The Effect of Substitution on the Photoreduction of Some Hindered Benzophenones[1]

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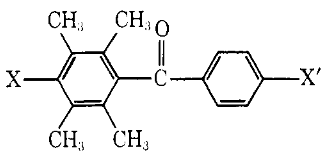
The photoreduction of 2,3,5,6-tetramethylbenzophenone (**1a**) and several of its 4 and 4′ (Cl, Br, OCH_3) derivatives with 2-propanol has been investigated. The products formed and the quantum yields for the disappearance of ketone, ϕ_B, depend on both the nature of the substituent and its position (4 or 4′). Substitution in the 4 position has little effect on ϕ_B while substitution in the 4′ position increases ϕ_B substantially relative to **1a**. Product analysis indicates that attack of a dimethylhydroxymethyl radical on the 4′ position of the hindered ketone leading to the formation of 1-(durylhydroxymethylene)-4-(dimethylhydroxymethyl)-2,5-cyclohexadiene (**10**) as an intermediate is an important step in the photochemistry of the ketones investigated.

In recent years the effect of substitution on the efficiency of the photoreduction of aromatic ketones has been the subject of several investigations.[2-5] The nature of this effect has been found to depend on the nature of the lowest triplet state of the molecule. Generally, aromatic ketones with lowest lying n–π* states exhibit normal, efficient photoreduction by alcohols while those with lowest lying or closely lying π–π* states show reduced reactivity. One problem which is encountered in the interpretation of these substituent effects is that most groups show both a resonance and an inductive effect simultaneously. Consequently the degree of involvement of each of these effects in the excited state is difficult to determine.

In this study, the photoreduction of 2,3,5,6-tetramethylbenzophenone and several of its 4 and 4′ derivatives **1a–g** with 2-propanol was investigated.



1a-g

1	X	X′
a	H	H
b	Br	H
c	Cl	H
d	OCH_3	H
e	H	Br
f	H	Cl
g	H	OCH_3

This series was chosen for several reasons, foremost among which is the fact that methyl substituents in both the 2 and the 6 positions inhibit the coplanarity of the duryl ring with the carbonyl group. The phenyl ring, however, can attain coplanarity without severe steric interactions. One anticipates that a substituent in the 4′position would interact with the carbonyl group both by resonance and induction while a substituent in the 4 position would interact primarily through induction. This assumption was supported by the uv spectra of these compounds which were identical for the derivatives substituted in the 4 position (**1a–d**), but experienced bathochromic shifts for those substituted in the 4′ position (**1e–g**). By comparing the effect on the efficiency of photoreduction of a substituent in the 4 position with the same substituent in the 4′ position, it was felt that a clearer picture of substituent interaction in the photoreduction process could be obtained.

Results and Discussion

Quantum yields (ϕ_B) relative to **1a** based on the disappearance of ketone were determined and are presented in Table I. Though the variations observed are difficult to interpret on the basis of known structure–reactivity relationships, two trends are evident. Substituents in the 4 position have only a slight effect on the quantum yields, while those in the 4′ position produce a marked increase in ϕ_B for each substituent.

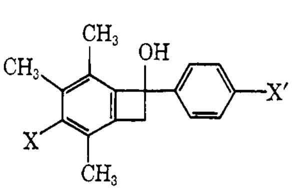
TABLE I

RELATIVE QUANTUM YIELDS OF DISAPPEARANCE OF 4- OR 4′-SUBSTITUTED 2,3,5,6-TETRAMETHYLBENZOPHENONES[a]

Ketone	ϕ_B
1a[b]	1.0
1b	0.5
1c	1.2
1d	1.2
1e	2.2
1f	4.3
1g	2.2

[a] All ketones are 0.01 *M* in 2.0 *M* 2-propanol–benzene. [b] Absolute quantum yield, 0.04.

Product analysis was accomplished using both preparative thin layer and column chromatography. Four classes of compounds were isolated and assigned structures **2**, **3**, **4**, and **5** based on elemental analysis and ir



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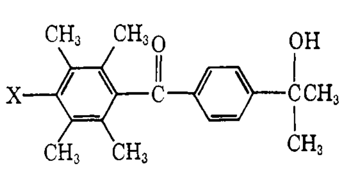

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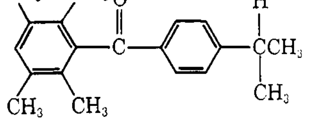

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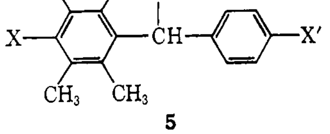

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(1) Presented in part at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 27 to Sept 1, 1972.

(2) J. N. Pitts, Jr., H. W. Johnson, and T. Kuwana, *J. Phys. Chem.* **66**, 2456 (1962).

(3) A. Becket and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963).

(4) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

(5) N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

and nmr spectroscopy. It is noteworthy that no pinacols were detected in any of these reactions.

The nature of the substituent and its position on the ring have a profound influence on both the products formed and their yields. Product analyses and other pertinent data for the ketones studied are presented in Table II.

TABLE II

PRODUCTS FORMED IN THE PHOTOREDUCTION OF 2,3,5,6-TETRAMETHYLBENZOPHENONE AND ITS 4- AND 4′-SUBSTITUTED DERIVATIVES[a]

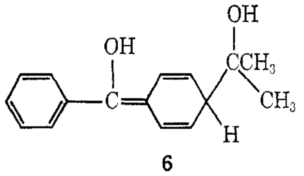
Ketone	Irradn period, hr	% ketone recovd[c]	% products 1a	2	3	4	5
1a	24	41.5		30	15		54
1b	40	56	59				
1c[b]	18.5	3.8		31			10
1d	18.5	62		5	11		84
1e	12	33	14	<1		14	<1
1f	2.5	61.5		26.5		38	
1g	12	1.8		70			21

[a] Irradiated solutions contained 0.5 g of ketone in 200 ml of 2.0 *M* 2-propanol–benzene. [b] The principal product in this reaction was an alkyl duryl ketone which has not yet been identified. [c] Based on total material isolated from column chromatography.

Benzocyclobutanol formation was observed in all cases except for the brominated derivatives **1b** and **1e**. In the case of **1b**, debromination is the only major primary photochemical process. Benzhydrols were formed in all cases except for the bromo compounds **1b** and **1e** and the 4′-chloro derivative **1f**. In the case of **1e** and **1f**, the two most reactive of the compounds studied, the lack of benzhydrol formation is compensated for by the formation of the isopropyl derivative (**4**), which is formed only in these two cases. The 4′-dimethylmethylol compound (**3**) was formed in detectable amounts only in the photoreduction of **1a** and **1d**.

The significance of these results becomes clear if one considers the problems that have existed in determining the mechanism of photoreduction. Though the photoreduction of benzophenone by alcohols has been known and studied for many years, the exact mechanism is still the subject of some controversy. Much of this controversy stems from attempts to explain the significance of the yellow color which develops during the photoreduction of carefully degassed solutions.[6–8] The origin of this color has been found to be a long-lived intermediate, the nature of which has remained in doubt for nearly 15 years.

Recently, enol structure **6** was proposed for this intermediate by several independent workers.[9–11] Still more recently, Weiner questioned the intermediacy of this structure in the photoreduction process.[12] Much of the problem arises from the fact that direct confirmation of this structure by product isolation or trapping has not been possible.[13] In the present study, product analysis clearly implicates an enol structure like **6** as an intermediate.



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The results of our work in conjunction with those published[11] earlier support the following mechanism for the photoreduction of **1a–g** in 2-propanol.

Steps 1 and 2 are similar to those previously proposed for benzophenone.[2,6,8] In the present work a quenching study using **1a** and piperylene gave a linear Stern–Volmer plot from which the apparent triplet lifetime, τ (0.54×10^{-7} sec), and the rate constant for hydrogen abstraction, k_r ($7.39 \times 2\ M \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$), were obtained. At 0.03 *M* piperylene concentration all reactions of **1a** were quenched.

The reaction in step 3 explains the formation of product types **3** and **4** and is analogous to the mechanism proposed for benzophenone.[11] The isolation of **3** provides direct evidence for the intermediacy of a structure such as **10** in the photoreactions of the hindered benzophenones. This intermediate may subsequently undergo either reaction 7, 8, or 9 depending on the substituent in the 4′ position. When either –H or –OCH_3 is in this position (except **1b**) the dark reaction, step 7, is the preferred route producing two ketyl radicals, **7**, and acetone in a manner proposed by Filipescu.[11] The ketyl radicals would then undergo disproportionation, step 10, yielding the benzhydrol, **5**, and starting ketone. Disproportionation rather than combination has been shown to be the preferred reaction between ketyl radicals produced by sterically hindered ketones.[14] Upon the admission of air at the conclusion of the photolysis, the intermediate **10** reacts with atmospheric oxygen to produce **3** (step 8).

When either –Cl or –Br is in the 4′ position (**1e** and **1f**), **10** undergoes two successive elimination reactions to yield **4**, presumably by way of **11**. This reaction is apparently possible because of the relatively weak C–X bond in the intermediate and does not occur with either –H or –OCH_3 in the 4′ position.

Further evidence for steps 7–10 is provided by the

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(6) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Amer. Chem. Soc.*, **81**, 1068 (1959).

(7) G. O. Schenck, W. Meder, and M. Pape, *Proc. U. N. Int. Conf. Peaceful Uses At. Energy, 2nd*, **29**, 2617 (1966).

(8) H. L. J. Bäckström, K. L. Appelgren, and R. J. V. Niklassen, *Acta Chem. Scand.*, **19**, 1555 (1965).

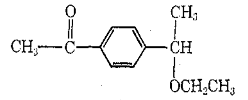
(9) H. L. J. Bäckström and R. J. V. Niklasson, *Acta Chem. Scand.*, **20**, 2617 (1966).

(10) D. C. Neckers, "Mechanistic Organic Photochemistry," Rheinhold, New York, N. Y., 1967, p 171.

(11) N. Filipescu and F. L. Minn, *J. Amer. Chem. Soc.*, **90**, 1544 (1968).

(12) S. A. Weiner, *J. Amer. Chem. Soc.*, **93**, 425 (1971).

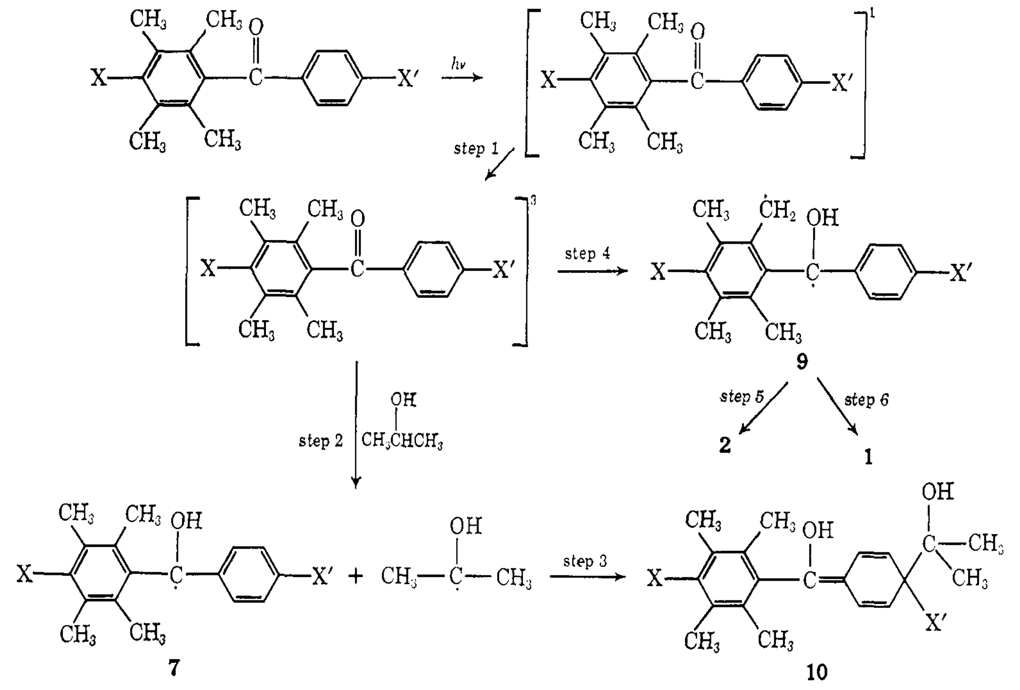
(13) A product having the structure i has been reported as being formed

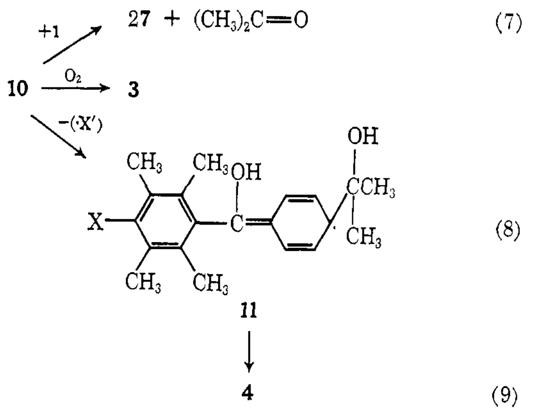


i

in the photoreduction of acetophenone in ethyl ether: B. D. Charlland, *Can. J. Chem.*, **47**, 687 (1969).

(14) F. D. Lewis, *Tetrahedron Lett.*, 1373 (1970).

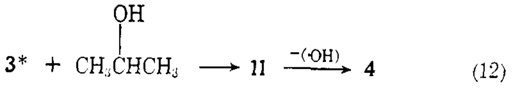




$$27 \longrightarrow 5 + 1 \qquad (10)$$

fact that irradiation of **3** (X = H) in 2 *M* 2-propanol in benzene produces **4** (eq 11 and 12). This shows that **3**

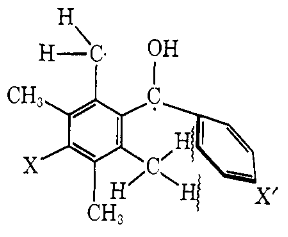
$$3 \xrightarrow{h\nu} 3^* \qquad (11)$$



$$3^* + \overset{\text{OH}}{\overset{|}{\text{CH}_3\text{CHCH}_3}} \longrightarrow 11 \xrightarrow{-(\cdot\text{OH})} 4 \qquad (12)$$

is not produced during the photolysis of **1a** but only after the admission of air since **4** was not detected with those ketones in which X′ = H (**1a**) or CH_3O (**1d**).

The photoenol formed in step 4 is similar to that reported in the photoreduction of 2-alkylbenzophenone[3,15,16] and 2,4,6-trialkylphenyl ketones.[17,18] An examination of molecular models shows that considerable steric interaction should be expected between the methyl group in the 6 position and the phenyl ring as shown in I.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Such interactions are not present in systems substituted only in the 2 position where a reversible enolization process is the favored reaction.[15] In the present case, however, a cyclization process leading to the formation of benzocyclobutanols (step 5) would relieve this crowding.

In the absence of phosphorescence data no definite conclusions can be made regarding the type of excited states involved. The results obtained in this study, however, allow for considerable speculation. Consider the methoxyl-substituted compounds **1d** and **1g**. In the case of **1g**, the methoxyl group can become conjugated with the carbonyl group thereby lowering the $\pi-\pi^*$ state. Since the major product in this instance was the cyclobutanol compound **2**, it may be tentatively concluded that the $^3[\pi-\pi^*]$ state is the photoreactive state involved. In contrast to this the methoxyl group in **1d** should exert an inductive effect on the system, thereby lowering the $n-\pi^*$ state relative to the $\pi-\pi^*$ state.[19] Since, with **1d**, the photoreduction yields mainly benzhydrol, **5**, the $^3[n-\pi^*]$ state must be involved in the reduction and the $^3[\pi-\pi^*]$ state in cyclobutanol formation.

Though the stereochemistry of the ketones investigated in this study differs significantly from that of benzophenone, it is not unreasonable to assume that the photochemical processes occurring in the two systems are the same. Whether the formation of intermediate **10** is due to unique steric factors involving the carbonyl group or whether all benzophenone photoreductions proceed by way of a similar intermediate cannot be determined directly from this work. If one assumes, however, that intermediates such as **10** are common to all benzophenone photoreductions, then, using stereo-

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

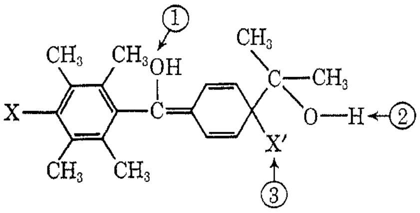
(16) E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2671 (1963).

(17) T. Matsuura and Y. Kitaura, *Tetrahedron*, **25**, 4487 (1969).

(18) Y. Kitaura and T. Matsuura, *Tetrahedron*, **27**, 1597 (1971).

(19) Y. Ogata, K. Takagi, and Y. Fujii, *J. Org. Chem.*, **37**, 4026 (1972).

chemistry as the main criterion of difference, the results obtained can be applied to the photoreduction of aryl ketones in general. There appear to be three critical centers on the intermediate, **10** (arrows), which determine the course of the dark reaction.



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As Filipescu, *et al.*, suggest, reaction could occur at ② through hydrogen abstraction by ketone.[11] This leads to benzopinacol in the case of benzophenone and to a benzhydrol in the case of hindered ketones. In the case of **1a–g**, however, owing to steric hindrance about the carbonyl group, this reaction is substantially suppressed.

When oxygen is introduced, a fast reaction occurs at ① in benzophenone and, because of hindrance, at ①, or ③ in the case of **1a**. When reaction occurs at ① and ② starting ketone is produced while reaction at ③ results in 4′ substitution. Further work is in progress on other hindered ketones and we hope to report these results in a subsequent paper.

Summary.—The photoreduction of several 4- or 4′-substituted duryl phenyl ketones yields at least four different classes of compounds indicated by structures **2–5**. The dimethylhydroxymethyl radical attacks the 4′ position of aryl ketones in a manner suggested by Filipescu and Minn.[11] If the substituent in the 4′ position is either –Cl or –Br, elimination of the halogen occurs, followed by elimination of –OH, yielding the 4′ isopropyl derivative **4**. The substituent and its position on the ring, 4 or 4′, has a profound influence on the nature of the products formed.

Experimental Section

Melting points are uncorrected and were determined on a Mel-Temp apparatus. The nmr spectra were recorded on a Joelco Model C-60HL spectrometer at 60 MHz using tetramethylsilane as an internal standard. Ir spectra were determined on a Perkin-Elmer Model 700 spectrophotometer, and uv spectra were measured on a Cary Model 15 spectrophotometer. The microanalyses were performed by Micro Analysis, Inc., Wilmington, Del. All solvents used in the photolysis studies were spectroscopic grade and were used as received. Benzene was obtained from Matheson Coleman and Bell and the 2-propanol from Fisher Scientific Co. The benzophenone and benzyhydrol used in the quantum yield determinations were recrystallized four times from petroleum ether (bp 60–80°) prior to use.

Synthesis of the Substituted Benzophenones.—The 4- and 4′-substituted derivatives were prepared by the Friedel-Crafts acylation of either durene or substituted durene with the appropriate benzoyl chloride according to the general method of Fuson.[20] The structure of the ketones prepared in this manner were confirmed by ir and nmr spectroscopy and either by a comparison with literature melting points or by elemental analysis.[21] Pertinent data for new compounds is listed in Table III.

TABLE III

1	Mp, °C	% yield[a]	Analyses, %
c	122–124	55	Calcd for $C_{17}H_{17}ClO$: C, 74.84; H, 6.29; Cl, 13.00. Found: C, 74.57; H, 6.37; Cl, 12.78.
d	153.5–154.5	74	Calcd for $C_{18}H_{20}O_2$: C, 80.55; H, 7.52. Found: C, 80.58; H, 7.58.
f	170.0–171.5	90	Calcd for $C_{17}H_{17}ClO$: C, 74.84; H, 6.29; Cl, 13.00. Found: C, 74.97; H, 6.33; Cl, 13.08.

[a] Based on Friedel-Crafts reaction.

Quantum Yield Determinations.—Quantum yields were measured using solutions of 0.01 M ketone and 2.0 M 2-propanol in benzene sealed under vacuum in 13-mm-o.d. Pyrex tubes after a minimum of five freeze–thaw cycles at a vacuum of <0.01 mm. Samples were irradiated in parallel using a Rayonet Model MGR-500 merry-go-round at 30 ± 1° using a filter solution of nickel sulfate and cobalt sulfate[22] to isolate the 3130-Å light from a Hanovia Type A 550-W lamp. The quantum yield of duryl phenyl ketone was determined using benzophenone benzhydrol actinometry.[23] Duryl phenyl ketone was in turn used as the standard for determination of the quantum yields of the substituted derivatives. Samples were analyzed for disappearance of ketone by observing the decrease in band intensity of the uv absorption spectra of diluted solutions of the isolated ketones after irradiation. The ketones were isolated from the reaction by thin layer chromatography and compared to nonirradiated samples treated in an analogous manner. Absorbancies were determined using an average of five wavelengths to measure the concentrations before and after irradiation.

Photolysis of 1a in 2 M 2-Propanol in Benzene.—A solution of duryl phenyl ketone (0.500 g) in 200 ml of 2 M 2-propanol in benzene was irradiated for 24 hr with the 3000-Å lamps. The solution was yellow at the end of the irradiation period. Evaporation of the solvent under reduced pressure gave a yellow oil. The oil was dissolved in petroleum ether–benzene (1:1) and chromatographed on a silica gel column (30 g). Elution with petroleum ether–benzene (1:5) gave 0.182 g of unreacted duryl phenyl ketone. Further elution gave 0.139 g of the hydrol derivative (**5a**) of duryl phenyl ketone and 0.078 g of a colorless oil. An ir spectrum of **5a** was virtually superimposable on that of the alcohol formed by the chemical reduction of duryl phenyl ketone with sodium. The naphthylurethane derivative of **5a** had mp 178–179.5° (lit.[20] 177–178.5°). The ir spectrum (neat) of **5a** showed peaks at 3350 (OH), 1010 and 1030 (C–O) cm^{-1}. The nmr spectrum ($CDCl_3$) showed the following bands: δ 7.25 (s, 5, Ar), 6.96 (s, 1, Ar), 6.40 (s, 1, CHOH), 2.20 (s, 3, CH_3), 2.10 (s, 3, CH_3).

The colorless oil was identified as the benzocyclobutanol derivative **2a**: ir 3350 (OH) and 1060 (C–O) cm^{-1}; nmr ($CDCl_3$) δ 6.99 (s, 5, Ar), 6.60 (s, 1, Ar), 3.10 (s, 2, CH_3), 2.64 (s, 1, OH), 2.02 (s, 3, CH_3), 1.98 (s, 3, CH_3), 1.80 (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.49; H, 7.57.

Further elution with chloroform–ether (9:1) gave 0.039 g **3** (X = H) as an oil with a yellow tint which crystallized upon standing. Recrystallization from benzene–petroleum ether gave a white solid: mp 127–128°; ir 3375 (OH), 1660 (C═O) cm^{-1}; nmr ($CDCl_3$) δ 7.57 (AB quartet, J = 9 Hz, 4, Ar), 6.95 (s, 1, Ar), 2.12 (s, 6, CH_3), 1.86 (s, 6, CH_3), 1.47 (s, 6, CH_3).

Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.03; H, 8.17. Found: C, 81.29; H, 8.17.

Photolysis of 1b in 2 M 2-Propanol in Benzene.—A 0.028 M solution (100 ml) in **1b** in 2 M 2-propanol was irradiated for 40 hr with the 3000-Å lamps. The solution was slightly yellow at the end of the irradiation. Evaporation of solvent under reduced pressure gave a light yellow oil. The oil was dissolved in hexane–benzene (1:1) and chromatographed on a column of 40 g of silica gel. Elution with benzene first gave 0.317 g of unreacted ketone followed by 0.146 g of duryl phenyl ketone, identified by a comparison of its ir spectrum with that of an authentic sample. Further elution with chloroform gave 0.039 g of a clear oil which appeared to be a mixture of durylphenylcarbinol (**5a**) and the

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[20] R. C. Fuson, B. C. McKusick and J. Mills, *J. Org. Chem.*, **11**, 60 (1946).

[21] Known compounds were synthesized by procedures described in the references that follow: **1a** and **1b**, R. C. Fuson and B. C. McKusick, *J. Amer. Chem. Soc.*, **65**, 60 (1943); **1e**, R. C. Fuson, W. S. Friedlander, and G. W. Parshall, *J. Amer. Chem. Soc.*, **76**, 5119 (1954); **1g**, R. C. Fuson, W. D. Emmons, and G. W. Parshall, *J. Amer. Chem. Soc.*, **76**, 5467 (1954).

[22] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

[23] W. M. Moore and M. Ketchum, *J. Org. Chem.*, **11**, 60 (1946).

cyclobutanol derivative (**2a**) of duryl phenyl ketone as shown by ir spectroscopy.

Photolysis of 1e in 2 *M* 2-Propanol in Benzene.—A solution of 0.500 g of **1e** in 200 ml of 2 *M* 2-propanol in benzene was irradiated for 12 hr with the 3000-Å lamps. The solution was dark yellow at the end of the photolysis. Evaporation of solvent under reduced pressure gave a brown oil which was dissolved in benzene–petroleum ether (1:1) and chromatographed on a silica gel (30 g) column. Elution with benzene–petroleum ether (1:3) gave 0.163 g of unchanged **1e**, identified by comparison of its ir spectrum with that of an authentic sample. Elution with benzene–petroleum ether (5:1) gave 0.094 g of a 1:1 mixture of duryl phenyl ketone and **4**, determined by ir and nmr spectroscopy. Further elution with benzene gave 0.026 g of products arising from the photolysis of **1a**.

Photolysis of 1c in 2 *M* 2-Propanol in Benzene.—Irradiation of 0.500 g of **1c** in 200 ml of 2 *M* 2-propanol in benzene for 18.5 hr produced a very slight yellow color in the solution. Evaporation of the solvent under reduced pressure gave an oil with a light yellow tint. The oil was dissolved in benzene–petroleum ether (1:1) and chromatographed on a 30-g column of silica gel. Elution with benzene–petroleum ether (5:1) gave 0.013 g of starting ketone identified by a comparison of its ir spectrum with that of an original sample. Further elution with benzene–petroleum ether (5:1) gave a mixture of 0.140 g of two hydroxyl-containing compounds as evidenced by their ir spectrum. Preparative tlc in benzene afforded the isolation of two white solids. The compound with the larger R_f value was identified as the hydrol derivative **5c**: ir (KBr) 3350 (OH), 1020 (C–O) cm^{-1}; nmr ($CDCl_3$) δ 7.17 (s, 5, Ar), 6.34 (s, 1, CHOH), 2.32 (s, 3, CH_3), 2.14 (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{19}ClO$: C, 74.29; H, 6.98; Cl, 12.90. Found: C, 74.28; H, 6.73; Cl, 13.04.

The compound with the lower R_f value was identified as the benzocyclobutanol derivative **2c**: ir 3325 (OH), 1460, 1150, 1065 (C–O) cm^{-1}; nmr ($CDCl_3$) δ 7.28 (s, 5, Ar), 3.36 (s, 2, CH_2), 2.70 (s, 1, OH), 2.28 (s, 3, CH_3), 2.18 (s, 3, CH_3), 2.02 (s, 3, CH_3).

Further elution with chloroform–ethyl ether (20:1) gave 0.065 g of a yellow oil. Its ir showed major absorptions at 3425 (w), 2925, 1690 (br), 1460, and 765 cm^{-1}. Tlc showed the presence of at least four components. The colored oil was not further investigated. Further elution with chloroform–ether (10:1) gave 0.130 g of an unidentified white solid. An ir spectrum (KBr) showed major absorptions at 3400, 2925, 1680 (C=O), 1450, 1380, 1120, and 1000 cm^{-1}. The nmr spectrum ($CDCl_3$) showed a well resolved quartet at δ 3.43 (J = 6 Hz) and a triplet at 1.2 (J = 6 Hz). Additional CH_3 peaks are present at δ 2.3 (6 H), 207 (6 H), and 1.13 (6 H). Most significant, however, was the fact that no bands appeared in the aromatic region.

Photolysis of 1f in 2 *M* 2-Propanol in Benzene.—A solution of 0.500 g of **1f** in 200 ml of 2 *M* 2-propanol in benzene was irradiated for a period of 2.5 hr with the 3000-Å lamps. The solution became very yellow within the first few minutes of irradiation and was dark yellow at the end of the photolysis. Evaporation of the solvent under reduced pressure gave a yellow oil. The oil was dissolved in benzene–petroleum ether (2:1) and chromatographed on a column of silica gel (30 g). Elution with benzene–petroleum ether (3:1) gave 0.295 g of unreacted **1f** which was identified by comparison of its ir spectrum with one of an authentic sample. Further elution with benzene–petroleum ether (5:1) gave 0.070 g of white solid, mp 107–108°, identified as structure **4**: ir (KBr) 1660 (C=O), 1600, 1250, 1190, cm^{-1}; nmr ($CDCl_3$) δ 7.34 (AB q, J = 8 Hz, 4, Ar), 6.88 (s, 1, Ar), 2.88 (septet, J = 7 Hz, 1, Ar), 2.17 (s, 6, CH_3), 1.93 (s, 6, CH_3), 1.28 (s, 3, CH_3), 1.17 (s, 3, CH_3).

Anal. Calcd for $C_{20}H_{24}O$: C, 85.65; H, 8.64. Found: C, 85.75; H, 8.57.

Further elution with benzene–petroleum ether (5:1) gave 0.049 g of a white solid, mp 98.5–99.5°, which was identified as the benzocyclobutanol derivative **2f**: ir (KBr) 3500 (OH), 1490, 1195, 1100 cm^{-1}; nmr ($CDCl_3$) δ 7.06 (s, 4, Ar), 6.72 (s, 1, Ar), 3.24 (s, 2, CH_2), 2.50 (s, 1, OH), 2.12 (s, 3, CH_3), 2.08 (s, 3, CH_3), 1.90 (s, 3, CH_3).

Anal. Calcd for $C_{17}H_{17}ClO$: C, 74.86; H, 6.28; Cl, 13.00. Found: C, 75.14; H, 6.36; Cl, 12.21.

Photolysis of 1g in 2 *M* 2-Propanol.—A solution of 0.500 g of **1g** in 200 ml of 2 *M* 2-propanol in benzene was irradiated for 12 hr with the 3000-Å lamps. The solution was very slightly yellow at the end of the irradiation period. Evaporation of the solvent under reduced pressure gave a light yellow oil which was dissolved in benzene–petroleum ether (5:1) and chromatographed on a silica gel (30 g) column. Elution with benzene–petroleum ether (5:1) gave 0.009 g of starting ketone which was identified by comparison of its ir spectrum with that of an authentic sample. Further elution with chloroform gave 0.109 g of a white solid, mp 116–117.5°, which was identified as the hydrol derivative **5g**: ir (KBr) 3500 (OH), 1040 cm^{-1}; nmr ($CDCl_3$) δ 7.21 (s, 1, Ar), 6.88 (AB q, J = 9 Hz, 4, Ar), 6.32 (s, 1, CHOH), 3.75 (s, 3, OCH_3), 2.22 (s, 6, CH_3), 2.12 (s, 6, CH_3).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.94; H, 8.22. Found: C, 79.84; H, 8.15.

Further elution with chloroform gave 0.343 g of a white solid, mp 113–114°, which was determined to be the benzocyclobutanol derivative **2g**: ir (KBr) 3500 (OH), 1170, 1040 cm^{-1} nmr ($CDCl_3$) δ 7.11 (AB q, J = 9 Hz, 4, Ar), 6.94 (s, 1, Ar), 3.77 (s, 3, OCH_3), 3.35 (s, 2, CH_2), 2.22 (s, 3, CH_3), 2.15 (s, 3, CH_3), 2.04 (s, 3, CH_3).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.55; H, 7.53. Found: C, 80.55; H, 7.73.

Photolysis of 1d in 2 *M* 2-Propanol in Benzene.—A solution of 0.500 g of **1d** in 200 ml of 2 *M* 2-propanol in benzene was irradiated for 18.5 hr. The solution was slightly yellow at the conclusion of the photolysis. Work-up of the reaction mixture as usual gave a light yellow oil which was dissolved in a small amount of benzene–petroleum ether (1:5) and chromatographed on a 30 g column of silica gel. Elution with benzene afforded 0.290 g of unchanged ketone. Elution with chloroform gave 0.149 g of a white solid, mp 101–102°, which was identified as the hydrol derivative **5d**: ir (KBr) at 3525 (OH), 1100, 1010 cm^{-1}; nmr ($CDCl_3$) δ 7.18 (s, 5, Ar), 6.34 (s, 1, CHOH), 3.60 (s, 3, OCH_3), 2.56 (s, 1, OH), 2.15 (s, 6, CH_3), 2.10 (s, 6, CH_3).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.94; H, 8.22. Found: C, 79.98; H, 8.11.

Further elution with chloroform–ether (9:1) gave 0.009 g of a clear oil. An ir spectrum (neat) of this material showed major absorptions at 3400 (OH), 1450, 1110, 775, and 715 cm^{-1}. Owing to the extremely low yield of this product, further analysis was not undertaken, although it appears, solely on the basis of the ir spectrum, that this substance is most likely the benzocyclobutanol derivative **2d**.

Elution with chloroform–ether (5:1) afforded 0.019 g of a clear oil. Tlc showed that this was a single product: ir (neat) 3425 (OH), 1660, 1330, 1230, 1110, 770 cm^{-1}; nmr ($CDCl_3$) δ 7.75 (AB q, J = 8 Hz, 4, Ar), 3.72 (s, 3, OCH_3), 2.20 (s, 6, CH_3), 2.13 (s, 6, CH_3), 1.60 (s, 6, CH_3). This information indicates that this compound has structure **3d**.

Registry No.—**1a**, 4885-14-7; **1b**, 40910-02-9; **1c**, 40910-03-0; **1d**, 40910-04-1; **1e**, 40910-05-2; **1f**, 40910-06-3; **1g**, 40910-07-4; **2a**, 40910-08-5; **2c**, 19020-69-0; **2d**, 40910-10-9; **2f**, 40910-11-0; **2g**, 40910-12-1; **3a**, 40910-13-2; **3d**, 40910-14-3; **4a**, 40910-15-4; **5a**, 40940-77-0; **5c**, 40910-16-5; **5d**, 40910-17-6; **5g**, 40910-18-7.