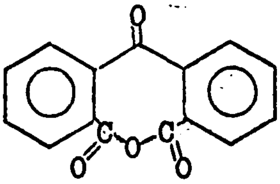
For ketones which were photooxidized to anthraquinone products, a fourth peak appeared in the gas chromatograms of the product mixtures. These anthraquinones were found to have slightly greater retention times than the phthalides. Anthraquinone formation is fully discussed in a later section.

Identification of 2-Benzoylbenzoic Acids and Other Products

Acidification of the sodium bicarbonate extract from a 24-hour long photooxidation reaction of 2,3'-dimethylbenzophenone in benzene gave a brown solid which was subsequently identified as 2-carboxy-3'-methylbenzophenone by its infrared spectrum and melting point.

The expected 2-carboxy-2'-methylbenzophenone was not isolated from any photolysis of 2,2'-dimethylbenzophenone. The acidified bicarbonate layer from a photooxidation reaction of this ketone in glacial acetic acid gave only a small amount of a black oil. Similar results were obtained when the photooxidation was run in benzene.

Although the anticipated 2-benzoylbenzoic acid was not isolated from the photooxidation of 2,2'-dimethylbenzophenone, the concurrent photooxidation of the two methyl groups of this ketone has been demonstrated by the isolation of the cyclic anhydride of benzophenone-2,2'-dicarboxylic acid XXV as a photolysis product.



XXV

An acetic acid solution of the ketone containing about 2% of hydrochloric acid was irradiated-aerated for 96 hours. The solid substance obtained as product was found by gas chromatography to contain 3-(2-methylphenyl)phthalide (16%) and an unknown (65%). Repeated crystallizations of the substance provided a pure compound. Nmr, ir, mass spectral, and elemental analyses showed that the compound at hand was XXV. The correct molecular ion at m/e 252 was observed in the mass spectrum and the melting point was the same as that reported in the literature. The unknown component of the product mixture was subsequently identified as this anhydride by peak enhancement gas chromatography. A reanalysis of other ketone photooxidation product mixtures than proved that this anhydride was indeed present as a minor product.

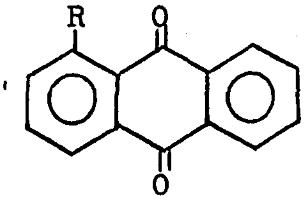
The only acidic product isolated from the photooxidations of 2,6-dimethylbenzophenone was 1-anthraquinonecarboxylic acid. The acid was identified by its infrared spectrum and melting point. Most photooxidations of this ketone gave only uncharacterizable black semisolids from the bicarbonate extracts.

The photochemical formation of cyclobutanols from alkyl o-methylphenyl ketones has been reported[61,15] (see Introduction). No cyclobutanols were isolated in the present study.

Anthraquinone Formation

The hitherto unreported formation of anthraquinones during the photooxidation of 2-methylbenzophenones[64] has been discovered. An irradiation-aeration of a benzene solution of 2,4-dimethylbenzophenone with the Hanovia lamp led to the isolation of 2-methylanthraquinone. Further experiments with 2-methyl-, 2,5-, and 2,3'-dimethylbenzophenone confirmed the generality of anthraquinone formation during irradiation-aeration in benzene solvent using the Hanovia lamp and the results are reported in Table 2. Indeed, the anthraquinones were the major products of the photolyses.

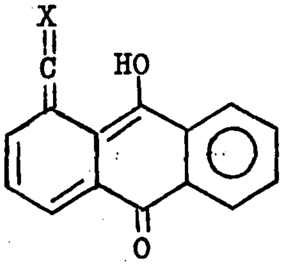
The anthraquinone which would be anticipated to arise from photooxidation of both 2,6- and 2,2'-dimethylbenzophenone would be 1-methylanthraquinone. However, this compound was never isolated or identified as a photooxidation product from either one of these ketones. In the light of recent investigations[58] on the photoreactivity of 1-methylanthraquinone, this is not surprising since any initially formed 1-methylanthraquinone would be expected to be readily consumed by further reaction. Yates[58] has shown that exposure of a benzene solution of 1-methylanthraquinone XVIIIa to sunlight in the presence of air for six days resulted in the formation of 1-anthraquinonecarboxylic acid XXVI (54%), anthraquinone (8%) and the dilactone XX. Previous studies by Yang[8] and Ullman[19,55] suggested to Yates[58] that the photooxidation of XVIIIa proceeded via photoenolization to XXVII which trapped molecular oxygen to form the peroxide XXVIII. Collapse of XXVIII would yield 1-formylanthraquinone XIX. Oxidation of XIX or its ketene tautomer XXIX could give XXVI while photodecarbonylation of XIX could lead to anthraquinone. In support of this mechanism, Yates[58] found that deuterium was incorporated into the methyl group when XVIIIa was irradiated without oxygen in CH_3OD-benzene and an irradiation-aeration of XVIIIa in acetic anhydride gave the aldehyde XIX.



XVIIIa, R = CH_3

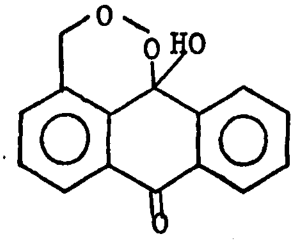
XIX, R = CHO

XXVI, R = CO_2H



XXVII, X = H_2

XXIX, X = O



XXVIII

In accordance with the work of Yates[58], an 8% yield of 1-anthraquinonecarboxylic acid XXVI was isolated from a photooxidation reaction of 2,6-dimethylbenzophenone in benzene (Table 2) and it can be concluded that 1-methylanthraquinone was therefore an intermediate.

The total lack of anthraquinone formation in the photooxidations of 2-methyl-, 2,4- and 2,5-dimethylbenzophenone in benzene at 350 nm (Rayonet) is very apparent from the product distribution data reported in Table 1 while the corresponding data in Table 2 show that when the Hanovia lamp is used instead, anthraquinone formation is now the dominant process. This marked difference in the product distribution is not likely due to an intensity difference between the two light sources since the radiated energy in the 350 nm range of both sources is comparable. The Hanovia lamp however, radiates a considerable amount of visible light (ca. 76 watts) while the 350 nm lamps do not. A dependence on the wavelength of the incident radiation is therefore indicated.

In order to check this hypothesis a photooxidation reaction of 2,5-dimethylbenzophenone in benzene was carried out in which the continuously aerated solution of the ketone was exposed to 350 nm light (Rayonet) simultaneously supplemented by a long wavelength 200 watt incandescent tungsten bulb. A 21% yield of 2-methylanthraquinone was now realized. Photooxidations of 2-methyl- and 2,4-dimethylbenzophenone were then conducted in the same manner to affirm the generality of this result and the data is reported in Table 4. From this data it is apparent that anthraquinone formation, totally lacking with the 350 nm source alone, was now almost comparable to that observed in the broad-spectrum Hanovia lamp experiments.

Control runs with the tungsten source alone were conducted and the data for these experiments is reported in Table 5. The 2-formylbenzophenone derived from the ketone was produced as the sole product in both 30 hr. photolyses, but no anthraquinone compound was present. Irradiations of longer duration with two 200 watt tungsten bulbs afforded significant conversions to the 2-formylbenzophenones accompanied by much smaller conversions to the phthalides and 2-benzoylbenzoic acids. Again, anthraquinone formation was not observed.

The foregoing sets of irradiations and resultant data as reported in Tables 1, 2, 4, and 5 allow the conclusion

Table 4

PHOTOOXIDATION OF 2-METHYLBENZOPHENONES IN BENZENE AT 350 nm (RAYONET) SUPPLEMENTED BY TUNGSTEN[1,2]

	Initial Ketone	Reaction	Product Distribution, % Yield[3]					Recovered Ketone
Ketone XIV Irradiated	Concentr. M	Time, hr.	XV %	XVI %	XVII %	XVIII %	Other⊕ %	XIV %
2-methyl	0.073	30	present	5	present	present	6⊛	present
2-methyl	0.073	48	*12	10	10	21	26⊛	6
2,4-dimethyl	0.068	30	22	8	23	15		20
2,5-dimethyl	0.068	30	*17	14	21	21		14

[1] One 200 watt incandescent tungsten filament bulb

[2] Volume of each solution irradiated was 220 ml and contained 3.14 g of ketone

[3] Based on starting ketone and calculated from glpc peak areas. Yield of acid (XVI) calculated from weight of acid isolated.

⊕Other products found: ⊛compound XXXVII

*Product mixture was later extracted with $NaHSO_3$ solution and reanalyzed by glpc - see Experimental section

Table 5

PHOTOOXIDATION OF 2-METHYLBENZOPHENONES IN BENZENE WITH TUNGSTEN[1,2]

Ketone XIV Irradiated	Initial Ketone Concentr. M	Reaction Time, hr.	No. of 200 W Tung. Bulbs	Product Distribution, % Yield*				Recovered Ketone XIV %
				XV %	XVI %	XVII %	XVIII %	
2-methyl	0.073	30	1	5	absent	absent	absent	95
2-methyl	0.073	144	2	60	6	18	absent	7
2,5-dimethyl	0.068	30	1	20	trace,?	absent	absent	80
2,5-dimethyl	0.068	165	2	50	15	14	absent	5

[1] 200 watt incandescent tungsten filament bulb

[2] Volume of each solution irradiated was 220 ml and contained 3.14 g of ketone

*Based on starting ketone and calculated from glpc peak areas. Yield of acid (XVI) calculated from weight of acid isolated to be made that the formation of anthraquinones in the photooxidation of 2-methylbenzophenones is a more than one photon process starting from the initial ketones.

Conclusive evidence that the anthraquinones require two activating wavelengths of incident light for production from the initial ketones is provided by the flash photolysis experiments of Tchir[72] on 2,4-dimethylbenzophenone. The first-formed fast transient XXX was assigned as the ketone triplet and was the precursor of the second fast transient XXXI postulated to be the enol triplet. The decay rates of both XXX and XXXI were insensitive to the presence of pure oxygen.

Photolysis through a filter solution which removed greater than 90% of the light between 380 and 550 nm produced a broad absorption spectrum which extended from 350 to 550 nm. It was shown that this spectrum was due to two long-lived transients which were assigned the two isomeric dienol structures, XXXII and XXXIII. In cyclohexane, transient XXXII absorbed between 350 and 430 nm (λmax ca. 390 nm) and transient XXXIII absorbed between 390 and 550 nm (λmax ca. 430 nm). In the presence of oxygen, their decay rates were greatly increased. The concurrent formation of both isomers permits the conclusion that there is free rotation about the central C-C bond in the transient XXXI. The faster decay rate observed for isomer XXXIII was accounted for by assuming a facile internal reketonization which cannot however, occur with the other isomer XXXII. The sensitivity of both decay rates to the presence of oxygen was believed to be due to the chemical reactions which we observe (vide infra) with oxygen.

Another transient XXXIV was produced when the ketone was flashed without the filter solution. Its absorption persisted for hours in degassed solution, but disappeared completely in about 30 s after the addition of air. The lifetimes of the isomeric dienols XXXII and XXXIII were now much shorter than when observed with the filter solution. The spectral characteristics of transient XXXIV were found to agree with those reported by Ullman[54] for an intermediate found in flash irradiation studies of 2-methylbenzophenone. Ullman had assigned the intermediate to 9,10-dihydro-9-anthranol VI, and transient XXXIV was therefore assigned the analogous dihydroanthranol structure. Tchir[70] has also flashed solutions of 2-methyl- and 2-isopropylbenzophenone and both of these ketones were found to give the same kind of transient enols as did the 2,4-dimethyl compound.

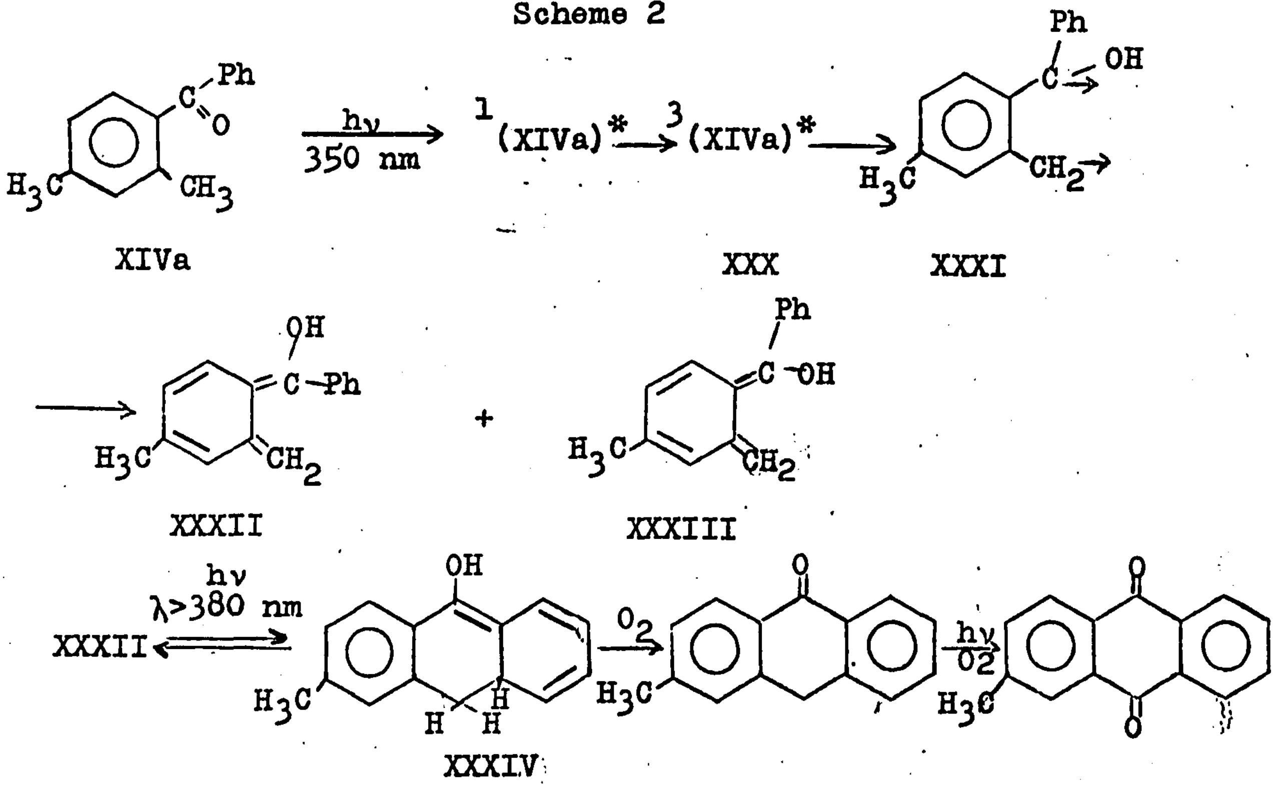
Hammond[73] has postulated on the basis of similar flash photolysis experiments that two isomeric enols are produced from both 2,4,6-trimethyl-4'-methoxybenzophenone and 2,4,6-triisopropyl-4'-methoxybenzophenone. Support for the assignment of the observed transients to the enols was obtained when it was found that the addition of organic bases such as triethylamine and 1,4-diazabicyclo[2.2.2]octane catalyzed the disappearance of the transients. This catalytic effect would be expected for the enol to ketone tautomerization. Ullman[19] has also observed similar base-catalysis in the 2-benzyl-3-benzoylchromone system.

From quenching studies, Hammond[73] concluded that the ketone triplet preceded enol formation. This is in agreement with the results of Zwicker, Grossweiner, and Yang[9].

The work of Matsuura and Kitaura[15] casts some doubt on the validity of the assignments made by Hammond[75]. They found that no deuterium was present in recovered 2,4,6-trimethylbenzophenone after the ketone had been irradiated in monodeuteriomethanol. However, the irradiation did produce a yellow color.

On the basis of the preceding flash photolysis studies of Tchir[70,72] and the experimental data accumulated in Tables 1, 2, 4, and 5, a mechanistic rationalization for anthraquinone formation in the photooxidation of 2-methylbenzophenones can be the following as illustrated with 2,4-dimethylbenzophenone:

Scheme 2



It is apparent from the flash studies of Tchir that both isomeric dienols XXXII and XXXIII are formed directly by a single photon process. The required energy is furnished by light in the 350 nm range which promotes the ketone to its triplet state.

The dihydroanthranol XXXIV is formed by the absorption of two photons: the initial ketone absorbs light in the 350 nm region and subsequently gives the enol XXXII (together with enol XXXIII) which then absorbs light in the visible region (λ>380 nm) and cyclizes to the tautomer XXXIV. This must be the case because in the flash experiments when the light was filtered to remove the visible portion of the spectrum (380 to 600 nm), the formation of XXXIV was now completely inhibited. These observations are consistent with the data reported in Tables 1, 2, 4, and 5. Anthraquinone formation is totally lacking in the irradiations conducted with the Rayonet (350 nm) apparatus because this source does not supply the short wavelength (λ>380 nm) visible light necessary for the formation of the dihydroanthranol. However, when the Rayonet apparatus is simultaneously supplemented by a tungsten bulb which emits the required short wavelength visible light, the dihydroanthranol is produced and subsequently oxidized to the observed anthraquinone product. The control runs with the tungsten source alone affirm the two photon process: no anthraquinones were produced. A small but apparently sufficient steady state concentration of the ketone enol was still produced to insure the occurrence of the rapid reaction with oxygen and subsequent formation of the other normal oxidation products.

The photooxidations in benzene with the Hanovia lamp readily yield anthraquinones since this source furnishes both light in the 350 nm region and in the short wavelength visible region (λ>380 nm).

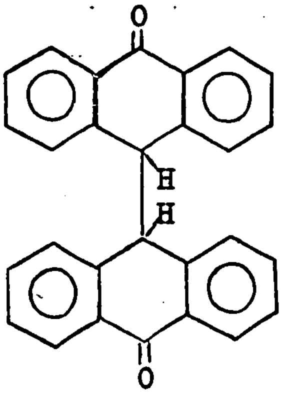
The photochemically reversible formation of the dihydroanthranol VI from 2-methylbenzophenone and its oxidation to anthrone has been reported by Ullman[54].

This reversibility is consistent with the results from the oxygen-free irradiations performed in the present study. Degassed benzene solutions of 2-methyl-, 2,4-, and 2,5-dimethylbenzophenone were irradiated for 24 hr. with the Hanovia lamp. No cyclization products were detected. Only a low yield of the corresponding pinacol was formed. When the irradiations were carried out at 350 nm (Rayonet), again only low quantum efficiency photopinacolization was detected[74].

Cyclization products were not obtained at elevated temperature during both oxygen-free and oxygen-saturated irradiations with 350 nm light (Rayonet). A degassed toluene solution of 2,4-dimethylbenzophenone maintained at 105-110° was irradiated in the Rayonet (350 nm) for 38 hr. Only a low yield of the pinacol was obtained. Another similar irradiation was conducted except that air was continuously bubbled through the solution. Products of types XV, XVI, and XVII were produced, but 2-methylanthraquinone was not present. It thus appears that thermal cyclization of the ketone photoenol is not an efficient process or is one that does not occur at all under these conditions.

Attempts to oxidize the dihydroanthranol transient VI with quinone, 2,3-dichloro-5,6-dicyanobenzoquinone, and 9,10-phenanthraquinone during the photolysis (Hanovia) of degassed benzene solutions of 2-methylbenzophenone were carried out. No cyclization products (i.e., anthrone or anthraquinone) were detected.

The facile conversion of anthrone to anthraquinone under the same conditions present during the 2-methylbenzophenone photooxidations has been verified by independent experiments. A benzene solution of anthrone was irradiated in a flowing air stream for 36 hr. with the Rayonet apparatus (350 nm). A 51% yield of anthraquinone was realized. A similar 7 hr. irradiation-aeration was performed using the Hanovia source. Anthraquinone was isolated in a 17% yield. In addition, an 11% yield of bianthrone XXXV was also isolated.



XXXV

Schönberg and Mustafa[75] have already reported that exposure of a benzene solution of anthrone to sunlight and air produces bianthrone. The photolysis of bianthrone in the presence of air to give anthraquinone has also been reported[76]. The production of bianthrone rather than anthraquinone as observed by Schönberg and Mustafa[75] was probably due to a concentration effect. Their anthrone concentration (3 g in 25 ml) was about ten times greater than that employed in this work and would therefore be expected to favor formation of the dimer XXXV. The isolation of bianthrone from the Hanovia photolysis and not from the Rayonet photolysis was probably due to the diminished photolysis time of the former, i.e. the residual bianthrone had not yet been photooxidized to anthraquinone.

However, during the photooxidation of the 2-methylbenzophenones, it is highly unlikely that the instantaneous concentration of the anthrone species at any time would be favorable to the formation of bianthrone type dimers. The anthraquinone would be formed directly from the anthrone intermediate. This is accordant with the work of Ullman[54] and the fact that no bianthrone compound was ever isolated from a ketone photooxidation in this study.

When the photooxidations (Hanovia) reported in Table 2 were run in glacial acetic acid media under otherwise identical conditions, the 2-formylbenzophenones, 3-phenylphthalides, and 2-benzoylbenzoic acids were produced, but no anthraquinones were present. The product distribution data is reported in Table 3. Tchir[70] has determined the lifetime of the 2,4-dimethylbenzophenone photoenol in acetic acid to be only about 25 µs. This indicates that the steady state concentration of the enol should be too low for it to absorb any light and thus be converted to the dihydroanthranol. Anthraquinone formation therefore, does not occur in this media. However, the rate constant for the oxygen addition to the enol must be sufficiently large that the other oxidation products are still obtained.

The formation of small amounts of 2-methylanthraquinone in two Hanovia photooxidations of 2,4-dimethylbenzophenone in acetic acid containing a few per cent concentrated hydrochloric acid is probably due to an inhibitory effect by protonic acids on the reketonization process, photoenol → ketone. This reverse tautomerization has been shown to be accelerated by small amounts of base such as triethylamine by Ullman[19] and Hammond[73] and partially inhibited by acids such as acetic or benzenesulfonic[19]. The lifetime of the 2,4-dimethylbenzophenone photoenol must therefore be greater in acetic acid-hydrochloric acid than in glacial acetic acid. Hydrogen bonding to photoenols is known to stabilize them[19].

The lower rate of reactivity observed in the photooxidations of 2,6-dimethylbenzophenone could be due to a relatively short-lived photoenol or the preferential reversion of the type XXXI intermediate to the ketone rather than the enol. Steric and/or electronic factors might be responsible for this behavior. However, steric effects seem to be ruled out since 2-isopropylbenzophenone gave the same kind of transient enol behavior as was observed with the

2,4-dimethyl case[70]. No photoenol of the 2,6-dimethyl compound has yet been detected by the "trapping" or "deuterium exchange" methods[14d]. Since 2,6-dimethylbenzophenone does photooxidize, an enol must form by analogy with the other 2-methylbenzophenones, but be too short-lived to be detectable by anything but a highly reactive co-reactant (i.e., O_2).

Anthraquinone formation has also been found to occur readily in acetic anhydride and in methanol solvents under conditions identical to those of the photolyses reported in Table 2 and 3. The anthraquinone yield attained in acetic anhydride is indicative of a photoenol lifetime intermediate between that in benzene and in glacial acetic acid.

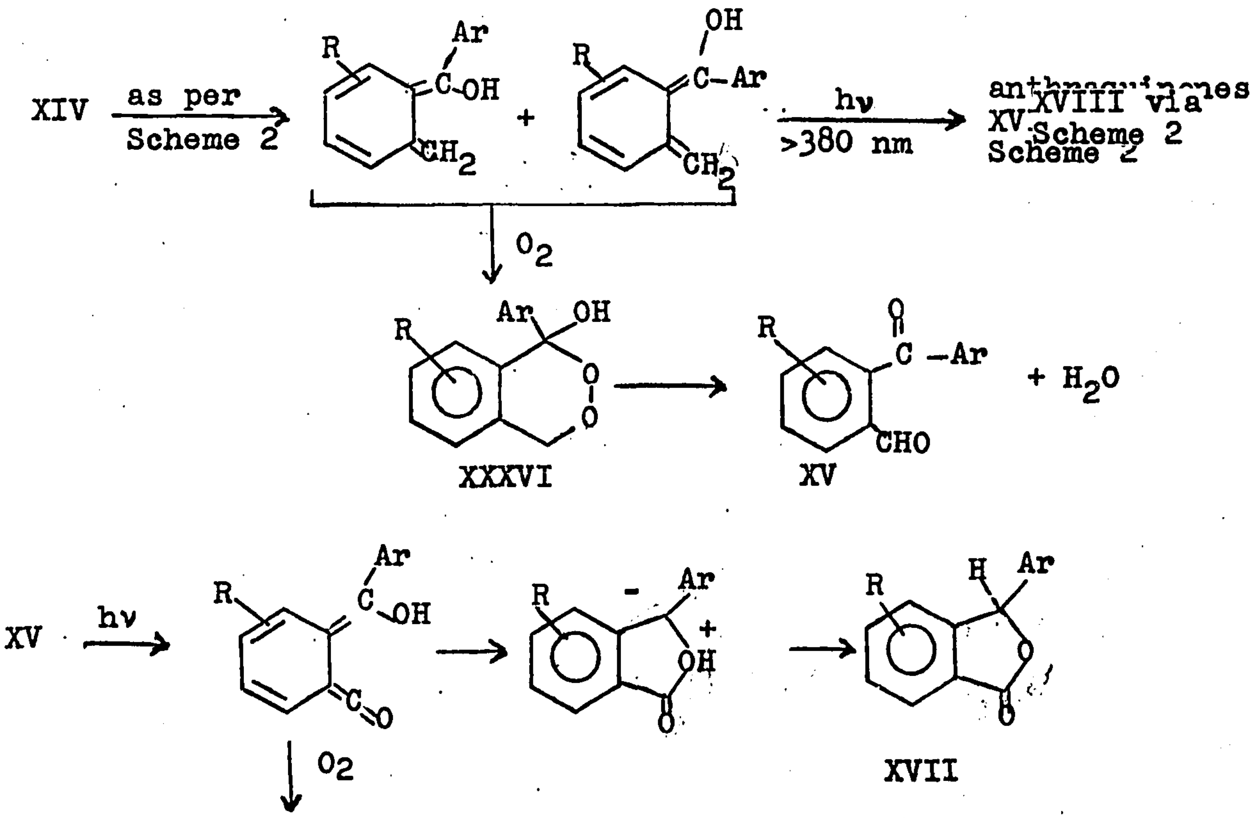
The preliminary flash photolysis experiments on 2-formylbenzophenone by Tchir[70] have already been mentioned. In ethanol a permanent photoproduct of yet unknown structure was formed. Tchir found that this product did not disappear when air was admitted and the amount formed did not appear to depend on whether the long wavelength filter was present or not. The spectrum of the photoproduct was noted to be very similar to that of 9,10-dihydroxyanthracene. If indeed the photoproduct is this compound, it could arise by an internal cyclization of the ketene XXIV. Subsequent oxidation could lead to anthraquinone[77,78]. In order to test this mechanism, a benzene solution of 2-formylbenzophenone was irradiated in the presence of air with the Hanovia lamp. The major product was 3-phenylphthalide in an 85% yield. No dihydroxyanthracene or anthraquinone was present. It may be concluded from this that anthraquinone formation in the photooxidation of 2-methylbenzophenones does not occur via the 2-formylbenzophenones.

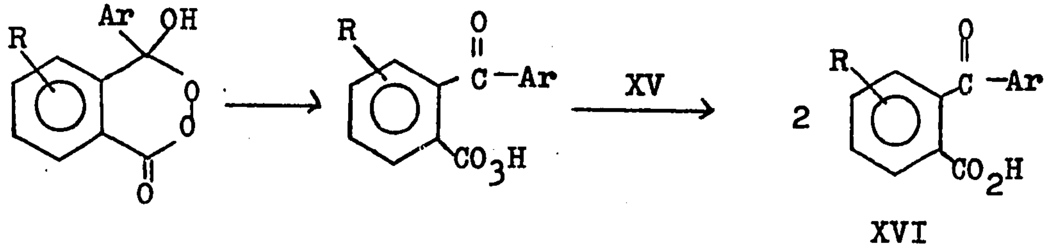
From the foregoing analysis, it may be concluded that the anthraquinone products in the photooxidation of 2-methylbenzophenones result from a Photo-Elbs cyclization of the appropriately disposed ketone photoenol with subsequent oxidation and require two activating wavelengths of incident light for production from the initial ketone.

Mechanism of the Reaction

A mechanistic rationalization for the production of 2-formylbenzophenones, 3-phenylphthalides, 2-benzoylbenzoic acids, and anthraquinones in the photooxidation of 2-methylbenzophenones can be the following:

Scheme 3





XVI

Evidence for the phenomenon of photoenolization of 2-methylbenzophenones has been provided by deuterium exchange[8,14a], Diels-Alder trapping[8,14b,21], flash spectroscopy[9,54,70,72], mass spectrometry[29], and dienol oxidation[14c,64].

The sensitivity of the ketone photoenols toward oxygen has been conclusively demonstrated by the flash photolysis experiments of Tchir[70,72] and Ullman[54]. The extreme reactivity of the photoenols derived from 2,4-dimethylbenzophenone has been illustrated by their rapid reaction with dimethyl acetylenedicarboxylate[70]. The rate constant for the reaction was found to be 10^4 to 10^5 times as large as the rate constant for the addition of the same dienophile to 2-phenylfuran[79]. A valid conclusion then can be that the photooxidation of 2-methylbenzophenones is initiated by the reaction between the photoenols and molecular oxygen. The photooxygenation of 1,3-diene systems is a well known process and can be regarded as a photoinduced Diels-Alder reaction in which molecular oxygen acts as a dienophile (see Introduction). The cyclic peroxide XXXVI would be the expected product from the 1,4-addition of molecular oxygen to the photoenol. No peroxides of type XXXVI were isolated in this work, but support for their intermediacy is found in the work of Yates[58], Ullman[55], and Matsuura[15] where the isolation of labile cyclic peroxides from oxygen and photoenolic compounds has been reported.

The intermediacy of the 2-formylbenzophenones XV and their conversion to the 3-phenylphthalides XVII and 2-benzoylbenzoic acids XVI has already been discussed. The ketene intermediate of type XXIV could also be utilized to account for the formation of the 2-benzoylbenzoic acids as well as the phthalides. The ketene could trap oxygen much in the same manner as has been proposed for the method of formation of the peroxides XXXVI. A redox reaction between the resultant peroxyacid and the 2-formylbenzophenone would provide an efficient pathway for the production of the 2-benzoylbenzoic acids[80]. A reaction of this sort ($RCHO + RCO_3H \rightarrow 2RCOOH$), of course, has excellent precedent in the Baeyer-Villiger synthesis.

A direct photooxidation of the aldehydes XV to the acids XVI without invoking the presence of the ketene can also be postulated since the direct light catalyzed conversion of benzaldehyde to benzoic acid has been established[81]. However, a ketene intermediate was attractive since it could reasonably be the precursor of both the 2-benzoylbenzoic acids and the phthalides.

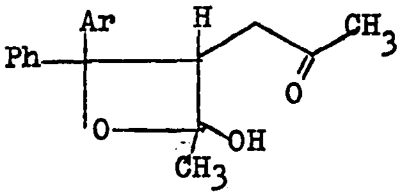
Some conclusions can be made regarding the electronic state of the oxygen participating in the reaction with the photogenerated ketone enols. The flash photolysis studies

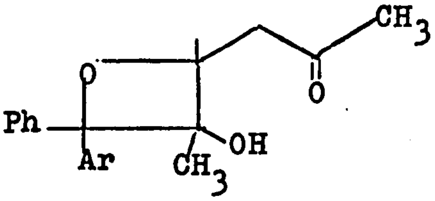
Tchir[70,72] have shown that oxygen does not affect the lifetime of the ketone triplet or the intermediate XXXI; hence, there can be no reaction between either of these species with oxygen. Tchir[70] has concluded that the absorption spectra detected for the photoenols must be for the ground state and not an excited state of these species to possess such long lifetimes. Therefore it appears that the well documented oxygen-activation mechanism, in which singlet oxygen generated by photosensitization reacts with ground state diene (see Introduction), is not operating in this system. Rather an addition of triplet ground state oxygen to the ground state dienol is suggested. One example of such a process has been found in the literature. This is a report of the dark reaction of oxygen with the dienic compound 1,3-diphenylisobenzofuran, to give 1,2-dibenzoylbenzene and a peroxide polymer[82].

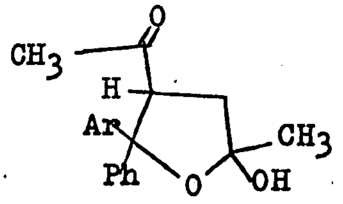
Further evidence for the participation of triplet ground oxygen has been provided from an experiment in which 2,5-dimethylbenzophenone in benzene was irradiated in the presence of 2,5-dimethylfuran and air. The furan is a well known singlet oxygen acceptor; in fact, most substrates have been found to be less reactive than 2,5-dimethylfuran toward oxygen[37]. However, the photooxidation of 2,5-dimethylbenzophenone was not quenched, the oxidation proceeding in the normal manner. The absence of singlet oxygen is thus indicated. In light of the extreme reactivity observed by Tchir[70] of the photoenols toward dimethyl acetylenedicarboxylate, such a conclusion might be overly commital. Indeed, the photoenols might be more reactive toward singlet oxygen than 2,5-dimethylfuran.

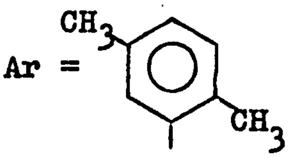
In conclusion, with the data on hand it appears likely that triplet ground oxygen is responsible for the photooxidation of 2-methylbenzophenones.

An unexpected and interesting reaction has been uncovered during the previously mentioned irradiation-aeration of 2,5-dimethylbenzophenone in the presence of 2,5-dimethylfuran. Gas chromatography showed that a new product was being rapidly formed in addition to the usual oxidation products of this ketone. This product was subsequently isolated in good yield and the elemental analysis was correct for a 1:1:1 adduct of 2,5-dimethylbenzophenone, 2,5-dimethylfuran, and water. The mass spectrum displayed the expected molecular ion at m/e 324. An unambiguous structural assignment on the basis of the nmr, ir, and mass spectral data could not be made. Plausible structures for this compound can be the following:







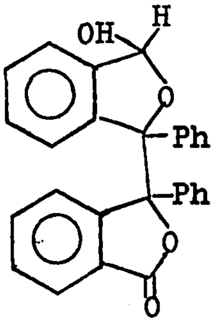


Mechanistically, the products can be envisioned to arise from the addition of a molecule of water to the 1:1 Paterno-Buchi cycloaddition adduct of the benzophenone and the furan with subsequent rearrangement. If indeed this is the mode of formation, the reaction observed here is the first example of a photoenolizable benzophenone partaking in a Paterno-Buchi photocycloaddition reaction.

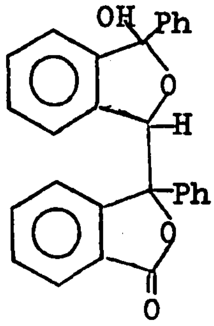
The photocycloaddition of a carbonyl compound to an olefin with the formation of an oxetane is known as the Paterno-Buchi reaction. The reaction has been found to be applicable to a wide variety of carbonyl compounds and olefins[83,3b,84]. Numerous examples of oxetane formation between diaryl ketones and furans have been reported[83]. However, 2-methylbenzophenone has been found to be unreactive in the photocycloaddition reaction with isobutylene, no oxetane product having been detected[83]. It was postulated that the photocycloaddition reaction was prevented by the rapid internal photoactivated hydrogen transfer (photoenolization) of the 2-methylbenzophenone and that this deactivation pathway can be expected to be general for other aromatic carbonyl compounds that can enolize.

Phthalide Dimer Formation

A benzene solution of 2-methylbenzophenone was irradiated in the presence of air with the Rayonet (350 nm) reactor simultaneously supplemented by a 200 watt incandescent tungsten bulb. The crystalline solid which was collected in low yield (ca. 6%) was subsequently found to be identical to a compound isolated by Pfau[85] to which was assigned the structure XXXVII.



XXXVII



XXXVIII

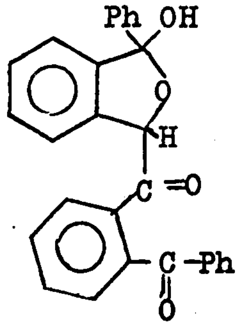
Pfau obtained this material in low yield (ca. 4%) from an irradiation (Rayonet, 350 nm) of a degassed benzene solution of 2-formylbenzophenone. The product mixture was also found to be rich in 3-phenylphthalide.

Structure XXXVII was proposed on the basis of ir, nmr, and mass spectral data. The mass spectrum did not display a parent peak at m/e 420, but rather one at m/e 402. This corresponds to a loss of water and is typical for a secondary alcohol[66]. The presence of a secondary hydroxyl group was indicated by the nmr spectrum in dimethylsulfoxide[86]. A one proton doublet appeared at δ6.66 (J = 3 Hz) vs. TMS which collapsed to a singlet upon dilution with D_2O. The ir spectrum (nujol) showed an intense absorption at 1780 cm^{-1} (carbonyl) and a weak absorption at 3530 cm^{-1} (-OH). The foregoing data is not consistent with the structure XXXVIII. Kagan[57] had assigned the analogous structure XI to the dimer obtained from o-phthalaldehyde on the basis of similar arguments. The dimeric compound XXXVII was not obtained from the irradiation-aeration of 2-methylbenzophenone at 350 nm (Rayonet) without the tungsten illumination. This experiment is reported in Table 1.

Another irradiation-aeration of 2-methylbenzophenone at 350 nm supplemented by a tungsten bulb was carried out for 48 hr. A 26% yield of the dimer XXXVII was realized in addition to the other normal oxidation products. The results are reported in Table 4. No dimer was obtained with tungsten illumination alone (Table 5) or from any photooxidation conducted with the Hanovia source (Table 2).

The conclusion can therefore be made that the dimer produced in the oxygen-saturated photolysis of 2-methylbenzophenone arises via the 2-formylbenzophenone intermediate. The formation of the dimer is unaffected by the presence of oxygen and requires 350 nm light supplemented by tungsten illumination for good conversions.

The carbene mechanism proposed by Cohen et al.[23] (see Introduction) cannot be responsible for the production of the dimer XXXVII. If this mechanism was operating, the final product would be XXXIX and not XXXVII.



XXXIX

The spectral data on hand do not agree with structure XXXIX. No long wavelength ketone carbonyls of the type in XXXIX are observed in the ir spectrum, and the nmr and mass spectral data do not indicate the presence of a tertiary hydroxyl function.

EXPERIMENTAL SECTION

All temperatures are uncorrected. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained with a Perkin-Elmer 257 spectrophotometer in pressed potassium bromide pellets, Nujol, and the neat state. Nmr spectra were recorded on either a Varian Associates A-60 or on a Hitachi Perkin-Elmer Model R-20A spectrometer using tetramethylsilane (TMS) as an internal standard. Data are presented in the order δ (multiplicity, number of protons, assignment). Element analyses were provided by Dr. G. I. Robertson of Florham Park, New Jersey. Mass spectra were run by J. E. Rowe on a Hitachi Perkin-Elmer RMU-6E double focusing sector mass spectrometer. Peak positions were assigned relative to peaks found in the fragmentation pattern of perfluorokerosene. Glpc chromatograms were obtained with a Hewlett-Packard Model 700-231 Laboratory Gas Chromatograph equipped with a thermal conductivity detector. Stationary phases, solid supports, and dimensions of columns used were: 10% Silicone Rubber UC-W98, Chromosorb W AW-DMCS-treated, 80-100 mesh, 6 ft. x 0.125 in.; 5% Silicone Gum Rubber OV-1, Diatoport S, 80-100 mesh, 6 ft. x 0.125 in. 2,4-, 2,5-, and 2,6-Dimethylbenzophenone were obtained from the Tensyn Division of Velsicol Chemical Corp. (Chicago, Ill.) and were vacuum redistilled. 2-Methylbenzophenone was purchased from Distillation Products Industries and was used as received. Benzene (reagent grade) for the photolyses was dried over sodium ribbon. Glacial acetic acid (reagent grade) employed in the photolyses was used as purchased.

Photochemical Apparatus

The Hanovia 450 watt medium pressure quartz mercury-vapor lamp was placed in a water cooled double-walled immersion well constructed of Pyrex glass. The immersion well was fitted into the outer Pyrex glass reaction vessel by means of a 50/60 standard tapered joint. The reaction vessel was equipped with two 10/30 standard tapered joints to which a gas inlet and outlet tube could be attached and a side arm to accommodate a reflux condenser. The oxidation reactions were carried out by delivering dry compressed air via the gas inlet tube to a capillary tipped bubbler tube in the reaction solution. The air was presaturated with solvent vapor by first bubbling the air through a volume of liquid solvent. For experiments which required degassing, nitrogen gas was admitted to the capillary tipped tube instead of air and the gas outlet tube was connected to a vacuum line. The system was purged with nitrogen and then evacuated. This procedure was repeated several times. Reaction vessels of 230, 350 and 430 ml capacities were employed.

Other photolyses were run in a Rayonet Model RPR-100 chamber reactor equipped with sixteen 350 nm mercury-vapor lamps. About 24 watts of light, 90% being in the 350 ± 10 nm range, are produced from these lamps.

Several 12 in. long Pyrex glass reaction tubes were employed in the Rayonet reactor photolyses. Each tube had a joint to accommodate a reflux condenser and a 10/30 standard tapered joint for a gas inlet tube. A gas outlet tube was connected to the top of the reflux condenser. Reaction tubes of 100, 120, 170 and 250 ml capacities were available. The air oxidation and degassing methods were the same as those described for the Hanovia apparatus.

A third light source was an ordinary 200 watt tungsten filament incandescent bulb (120 volt, 60 cycle ac current). All photolyses with this source were conducted within the cavity of the Rayonet reactor with the tungsten bulb suspended inside the cavity and with the same photochemical glassware previously described.

In all photolysis experiments, agitation was provided by magnetic stirring. A flow rate of approximately 4 ml/min. of air was used for all photooxidation reactions. All photochemical glassware was made of Pyrex glass specially constructed by Custom Scientific Glass Co., Wilmington, Delaware.

A standard work-up procedure was followed for each photooxidation experiment unless otherwise noted. For photolysis-aerations run in acetic acid, the mixture was first concentrated in vacuo or via a forced draft and the resultant oil was then redissolved in ca. 200 ml of toluene. Each final reaction mixture in benzene media was used as is without concentration. The toluene (or benzene) mixture was filtered to remove any insoluble matter. The organic solution was extracted with saturated sodium bicarbonate solution (three 60 ml portions) and saturated sodium chloride solution (one 60 ml portion). The organic phase was filtered again if necessary and dried (anhydrous $MgSO_4$). Removal of the solvent in vacuo afforded the residual final product mixture which was usually an oil. The oil was analyzed by glpc using authentic materials for peak enhancement whenever possible. Yields were calculated from glpc peak areas and are based on the starting ketone. The combined bicarbonate extracts were filtered and acidified with dilute (ca. 6M) hydrochloric acid. The precipitated matter was collected and vacuum oven dried. One or two crystallizations were usually required to provide an acid of reasonable purity. The acids were identified by ir and mp.

Preparation of 2,2'-Dimethylbenzophenone

The method used by Sarver[14e] to prepare this ketone was followed and a yield of 50% was obtained. Purification of the ketone was effected by sublimation in vacuo. This procedure gave colorless needles, mp 63-4° (literature[87] mp 62°).

Preparation of 2,3'-Dimethylbenzophenone

The method of Newman and McCleary[88] was employed to prepare this ketone. The product was collected by vacuum distillation, bp 126-131° at 0.14 torr (literature[88] bp 228-231° at 24 torr); ir (neat) 1670 cm^{-1} (C=O).

Preparation of 2-Hydroxymethylbenzhydrol

This compound was prepared by the sodium dihydro-bis (2-methoxyethoxy) aluminate reduction of 2-benzoylbenzoic acid according to the method of Heindel et al.[89] Their procedure was followed exactly.

Preparation of 2-Formylbenzophenone

The published[90] selenium dioxide oxidation of 2-hydroxymethylbenzhydrol was used to synthesize this ketoaldehyde. White crystals of 2-formylbenzophenone were obtained, mp 66-7° (lit.[90] 64-7°); ir (KBr) 1665 (broad), 1600, 1570, 1280, and 1200 cm^{-1}.

Photooxidation of 2,4-Dimethylbenzophenone - Isolation of 2-Methylanthraquinone

A solution of 4.08 g (0.019 mol) of 2,4-dimethylbenzophenone in 350 ml of benzene was irradiated with the Hanovia lamp for 5 hr. while being continuously saturated with air. The orange reaction mixture was filtered to remove some yellow orange solid and the filtrate was evaporated to a thick oil. The oil was dissolved in 100 ml of diethyl ether and the resultant solution was extracted with three 40 ml portions of sodium bicarbonte solution and 40 ml of saturated sodium chloride solution. The ether solution was dried over anhydrous magnesium sulfate. The filtrate was concentrated in vacuo and the residue was dissolved in 1:1 mixture of benzene and 100% ethanol. The benzene-ethanol mixture was removed in vacuo. This treatment was repeated ca. 4 times to remove residual water. The final gummy residue weighed 3.41 g; ir (neat) 1770 (broad) and 1660 cm^{-1}. All attempts to induce crystallization failed. The oil was distilled at 0.35 torr but no really constant boiling fraction was observed. Two fractions were collected: cut #1, bp to 200°; and cut #2, bp 200-230°. Trituration of cut #2 with cold 100% ethanol gave a yellow solid which was crystallized several times from ethanol. Yellow crystals of mp 183-185° were obtained. This material was found to be identical in all respects with an authentic sample of 2-methylanthraquinone. Ir (KBr) 1670, 1590 cm^{-1}; nmr ($CDCl_3$) δ 2.52 (s, 3, CH_3) and 7.2-8.5 (m, 7, aromatic protons). Lit.[91] mp 177-179°.

Anal. Calcd for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54.
Found: C, 80.79; H, 4.52.

More 2-methylanthraquinone was produced by trituration of cut #1 with ethanol. The total yield isolated was 0.33 g (8%). Gas chromatography analysis of the trituration filtrates proved the presence of more 2-methylanthraquinone and 6-methyl-3-phenylphthalide.

Acidification of the bicarbonate extracts with dilute hydrochloric acid gave a yellow solid 0.6 g (12%) which was subsequently identified as 2-benzoyl-5-methylbenzoic acid, mp 148-150° (lit.[64] mp 149-150°) after ca. two crystallizations.

Photooxidation of 2,6-Dimethylbenzophenone - Isolation of 4-Methyl-3-phenylphthalide

A solution of 6.0 g (0.028 mol) of 2,6-dimethylbenzophenone in 350 ml of glacial acetic acid was irradiated with the Hanovia lamp in a flowing air stream for 24 hr. The clear yellow solution was concentrated to an oil. The oil was dissolved in toluene and the solution was extracted thoroughly with saturated sodium bicarbonate solutions and once with saturated sodium chloride solution. The toluene solution was dried ($MgSO_4$) and concentrated <u>in vacuo</u>. The resultant oil was analyzed by glpc and the results are reported in Table 3. Trituration of the oil with cold 100% ethanol provided a crystalline yellow solid, 0.84 g. After several crystallizations from ethanol, a crystalline yellow solid was obtained, mp softened 130°, melted 131.5-132.5°, which was analytically pure 4-methyl-3-phenylphthalide. Ir (KBr) 1745 (C=O), 1600, and 1290 cm^{-1}; nmr ($CDCl_3$) δ 1.94 (s, 3, CH_3), 6.28 (s, 1, benzylic H), and 6.95-7.90 (m, 8, aromatic protons); mass spectrum m/e 224 (molecular ion), 209, 195, 178, 165, 147, 119, 105, 91, and 77.

<u>Anal</u>. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39.
Found: C, 80.60; H, 5.36.

Acidification of the bicarbonate washes gave only a black semisolid, 0.73 g.

<u>Photooxidation of 2,2'-Dimethylbenzophenone - Isolation of 3-(2-Methylphenyl)phthalide</u>

A solution of 6.15 g (0.029 mol) of 2,2'-dimethylbenzophenone in 430 ml of glacial acetic acid was photolyzed with the Hanovia lamp in a flowing air stream for 24 hr. The solution was concentrated to an oil which was taken up in toluene. The toluene solution was thoroughly extracted with saturated sodium bicarbonate solution, once with saturated sodium chloride solution and dried ($MgSO_4$). Concentration <u>in vacuo</u> afforded an oil which was analyzed by glpc (Table 3). On standing the oil solidified. The semisolid was redissolved in the minimum amount of hot ethanol and refrigerated. A 2.55 g yield of yellow needles was collected; ir (Nujol) 1760 cm^{-1} (intense) and starting ketone C=O absent. Several more crystallizations from ethanol afforded analytically pure light tan crystals of 3-(2-methylphenyl)phthalide, mp 112-114°. Ir (KBr) 1740 (wide, intense, C=O), 1600, 1455, and 1280 cm^{-1}; nmr ($CDCl_3$) δ 2.37 (s, 3, CH_3), 6.56 (s, 1, benzylic H), and 6.66-8.13 (m, 8, aromatic protons); mass spectrum m/e 224 (molecular ion), 209, 195, 190 (metastable), 179, 165, 152, 143 (metastable), 133, 119, 104, and 105.

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

Found: C, 80.23; H, 5.32.

Photooxidation of 2,2'-Dimethylbenzophenone - Isolation of the Anhydride of Benzophenone-2,2'-dicarboxylic acid XXV

A solution of 5.0 g (0.024 mol) of 2,2'-dimethylbenzophenone in 220 ml of glacial acetic acid containing 4.0 ml of concentrated hydrochloric acid was irradiated in a flowing air stream for 96 hr with the Hanovia lamp. The solvent was removed and the oil taken up in toluene. The toluene solution was thoroughly washed with saturated sodium bicarbonate solution, sodium chloride solution, and dried ($MgSO_4$). Removal of the toluene *in vacuo* afforded an oil which solidified on standing. Gas chromatographic analysis showed that the solid contained 3-(2-methylphenyl)phthalide (16%) and an unknown (65%). The solid was dissolved in boiling ethanol and cooled to yield a fine-grained tan solid. The solid was purified by several crystallizations from ethanol and gave the analytical specimen, white crystals of mp 214-214.5°,

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which was subsequently identified as the anhydride of benzophenone-2,2'-dicarboxylic acid XXV (lit.[92]mp 212°). Ir (KBr) 1790 (wide, strong), 1610, 1460, and 3530 cm^{-1} (weak); nmr ($CDCl_3$) δ 7.10-8.20 (m, aromatic protons); mass spectrum m/e 252 (molecular ion), 223, 208, 180, 152, 149, 126, 104, 76, and 50.

Anal. Calcd for $C_{15}H_8O_4$: C, 71.43; H, 3.20.
Found: C, 71.46; H, 2.92.

The unknown component (65%) was subsequently confirmed as this anhydride by peak enhancement gas chromatography on the original mixture.

Only a black semisolid was produced from the bicarbonate washes on acidification with dilute hydrochloric acid. Attempts to ring-open this anhydride with 5% aqueous NaOH were unsuccessful (two hr. heating at steam bath temperatures).

Photooxidation of 2,3'-Dimethylbenzophenone - Isolation of 3'-Methylbenzophenone-2-carboxylic Acid

A solution of 6.15 g (0.029 mol) of 2,3'-dimethylbenzophenone in 430 ml of sodium dried benzene was irradiated in a flowing air stream with the Hanovia lamp for 24 hr. The reaction solution was worked up by the standard method. The glpc analysis of the product oil is reported in Table 2.

Acidification of the bicarbonate layer afforded 0.74 g of crude acid. After two crystallizations from boiling benzene, 3'-methylbenzophenone-2-carboxylic acid of mp 160-161° was obtained (lit.[93] mp 162.2-162.4°); ir (KBr) 1660-1700 cm^{-1} (broad). The yield was 10%.

Photooxidation of 2,6-Dimethylbenzophenone - Isolation of 1-Anthraquinonecarboxylic Acid

A solution of 3.64 g (0.017 mol) of 2,6-dimethylbenzophenone in 200 ml of benzene was irradiated with the Hanovia lamp in a flowing air stream for 24 hr. The immersion well was coated with a yellow solid and some solid was present in suspension. The solid (0.2 g) was collected by filtration; ir (KBr) 1650-1770 (broad) and 1600 cm^{-1}, sample very impure. This solid was not characterized further. The clear filtrate was thoroughly extracted with saturated sodium bicarbonate solution and washed with saturated sodium chloride solution. After drying ($MgSO_4$) the solution was concentrated *in vacuo* to an oil. The oil was analyzed by glpc and the analysis is reported in Table 2.

The combined sodium bicarbonate extracts were acidified with dilute hydrochloric acid to afford 0.32 g of tan solid, mp 164-166°. Two crystallizations from n-PrOH gave a tan-yellow solid, mp 290-292° dec, which was identified as 1-anthraquinonecarboxylic acid (lit.[94] mp 293-4°). The yield was 8%. Ir (KBr) 1700, 1670, 1575, 1325, and 1280 cm^{-1}.

Photooxidation of 2,4-Dimethylbenzophenone - Attempted Preparation of 6-Methyl-3-phenylphthalide

Run 1:

A solution of 3.77 g (0.018 mol) of 2,4-dimethylbenzophenone in 220 ml of glacial acetic acid containing 4.0 ml of concentrated hydrochloric acid was irradiated with the Hanovia lamp for 26 hr in a flowing air stream. Two more identical runs were made and the three reaction solutions were combined. The solvent was removed to yield an oil. The toluene solution of this oil was thoroughly extracted with saturated sodium bicarbonate solution, washed with saturated sodium chloride solution, and dried ($MgSO_4$). Removal in vacuo of the toluene afforded an oil which gradually turned semisolid on standing; ir (neat) 1770 (intense, wide), 1705, 1665, and 1600 cm^{-1}. Gas chromatographic analysis showed that the oil composition was 2-methylanthraquinone (10%), 6-methyl-3-phenylphthalide (41%), 2-formyl-4-methylbenzophenone (2%) and 2,4-dimethylbenzophenone (47%). After ca. three crystallizations from ethanol an amorphous white solid was obtained, mp 86-88°; ir (Nujol) 1760, 1460, 1300, 1065, and 980 cm^{-1}. This infrared spectrum was very similar to that of authentic 5-methyl-3-phenylphthalide. Gas chromatography detected only one component.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80,34; H, 5.39.
Found: C, 81.07; H, 5.90.

Run 2:

A solution of 7.00 g (0.033 mol) of 2,4-dimethylbenzophenone in 220 ml of glacial acetic acid containing 5.0 ml of concentrated hydrochloric acid was irradiated with the Hanovia lamp for 96 hr. in a flowing air stream. The work-up procedure was the same as that in Run 1. The residual final oil was analyzed by gas chromatography and its composition was found to be 6-methyl-3-phenylphthalide (75%), 2-formyl-4-methylbenzophenone (8%) and 2,4-dimethylbenzophenone (12%); ir (neat) 1770, 1665, and 1600 cm^{-1}.

On acidification of the bicarbonate layer a black-brown amorphous semisolid mass (5.0 g) was produced.

Run 3:

A solution of 5.00 g (0.024 mol) of 2,4-dimethylbenzophenone in 220 ml of glacial acetic acid containing 4.0 ml of concentrated hydrochloric acid was photolyzed with the Hanovia lamp for 96 hr. in a flowing air stream. The work-up treatment was as per Runs 1 and 2. The composition of the oil was determined by gas chromatography to be 2-methylanthraquinone (13%), 6-methyl-3-phenylphthalide (32%), 2-formyl-4-methylbenzophenone (1%), and 2,4-dimethylbenzophenone (53%).

Acidification of the bicarbonate washes gave 2.59 g of an amorphous, black tarry substance.

Photooxidation of 2,3'-Dimethylbenzophenone - Attempted Preparation of 3-(3-Methylphenyl)phthalide

A solution of 5.00 g (0.024 mol) of 2,3'-dimethylbenzophenone in 220 ml of glacial acetic acid containing 4.0 ml of concentrated hydrochloric acid was irradiated with the Hanovia lamp for 96 hr. while being continuously saturated with air. Work-up was in the standard manner, giving an oily product which was found by gas chromatography to be a mixture of seven components. One unidentified component represented 49% of the oil. Peak enhancement with authentic 2-methylanthraquinone showed that the oil was devoid of this compound.

The acidified bicarbonate extracts gave 2.33 g of brown solid. A portion of this solid after ca. two crystallizations from benzene gave as a tan solid, mp 160-161°, 3'-methylbenzophenone-2-carboxylic acid (lit.[93] mp 162.2-162.4°). The yield was 41%.

Photooxidation of 2-Methyl-, 2,4-Dimethyl-, and 2,5-Dimethylbenzophenone in Glacial Acetic Acid at 350 nm.

A glacial acetic acid solution of each ketone in the immersion well-reaction vessel apparatus was photolyzed in the Rayonet reactor (350 nm) according to the following general procedure.

A solution of 0.024 mol of the ketone in 160 ml glacial acetic acid was irradiated for 24 hr. in a flowing air stream. The reaction mixture was concentrated *in vacuo* and the resultant oil was completely dissolved in diethyl ether. The ether solution was extracted with saturated sodium bicarbonate solution (2 x 30 ml portions) and with saturated sodium chloride solution (1 x 30 ml portion) and then dried ($MgSO_4$). Concentration of the solution afforded an oil which was dissolved in a 1:1 mixture of benzene and ethanol. The benzene-ethanol was distilled off *in vacuo*. This procedure was repeated ca. 3 times to remove residual water. The final oily residue was analyzed by glpc and the results are reported in Table 1. The infrared spectra (neat) of these oils displayed sharp intense absorptions at 1770 (phthalide C=O) and 1665 (ketone C=O) cm^{-1}.

The 2-benzoylbenzoic acids were obtained and identified according to the standard work-up procedure. The yields are reported in Table 1. Authentic samples of the three acids[64] were on hand to facilitate identification by ir and mp.

Photooxidation of 2-Methyl-, 2,4- and 2,5-Dimethylbenzophenone in Benzene at 350 nm.

For 2-methyl- and 2,5-dimethylbenzophenone a solution of 5.0 g of the ketone in 350 ml of benzene was photolyzed-aerated in the Rayonet reactor at 350 nm for 30 hr. Three runs were made with 2,4-dimethylbenzophenone at concentrations of 6.0, 5.0 and 7.0 g of ketone in 350 ml benzene with reaction times of 67, 72 and 114 hr., respectively. Glpc analyses and acid yields are reported in Table 1.

The final product mixtures from the 2-methyl- and the 67 hr. 2,4-dimethylbenzophenone photolyses were analyzed by gas chromatography-mass spectrometry[65]. For 2-methylbenzophenone the mass spectrum of the middle glpc peak was m/e 210 (molecular ion), 181, 165, 152, 133, 105, 77 and 51; this spectrum was identical to that of authentic 2-formylbenzophenone. The glpc peak was enhanced with authentic 2-formylbenzophenone. For 2,4-dimethylbenzophenone the mass spectrum of the middle glpc peak was m/e 224 (molecular ion), 209, 195, 181, 165, 152, 119, 105, 91, 77, and 51.

Photooxidation of 2-Methyl-, 2,4-, 2,5-, 2,3'-, 2,2'- and 2,6-Dimethylbenzophenone in Benzene-Hanovia Lamp

A benzene solution of the ketone was irradiated in a flowing air stream in the immersion well-reaction vessel apparatus with the Hanovia lamp. The standard work-up procedure was followed in each case. The initial ketone concentrations, reaction times and product distributions are reported in Table 2.

Photooxidation of 2-Methyl-, 2,4-, 2,5-, 2,3'-, 2,2'- and 2,6-Dimethylbenzophenone in Glacial Acetic Acid-Hanovia Lamp

Glacial acetic acid solutions of the ketones were irradiated with the Hanovia lamp while being continuously saturated with air. The work-up procedure was standard in all cases. Initial ketone concentrations, reaction times and product distributions are reported in Table 3. Those reactions which gave previously unreported compounds (e.g. 3-(2-methylphenyl)phthalide) are described (*vide infra*) elsewhere in the Experimental Section.

Photooxidation of 2,5- and 2,4-Dimethylbenzophenone - 350 nm with Tungsten

The Hanovia immersion well-reaction vessel apparatus was used to contain the reaction solution and was placed inside the Rayonet cavity. A 200 watt incandescent tungsten bulb was suspended within the Rayonet cavity. The solution of 3.14 g (0.015 mol) of the ketone in 220 ml of benzene was irradiated (350 nm lamps plus tungsten bulb) in a flowing air stream for 30 hr. The reaction was worked-up and analyzed in the standard manner and the product yields are recorded in Table 4.

Photooxidation of 2-Methylbenzophenone - 350 nm with Tungsten

Run 1:

A solution of 3.14 g (0.016 mol) of 2-methylbenzophenone in 220 ml of benzene contained in the immersion well-reaction vessel apparatus was placed inside the Rayonet cavity along with a 200 watt incandescent tungsten bulb. The solution was irradiated (350 nm lamps plus tungsten bulb) in a flowing air stream for 30 hr. The reaction solution was filtered to remove some white crystalline solid (0.10 g) and treated in the standard manner to afford the final product oil which became semicrystalline on standing. Trituration with ethanol gave 0.3 g of white solid. The two crops of white solid displayed the same infrared spectrum; (KBr) 3520, 1770, 1595, and 1240 cm^{-1}; (Nujol) 3530, 1780, 1595, 1245, 1290, 1070 and 1000 cm^{-1}; mp sublimed >240°, softened 263°, slow melting 268-278°. The trituration filtrate was found to contain anthraquinone, 3-phenylphthalide, 2-formylbenzophenone and 2-methylbenzophenone by glpc analysis. The white solids were combined and crystallized several times from boiling toluene to yield light tan crystals, mp 273-277°; ir (Nujol) 3530, 1780, 1595, 1470, 1450, 1290, 1245, 1070, and 1000 cm^{-1}; mass spectrum m/e 402, 211, 210, 209, 194, 181, 166, 165, 164, and 163; nmr (DMSO) δ 6.66 (d, 1, J = 3 Hz., collapsed to a singlet on dilution with D_2O, $\underline{H}$C(OH)), and 6.9-8.2 (m, 18, aromatic protons). This material was found to be identical to an authentic specimen of compound XXXVII[85]. The yield of XXXVII was 6%.

Anal. Calcd for $C_{28}H_{20}O_4$: C, 79.98; H, 4.79.

Found: C, 80.60; H, 4.30.

Run 2:

This 48 hr. irradiation-aeration was conducted exactly according to the directions in Run 1. A 1.77 g (26%) yield of the dimer XXXVII was isolated. The product distribution is reported in Table 4.

Irradiation-Aerations of 2-Methyl- and 2,5-Dimethylbenzophenone with Tungsten Illumination

The experimental procedure was the same for both ketones.

A solution of 3.14 g of the ketone in 220 ml of benzene was charged to the immersion well-reaction vessel apparatus and the assembly was placed inside the Rayonet chamber. The solution was irradiated in a flowing air stream with one or with two 200 watt incandescent tungsten filament bulbs. The reactions were worked-up and analyzed in the standard manner. The reaction times, illumination conditions, and product yields are listed in Table 5.

Photooxidation of 2,4-Dimethylbenzophenone in Acetic Anhydride-Hanovia Lamp

A solution of 5.00 g (0.024 mol) of 2,4-dimethylbenzophenone in 220 ml of acetic anhydride was photolyzed with the Hanovia lamp for 24 hr. in a flowing air stream. The acetic anhydride was evaporated, leaving an oil. The oil was washed in the standard manner to afford a dark residual oil. The analysis of this oil by gas chromatography (expressed as % yield) was: 2-methylanthraquinone (19%), 6-methyl-3-phenylphthalide (54%), 2-formyl-4-methylbenzophenone (3%), and recovered 2,4-dimethylbenzophenone (13%). An amorphous solid (mp >300°, 0.86 g) was precipitated during the bicarbonate extractions and was not characterized further.

The sodium bicarbonate layer was acidified to afford 0.44 g of brown solid which was subsequently identified by ir and mp as 2-benzoyl-5-methylbenzoic acid[64]. The yield was 8%.

Photooxidation of 2,5-Dimethylbenzophenone in Methanol-Hanovia Lamp

A solution of 5.0 g (0.024 mol) of 2,5-dimethylbenzophenone in 350 ml of absolute methanol was irradiated in a flowing air stream with the Hanovia lamp for 24 hr. The reaction mixture was concentrated to ca. 75 ml at which point much solid appeared. The orange solid (1.04 g) was filtered off; ir (Nujol) 1775, 1730, 1670 and 1605 cm^{-1}. Glpc analysis showed that it contained 2-methylanthraquinone, 6-methyl-3-phenylphthalide, 2-formyl-4-methylbenzophenone and starting ketone. The filtrate was evaporated to a viscous oil which glpc showed contained the aforementioned products in the ratio 4:9:8:1.

Extraction of 2-Methylbenzophenone Photooxidation Product Mixtures with Sodium Bisulfite

The product mixture derived from the photooxidation reaction of each 2-methylbenzophenone was extracted with a saturated aqueous solution of sodium bisulfite according to the general procedure outlined below. Those product mixtures which were treated in this fashion are designated in Tables 1, 2 and 4.

An approximate 1 g portion of the product mixture was dissolved in ca. 100 ml of toluene. The toluene solution was extracted with saturated aqueous sodium bisulfite solution (four 50 ml portions). The toluene layer was filtered, dried ($MgSO_4$) and concentrated *in vacuo* to afford an oil which was analyzed by glpc. A comparison of the product oil chromatograms obtained before and after the bisulfite treatment was made to determine the relative 2-formylbenzophenone concentration change. In each case, the phthalide: 2-formylbenzophenone peak area ratio was larger after the bisulfite extractions.

Extended Irradiations of the Photooxidation Product Mixtures of 2-Methylbenzophenones

A photooxidation product mixture from 2-methyl-, 2,5- and 2,4-dimethylbenzophenone was irradiated according to the following scheme. The product mixtures treated in this way are denoted in Table 1.

Two aliquot portions of each product mixture were taken. One aliquot was dissolved in benzene and the other in glacial acetic acid containing 1% of concentrated hydrochloric acid. Each solution was then treated separately. The solution was charged to a Pyrex tube in the Rayonet reactor and was degassed and maintained under a nitrogen atmosphere during a 24 hr. irradiation (350 nm). In addition, for 2,4-dimethylbenzophenone, the irradiations were also carried out with the Hanovia lamp. The solution was concentrated to yield an oil which was analyzed by glpc. A comparison of the product oil chromatograms obtained before and after the extended irradiation treatment was made to establish the relative 2-formylbenzophenone concentration change. For each ketone, the phthalide: 2-formylbenzophenone peak area ratio was larger after the extended irradiation in benzene while in the acid media, no 2-formylbenzophenone remained.

Photooxidation of 2-Formylbenzophenone

A solution of 1.5 g (0.007 mol) of 2-formylbenzophenone in 220 ml of benzene was photolyzed in a flowing air stream with the Hanovia lamp for 24 hr. The mixture was filtered to remove 0.33 g of solid which was not characterized, but did not contain any anthraquinone; ir (KBr) poorly resolved, 1670-1800 cm^{-1}. The filtrate was taken through the standard work-up treatment to yield a semisolid residue. The composition of the residue was 3-phenylphthalide (85%), 2-formylbenzophenone (4%) and benzophenone (9%) according to glpc analysis.

The acidified bicarbonate layer gave 0.03 g of a black amorphous material.

Kinetic Studies - Photooxidation of 2-Methylbenzophenones

The general procedure employed was to charge the immersion well-reaction vessel apparatus with a solution of the 2-methylbenzophenone. The solution was irradiated in the flowing air stream with the Hanovia lamp in the normal manner. A 3 ml aliquot was removed every half hour during the course of the photolysis. The aliquots were then analyzed by glpc. The ketone photooxidations monitored by this technique and the length of reaction time covered were 5.0 g (0.024 mol) 2,5-dimethylbenzophenone in 350 ml benzene, 20 hr.; 6.15 g (0.029 mol) 2,5-dimethylbenzophenone in 430 ml glacial acetic acid, 17 hr.; 6.15 g (0.029 mol) 2,6-dimethylbenzophenone in 430 ml glacial acetic acid, 21 hr.; and 5.72 g (0.029 mol) 2-methylbenzophenone in 430 ml glacial acetic acid, 9 hr.

Dark Reaction of 2-Methylbenzophenone with Air

A stream of air was continuously bubbled through a solution of 1.0 g (0.005 mol) of 2-methylbenzophenone in 80 ml of benzene for 96 hr. The solution was kept in the dark during the aeration. The benzene was distilled off *in vacuo* and the resultant oil was found to be unchanged and pure 2-methylbenzophenone by ir and glpc.

Photooxidation of Anthrone - Hanovia Lamp

A solution of 3.56 g (0.018 mol) of anthrone in 220 ml of benzene was irradiated with the Hanovia lamp for 7 hr. A considerable amount of solid was present in suspension after about 1-2 hr. had elapsed. The solvent was removed *in vacuo* giving an orange solid residue which was dissolved almost completely in 100 ml of boiling chloroform, filtered and refrigerated. The insoluble residue weighed 0.11 g, mp >300°, and was not characterized further. A 0.1 g yield of yellow-orange needles, mp sublimed >200°, melted 278-284°, crystallized from the solution. The infrared spectrum of this sample was identical to that of a pure specimen of anthraquinone (lit.[95] mp 286°, sublimes); ir (KBr) 1670, 1575, 1280, 1165, 930, 805, and 680 cm^{-1}. The filtrate was concentrated to a solid. The solid was slurried with two portions of hot toluene. A second crop of anthraquinone (0.54 g) crystallized from the cooled toluene filtrate solution bringing the total yield to 0.64 g (17%). The toluene insoluble residue was again slurried with hot toluene. A brown solid (0.77 g, mp 250°, very gradual) crystallized from the cooled toluene filtrate. The infrared spectrum of this solid was identical to that of an authentic sample of bianthrone, mp 265-270° (lit.[96] mp 250° dec); ir (KBr) 1655, 1595, 1460, 1310, 1170, 1155, 1095, 930, 790, and 685 cm^{-1}. The yield was 11%.

Photooxidation of Anthrone - 350 nm Rayonet

A solution of 4.0 g (0.021 mol) of anthrone in 250 ml of benzene contained in a Pyrex tube was irradiated for 36 hr. in the Rayonet at 350 nm. Air was bubbled through the reaction solution during the irradiation. The solvent was removed *in vacuo* to afford an orange solid residue, 4.52 g. The residue was sublimed *in vacuo* at 220° to yield 2.20 g of orange solid, mp 280-286° sublimed to needles. The infrared spectrum was identical to that of an authentic sample of anthraquinone (lit.[95] mp 286°, sublimes). The yield was 51%.

Attempted Photo-Elbs Reactions of 2-Methyl-, 2,4-Dimethyl- and 2,5-Dimethylbenzophenone

The following procedure was carried out with each of the three ketones.

A solution of 0.024 mol of the benzophenone in 350 ml of sodium dired benzene was degassed and kept under nitrogen. The solution was irradiated for 24 hr. with the Hanovia lamp. A semisolid yellow residue was obtained after removal of the benzene *in vacuo*. Glpc analysis of the residue detected only two components, starting benzophenone and its corresponding benzhydrol. The benzhydrol peak was also enhanced by the addition of the corresponding pinacol to the reaction residue.

Authentic samples of the benzhydrols and pinacols[74,14f] were available for peak enhancement.

Attempted Photoinduced Elbs Reactions of 2,4-Dimethylbenzophenone

Method 1:

A solution of 4.0 g (0.019 mol) of 2,4-dimethylbenzophenone in 230 ml of toluene was degassed and maintained under nitrogen gas. The solution was kept at 105-110° while it was irradiated in the Rayonet reactor (350 nm) for 38 hr. Concentration of the yellow solution afforded an oil whose ir spectrum was identical to that of authentic 2,4-dimethylbenzophenone. Glpc detected three components; starting ketone, a trace of 2,4-dimethylbenzhydrol and a negligible trace of an unknown.

Method 2:

A solution of 3.0 g (0.014 mol) of 2,4-dimethylbenzophenone in 250 ml of toluene was charged to a Pyrex tube in the Rayonet reactor. Air was continuously bubbled through the solution maintained at 105-110° during a 24 hr. irradiation at 350 nm. The yellow reaction solution was worked up in the standard manner. Glpc analysis of the product oil found the following components and percent yields: 2-methylanthraquinone (absent), 6-methyl-3-phenylphthalide (10%), 2-formyl-4-methylbenzophenone (17%) and starting ketone (15%). The yield of 2-benzoyl-5-methylbenzoic acid was 25%.

Irradiation of 2-Formylbenzophenone in the Presence of Dimethyl Acetylenedicarboxylate

A thoroughly degassed solution of 1.42 g (6.7 mmol) of 2-formylbenzophenone and 1.10 g (7.8 mmol) of dimethyl acetylenedicarboxylate in 120 ml of sodium dried benzene was photolyzed in the Rayonet reactor (350 nm lamps) for 30 hr. under a nitrogen atmosphere. The benzene was removed by flash distillation in vacuo and the resultant oil was triturated with cold CCl_4 to afford 0.30 g of brown solid; ir (KBr) 1740 cm^{-1}. The sample was shown to be identical to an authentic specimen of 3-phenylphthalide (mp and ir comparison).

Photolysis of 2-Methylbenzophenone in the Presence of Quinone

Run 1:

A thoroughly degassed solution of 5.0 g (0.025 mol) of 2-methylbenzophenone and 6.51 g (0.060 mol) of quinone in 350 ml of sodium dried benzene was maintained under a nitrogen atmosphere during a 24 hr. irradiation with the Hanovia lamp. The solvent was distilled in vacuo, leaving a dark semisolid residue. Glpc analysis showed that anthrone was absent.

Run 2:

This reaction was carried out as per directions for Run 1 except the reactant concentrations were 5.0 g (0.025 mol) of 2-methylbenzophenone and 5.49 g (0.051 mole) of quinone in 350 ml of benzene and the reaction time was 12 hr. The product oil again was devoid of anthrone as shown by glpc analysis.

Photolysis of 2-Methylbenzophenone in the Presence of 9,10-Phenanthraquinone

Run 1:

A mixture of 2.85 g (0.014 mol) of 2-methylbenzophenone and 1.18 g (0.006 mol) of 9,10-phenanthraquinone in 200 ml of sodium dried benzene was degassed and maintained under a nitrogen atmosphere. The mixture was photolyzed with the Hanovia lamp for 24 hr. The mixture became clear after 1 hr. of irradiation. The benzene was removed *in vacuo*, leaving an oil. Gas phase chromatography using authentic anthrone for peak enhancement showed that this component was not present in the product oil.

Run 2:

This reaction was carried out in the same manner as Run 1 except that the initial concentration of 9,10-phenanthraquinone was 4.00 g (0.019 mol) in 200 ml of benzene. The resultant black product oil was found to be devoid of anthrone by gas chromatography.

Photolysis of 2-Methylbenzophenone in the Presence of 2,3-Dichloro-5,6-dicyanobenzoquinone

A solution of 3.0 g (0.015 mol) of 2-methylbenzophenone and 6.6 g (0.029 mol) of 2,3-dichloro-5,6-dicyanobenzoquinone in 230 ml of sodium dried benzene was degassed and maintained under a nitrogen atmosphere. The solution was irradiated for 12 hr. with the Hanovia lamp, after which time the irradiation was terminated due to an extensive solid coating on the immersion well. After the coating was removed with an acetone wash the reaction mixture was degassed again and held under nitrogen gas. The irradiation was continued for an additional 23 hr. The solvent was removed in vacuo to yield a solid residue. No anthrone was detected in this residue by peak enhancement gas chromatography using authentic anthrone.

Photooxidation of 2,5-Dimethylbenzophenone in the Presence of 2,5-Dimethylfuran

A solution of 5.0 g (0.024 mol) of 2,5-dimethylbenzophenone and 5.7 g (0.059 mol) of freshly distilled 2,5-dimethylfuran in 350 ml of sodium dried benzene was charged to the immersion well-reaction vessel. A stream of air was bubbled through the solution during a 6.5 hr. irradiation with the Hanovia lamp. Aliquots (3 ml) were taken from the reaction at 2.0, 3.5 and 5.0 hr. of elapsed reaction time. Each aliquot was analyzed by glpc. The composition of each aliquot was approximately the same, i.e. no significant change in the concentration of any component was noted over the 3.0 hr. period. The concentrations of 5-methyl-3-phenylphthalide and 2-formyl-5-methylbenzophenone increased slightly (ca. <5%) over the 3.0 hr. The composition was an unknown (35%), 2-methylanthraquinone (8%), 5-methyl-3-phenylphthalide (1%), 2-formyl-5-methylbenzophenone (15%), and 2,4-dimethylbenzophenone (35%). The last aliquot was also shown to contain considerable 2,5-dimethylfuran.

The clear yellow reaction solution was concentrated in vacuo to yield a semisolid residue. Trituration of the residue with cold methanol produced a white solid which was collected by filtration; 2.1 g mp 149-151°; ir (Nujol) 3400 (sh) and 1695 (sh) cm^{-1}. The solid was crystallized several times from methanol to afford white crystals of mp 160.5-162°. Elemental analyses indicated that this material was a 1:1:1 adduct of 2,5-dimethylbenzophenone, 2,5-dimethylfuran, and water. Peak enhancement glpc showed that this substance was the same unknown (35%) found in the reaction aliquots. The compound gave a positive iodoform test.

Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46.
Found: C, 77.60; H, 7.30.

Ir (Nujol) 3400 (sh) and 1695 (sh) cm^{-1}; ir ($CHCl_3$) 1700 (sh) cm^{-1}; nmr ($CDCl_3$) δ 1.23 (s, 3, CH_3), 1.45 (s, 3, CH_3), 2.00 (s, 3, CH_3), 2.31 (d, 2, J = 3 Hz, $C\underline{H}-CH_2$), 2.43 (s, 3, CH_3), 4.29 (t, 1, J = 3 Hz, $CH-C\underline{H_2}$), 6.20 (s, 1, OH) and 6.70-7.45 (m, 8, aromatic protons); mass spectrum m/e 324 (molecular ion), 306, 288, and 263.

The oil left after removal of the white solid by methanol trituration was examined by ir (neat) and showed absorptions at 1775, 1719 (broad) and 1670 cm^{-1}. Glpc showed that its composition was the unknown (38%), 2-methylanthraquinone (12%), 5-methyl-3-phenylphthalide (6%), 2-formyl-5-methylbenzophenone (19%), and 2,4-dimethylbenzophenone (24%). Part of the oil was extracted thoroughly with saturated $NaHCO_3$ solution. The bicarbonate layer was acidified and then extracted with benzene. Evaporation of the benzene produced a semicrystalline product whose ir (Nujol), although not a peak-for-peak match with the ir of authentic 2-benzoyl-4-methylbenzoic acid, did contain all the peaks of the authentic acid.

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