

Photolysis of 2-(Benzyloxy)-4-(dodecyloxy)benzophenone and 2-Isopropoxy-4-methoxybenzophenone

G. R. LAPPIN* AND J. S. ZANNUCCI

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662

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The photolysis of 2-(benzyloxy)-4-(dodecyloxy)benzophenone (**1b**) or of 2-isopropoxy-4-methoxybenzophenone (**9**) proceeded mainly *via* ring closure between the carbonyl carbon and the α carbon of the 2 substituent to give 6-(dodecyloxy)-2,3-dihydro-2,3-diphenyl-3-benzofuranol (**4b**) or 2,3-dihydro-2,2-dimethyl-6-methoxy-3-phenyl-3-benzofuranol (**12**), respectively. The quantum efficiencies for disappearance of starting ketone and for cyclization decreased significantly with an increase in solvent polarity. The lifetime of the excited state, believed to be $^3(n, \pi^*)$, was about 3×10^{-8} sec, unusually short for a benzophenone. Further photolysis of **1b** or **4b** resulted in dehydration to give 6-(dodecyloxy)-2,3-diphenylbenzofuran (**6a**) and partial cyclization of **6a** to 11-(dodecyloxy)benzo[*b*]phenanthro[9,10-*d*]furan (**5**), but further photolysis of **12** gave only 2-hydroxy-4-methoxybenzophenone. Both **1b** and **9** gave the corresponding 4-alkoxy-2-hydroxybenzophenone as a minor product.

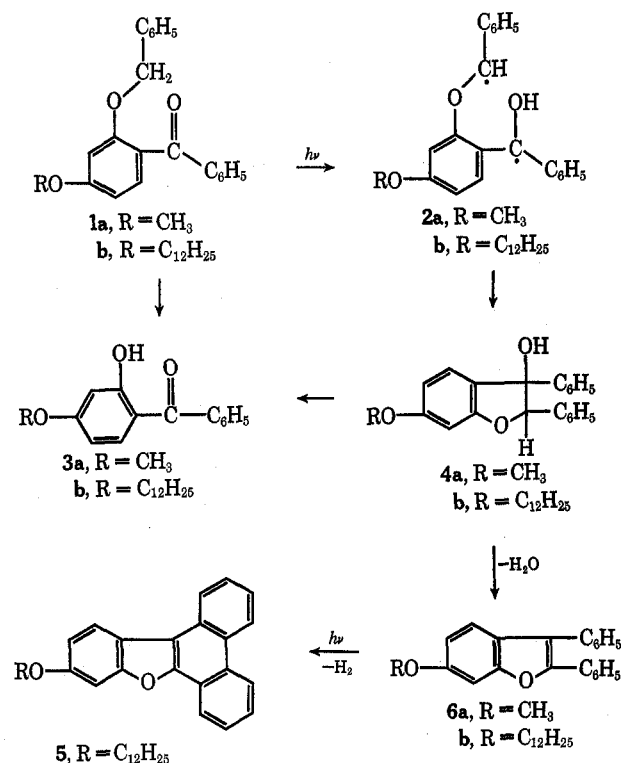
In a preliminary communication we reported that the photolysis of 2-(benzyloxy)-4-methoxybenzophenone (**1a**) gave 6-methoxy-2,3-diphenylbenzofuran (**6a**) and a small amount of 2-hydroxy-4-methoxybenzophenone (**3a**).¹ We now report a further investigation of the photochemistry of two 2,4-dialkoxybenzophenones, 2-(benzyloxy)-4-(dodecyloxy)benzophenone (**1b**) and 2-isopropoxy-4-methoxybenzophenone (**9**). Because the nature of the 4-alkoxy group has no significant effect on the photochemistry of **1** or **9**, these specific compounds were chosen for experimental convenience. The reaction products from **1b** were more easily separated than those from **1a**. The 4-methoxy substituent in **9** facilitated identification of the products by nmr analysis.

Results and Discussion

Photolysis of 2-(Benzyloxy)-4-(dodecyloxy)benzophenone (1b).—The photolysis of **1b** in cyclohexane (310 nm, 7 hr) gave 6-(dodecyloxy)-2,3-dihydro-2,3-diphenyl-3-benzofuranol (**4b**) in 67% yield ($\phi = 0.56$) and 4-(dodecyloxy)-2-hydroxybenzophenone (**3b**) in 6% yield ($\phi = 0.07$). Although benzyl phenyl ether² and other alkoxybenzenes undergo photorearrangement to 2- and 4-alkylphenols, no products of such a rearrangement of **1b** were found. Prolonged photolysis of **1b** (310 nm, 87 hr) or of **4b** (310 nm, 29 hr) resulted in dehydration to the benzofuran **6b** in high yield and a partial cyclization of this compound to 11-(dodecyloxy)benzo[*b*]phenanthro[9,10-*d*]furan (**5**). A small amount of **3b** was also found. The analogous photocyclization of 2,3-diphenylfuran has been reported.³ These reactions are shown in Scheme I.

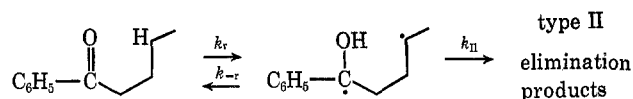
The ultraviolet spectrum of **1b** (Figure 1) is similar to that of benzophenone except that in hexane the (n, π^*) band [uv max 340 nm (ϵ 380)] is a shoulder on the (π, π^*) band [uv max 307 nm ($\epsilon = 6485$)]. Because the photocyclization of **1b** proceeds efficiently at 360 nm and can be completely quenched by 2 *M* piperylene, the reaction probably proceeds from the $^3(n, \pi^*)$ by intramolecular abstraction of a benzylic hydrogen to give the diradical **2b** which collapses to **4b**. A similar mechanism has been proposed for the photocyclization of 4,6-di-*tert*-butyl-2-methoxybenzophenone to give 5-*tert*-

SCHEME I
PHOTOLYSIS OF 1



butyl-7-methoxy-3,3-dimethylindan-1-ol, except that in the latter reaction hydrogen is abstracted from a methyl group of the *tert*-butyl moiety.⁴

The effect of solvent polarity on the photolysis of **1b** (Table I) was unexpected. Both the quantum efficiency for disappearance of **1b**, ϕ_d , and the quantum efficiency for cyclization to **4b**, ϕ_c , decrease by a factor of more than 3 as the solvent polarity increases in this series. This solvent effect is the reverse of that observed by Wagner for the type II photoelimination reaction of valerophenone which proceeds through a biradical similar to **2b**.⁵



(1) G. R. Lappin and J. S. Zannucci, *Chem. Commun.*, 1113 (1969).

(2) D. P. Kelly, J. T. Pinkey, and R. D. Rigby, *Tetrahedron Lett.*, 5953 (1966).

(3) A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, **88**, 3759 (1966).

(4) E. J. O'Connell, Jr., *ibid.*, **90**, 6550 (1968).

(5) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

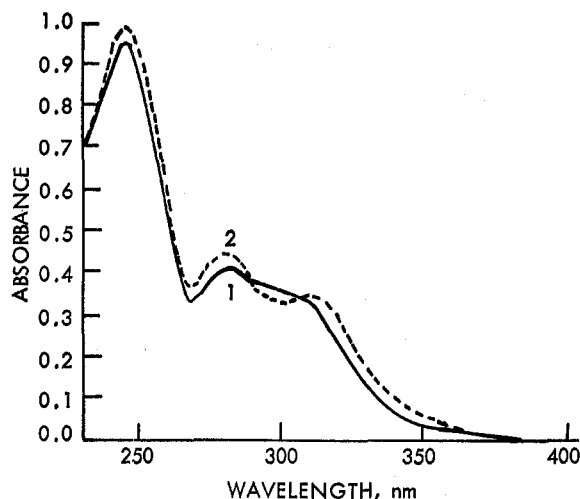


Figure 1.—Absorption spectra (0.100 g/l., 0.25-cm cell) of (1) 2-(benzyloxy)-4-(dodecyloxy)benzophenone, and (2) 4-(dodecyloxy)-2-isopropoxybenzophenone.

TABLE I
QUANTUM EFFICIENCIES AND TRIPLET LIFETIMES FOR
PHOTOLYSIS OF **1b** IN VARIOUS SOLVENTS

Solvent	ϕ_d^a	ϕ_o^b	$\tau \times 10^8$ sec ^c	ϕ_{ic}^d
Cyclohexane	0.70	0.56		
Benzene	0.69	0.54	4.8	0.84
Dichloromethane	0.57	0.35		0.78
Acetone	0.38	0.22	2.3	
Acetonitrile	0.23	0.13	2.5	0.70
<i>tert</i> -Butyl alcohol	0.21	0.12	2.3	

^a ϕ_d is for disappearance of **1b**. ^b ϕ_o is for appearance of **4b**. ^c Obtained from Stern-Volmer plots for piperylene quenching. Diffusion controlled quenching was assumed, and k_{diff} was calculated from η by using the Debye equation. ^d ϕ_{ic} is quantum efficiency for intersystem crossing as measured by sensitization of piperylene isomerization.

Wagner attributed the increase in quantum efficiency for elimination from 0.46 in hexane to 1.0 in acetonitrile to solvation of the hydroxyl hydrogen in the biradical, which impeded back abstraction of the hydrogen to regenerate valerophenone, thus reducing k_{-r} . Solvent polarity should have little effect on k_{II} ; hence, the efficiency of the type II elimination was greatly increased in polar solvents.

Four possible explanations were considered for the decrease in ϕ_d and ϕ_o observed in polar solvents. First, in polar solvents an inversion of excited states might occur; this inversion would result in the population of the unreactive $^3(\pi, \pi^*)$. For acetophenone, Lamola found the first excited triplet to be $^3(n, \pi^*)$ in nonpolar solvents but the $^3(\pi, \pi^*)$ was lowest lying in polar solvents.⁶ Such an inversion of excited states might be expected for **1b** because the lowest lying triplet for acetophenones substituted with methoxyl has been shown to be $^3(\pi, \pi^*)$.⁷ Second, the observed effect of solvent polarity on the photolysis of **1b** might also arise from inefficient intersystem crossing to the triplet in polar solvents. Third, the reaction of the $^3(n, \pi^*)$ of **1b** might lead to different products in polar solvents than in nonpolar solvents. Finally, interaction between the polar solvent and the biradical **2b** might affect the relative importance of cyclization and return to the

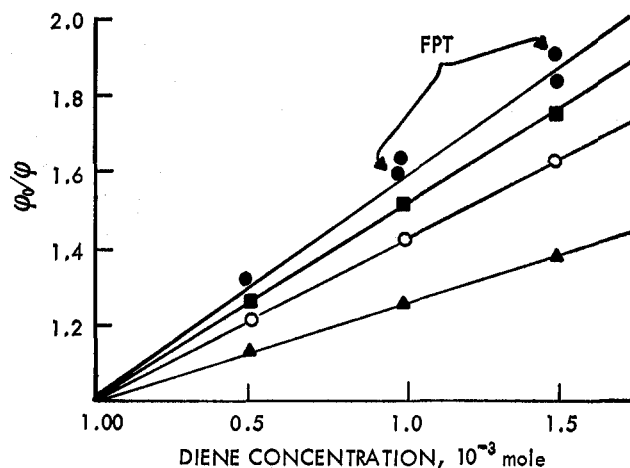


Figure 2.—Stern-Volmer plot for quenching photolysis of **1b** by *cis*-piperylene in acetonitrile (●), benzene (O), acetone (■), and *tert*-butyl alcohol (Δ). FPT: these two points were determined by freeze-pump-thaw degassing; all other points were determined by nitrogen-flow degassing.

ground state but with results apparently opposite to those observed by Wagner.

To choose among these alternatives, we determined triplet lifetimes and the efficiencies of intersystem crossing for the photolysis of **1b** in benzene, acetone, acetonitrile, and *tert*-butyl alcohol. Linear Stern-Volmer plots (Figure 2) were obtained for photolysis of **1b** in the presence of *cis*-piperylene in all four solvents. These data led to nearly the same triplet lifetime ($\tau \approx 3 \times 10^{-8}$ sec) in the four solvents (Table I). Wagner and Kempainen found that the triplet lifetime for valerophenone was increased from 7.1×10^{-9} sec for the parent compound to 4.5×10^{-7} sec for *p*-methoxyvalerophenone and attributed this to a change from $^3(n, \pi^*)$ to $^3(\pi, \pi^*)$ for the lowest excited state in *p*-methoxyvalerophenone.⁸ If the triplet of **1b** had $^3(\pi, \pi^*)$ character in polar solvents, τ should have increased significantly. Our data show a small decrease in τ in polar solvents; hence, the same excited state of **1b** is involved in its reactions in either polar or nonpolar solvents. Although Kearns found the lowest excited state of *p,p'*-dimethoxybenzophenone to be $^3(n, \pi^*)$,⁹ we considered the possibility that the lowest triplet for **1b** was $^3(\pi, \pi^*)$ in both polar and nonpolar solvents. However, the phosphorescence lifetime of **1b** in either EPA (5.4×10^{-3} sec) or 1:1 heptane-pentane (3.2×10^{-3} sec) is of the magnitude expected for a benzophenone $^3(n, \pi^*)$ (*ca.* 10^{-3} sec) rather than that expected for the $^3(\pi, \pi^*)$ (*ca.* 1 sec).¹⁰ These results confirm our conclusion that the $^3(\pi, \pi^*)$ makes no significant contribution to the photochemistry of **1b**. Triplet counting by the piperylene isomerization technique¹¹ did show a small decrease in the efficiency of intersystem crossing, ϕ_{ic} (Table I), but this effect was too small to account for the large solvent effect we observed. Product analysis showed no observable effect of solvent polarity on the photolysis products of **1b**; hence, a change in reaction path cannot account for the solvent

(8) P. J. Wagner and A. E. Kempainen, *J. Amer. Chem. Soc.*, **90**, 5898 (1968).

(9) D. R. Kearns and W. A. Case, *ibid.*, **88**, 5087 (1966).

(10) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *ibid.*, **89**, 5466 (1967).

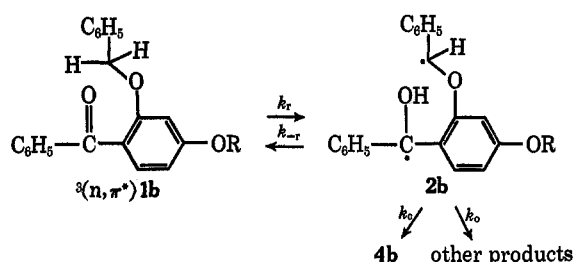
(11) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(6) A. A. Lamola, *J. Chem. Phys.*, **47**, 4810 (1967).

(7) T. Takemura and H. Baba, *Bull. Chem. Soc. Jap.*, **42**, 2756 (1969).

effect. We conclude, therefore, that the biradical **2b** is formed with high efficiency in both polar and non-polar solvents and that the observed effect of solvent polarity occurs because of interaction between **2b** and the polar solvent. Whether solvation of a diradical intermediate leads to an increase in ϕ_d , as observed by Wagner,⁵ or to a decrease in ϕ_d , as we report, for a ketone depends on the nature of the reaction paths available to the two radicals.

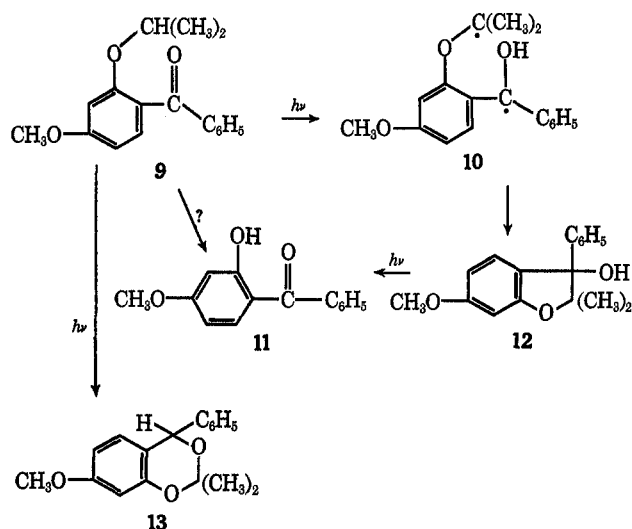
We propose the following mechanistic scheme for the photolysis of **1b**.



The intramolecular hydrogen abstraction (**1b*** \rightarrow **2b**) involves a seven-membered transition state and so should be very rapid. Thus, the lifetime of the triplet state of **1b** should be shorter than the expected lifetime for a benzophenone triplet ($\tau \approx 10^{-6}$ sec) where intermolecular hydrogen abstraction is involved in accord with our observation of $\tau \approx 3 \times 10^{-8}$ sec. In nonpolar solvents, **2b** efficiently cyclizes to **4b** ($k_c \gg k_{-r}$). Solvation of **2b** by a polar solvent should reduce k_{-r} by interference with the back abstraction of hydrogen, as it does for valerophenone. However, the effect of a reduction in k_{-r} on the disappearance of starting ketone depends on what alternative reaction paths are available to the biradical. The biradical from valerophenone has available a facile elimination reaction which can proceed without regard to any particular molecular orientation or solvent effect; hence, the loss of valerophenone becomes more efficient when k_{-r} is reduced. For **3b**, the only significant alternative to reverse hydrogen abstraction is cyclization. It seems reasonable that solvation of **3b** would also reduce k_c , because the solvent sheath might well impede assumption of the geometry necessary for cyclization. Indeed, Wagner, observed a similar effect in the cyclization of valerophenone to a cyclobutanol, which occurred as a minor side reaction competing with elimination.⁵ If k_o is decreased more than k_{-r} in polar solvents and if k_o , the rate of formation of all other products, remains relatively unchanged, then the rate at which **1b** disappears will decrease in polar solvents. The effect of polar solvents, although it arises from the same interaction of solvent and biradical, becomes the reverse of that observed by Wagner.

Photolysis of 2-Isopropoxy-4-methoxybenzophenone (9).—Photolysis of **9** in benzene (310 nm, 7 hr) gave not only the products expected from the results with **1b**, 2,3-dihydro-6-methoxy-2,2-dimethyl-3-phenyl-3-benzofuranol (**12**, 44% yield) and 2-hydroxy-4-methoxybenzophenone (**11**, 14% yield), but an unexpected product, 7-methoxy-2,2-dimethyl-4-phenyl-1,3-benzodioxane (**13**) in 28% yield (Scheme II). No product analogous to **13** was detected in the photolysis of **1b**; hence, some reaction path which is available to **9** is not available to **1b**. The effect of solvent polarity was less extensively studied for **9** than for **1b**, but the

SCHEME II
PRODUCTS FROM PHOTOLYSIS OF 9



SCHEME III

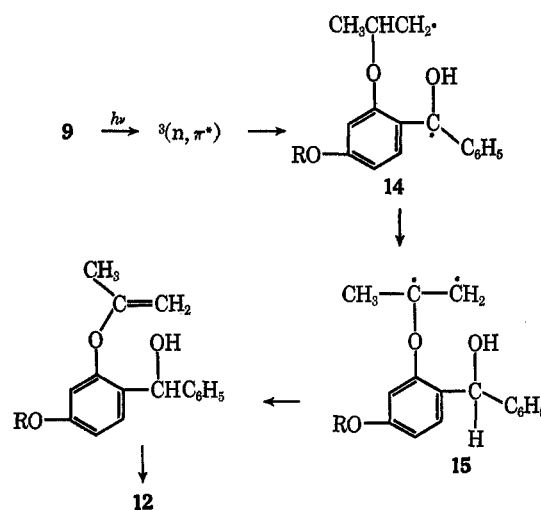


TABLE II
QUANTUM EFFICIENCIES FOR THE PHOTOLYSIS OF 9
IN CYCLOHEXANE AND ACETONITRILE

Solvent	ϕ_d^a	ϕ_{12}^b	ϕ_{13}^c
Cyclohexane	0.51	0.26	0.15
Acetonitrile	0.14	0.023	0.005

^a ϕ_d is for disappearance of **9**. ^b ϕ_{12} is for the appearance of **12**.
^c ϕ_{13} is for the appearance of **13**.

data in Table II show that polar solvents repress the loss of ketone and the cyclization to the benzofuranol to a greater extent than for **1b**. Cyclization to the 1,3-benzodioxane is decreased markedly in acetonitrile.

Although the cyclization to **12** undoubtedly involves the biradical **10**, the formation of **13** is less easily accounted for. It is not formed by a ring expansion of **12**; photolysis (310 nm, 24 hr) of **12** gave only **11** and unreacted **12**. In fact, the relative amounts of **11** formed by photolysis of **9** and **12** lead us to believe that the most of the **11** isolated in the photolysis of **9** is actually a secondary product arising from **12**. Bimolecular reactions involving hydrogen exchanges between **9** and the biradical **10** could also produce **13**. However, when the photolysis of **9** (benzene solution, 310 nm, 7 hr) was carried out over a range of concen-

trations from 0.002 *M* to 0.074 *M*, the ratio of **13** to **12** remained constant at 0.25; hence, any bimolecular reaction mechanism can be eliminated. Scheme III shows a tentative mechanism for the formation of **12**. The second intramolecular hydrogen abstraction (**14** → **15**) involves a six-membered transition state and should occur readily. This mechanism accounts for the failure of **1b** to give a product analogous to **13**.¹² However, we cannot offer any unequivocal explanation for the formation of **13**.

Experimental Section

Preparation of 2-(Benzyloxy)-4-(dodecyloxy)benzophenone (1b).—Benzyl bromide (25.2 g, 0.2 mol) was added to a solution of 76 g (0.2 mol) of 4-(dodecyloxy)-2-hydroxybenzophenone and 11.2 g (0.2 mol) of potassium hydroxide in 500 ml of ethanol. This solution was refluxed for 18 hr and then evaporated to dryness in a rotary evaporator. The residue was extracted with 200 ml of ether, and the ether solution was extracted twice with 50-ml portions of 10% aqueous NaOH solution and then twice with 50 ml of water. The ethereal extract was dried over anhydrous Na₂SO₄ and concentrated. The residue was recrystallized twice from ethanol to give 63 g (67%) of **1b**, mp 56–58°.

Anal. Calcd for C₃₂H₄₀O₃: C, 81.40; H, 8.47. Found: C, 81.59; H, 8.55.

Preparation of 2-Isopropoxy-4-methoxybenzophenone (9).—This compound was prepared in the same way as **1b** from 45.6 g (0.2 mol) of 2-hydroxy-4-methoxybenzophenone and 24.6 g (0.2 mol) of 2-bromopropane. The yield of white crystals was 23 g (46%), mp 57–59°.

Anal. Calcd for C₁₇H₁₈O₃: C, 75.59; H, 6.67. Found: C, 75.35; H, 6.60.

General Irradiation Procedure.—Benzene was washed with sulfuric acid and with water, dried over MgSO₄, and distilled. All other solvents were dried over MgSO₄ and distilled.

Samples were irradiated under nitrogen in 12-mm-o.d. Pyrex glass tubes closed by a serum cap. Dissolved oxygen was removed by bubbling nitrogen (20 ml/min) through 6 ml of solution from a 27-gage hypodermic needle for 2 min.¹³ Piperylene quenching and triplet counting experiments (Table I) were carried out in a "merry-go-round." The light source was a Hanovia 550-W medium-pressure arc; the 366-nm band was isolated by Corning 0-52 and 7-37 filters in series. Piperylene isomers were analyzed by glc on a 1/8 in. × 30 ft column packed with 25% 3,3'-oxydipropionitrile on 60–80-mesh Chromosorb P solid support. **1b** and **4b** (data in Table I) were determined by glc at 310° on a 0.25 in. × 10 ft column packed with 25% Lexan polycarbonate on 40–60-mesh Chromosorb W solid support. The data for the disappearance of **9** were also obtained with this glc column under the same conditions. Quantum yields were determined by uranyl oxalate actinometry.¹⁴ A Rayonet photochemical reactor fitted with 310-nm lamps was used for all other irradiations.

Photolysis of 2-(Benzyloxy)-4-(dodecyloxy)benzophenone (1b). **A.**—A solution of 500 mg of **1b** in 100 ml of cyclohexane was irradiated for 7 hr. The yellow solution was concentrated to a small volume and chromatographed on two 20 cm × 20 cm × 2 mm silica gel thin layer plates with 1:1.5 isooctane–methylene chloride mixture. The clear oil, 338 mg (67.5%), which was obtained was crystallized from ethanol to yield a white, crystalline material, mp 64–65°, identified as 6-(dodecyloxy)-2,3-di-

hydro-2,3-diphenyl-3-benzofuranol (**4b**): nmr (CDCl₃) δ 6.2–7.6 (m, 13 H, aromatic), 5.60 (s, 1 H, benzylic), 3.95 (m, 2 H, CH₂O), 2.25 (s, 1 H, OH), 1.25 (2 OH, CH₂), and 0.90 (t, 3 H, CH₃).

Anal. Calcd for C₃₂H₄₀O₃: C, 81.40; H, 8.47. Found: C, 81.69; H, 8.52.

Also isolated was 30 mg (6%) of 4-(dodecyloxy)-2-hydroxybenzophenone (**3b**), mp 50–52°. Mixture melting point and ir were identical with those of an authentic sample.

B.—**1b** (3.0 g) in hexane (100 ml) was irradiated for 87 hr. The yellow solution was evaporated to a small volume, cooled (–70°), and filtered. Decolorization and recrystallization from hexane (–70°) furnished 0.32 g (10.5%), mp 104–105°, of a white crystalline material identified as 11-(dodecyloxy)benzo[*b*]phenanthro[9,10-*d*]furan (**5**): nmr (CDCl₃) δ 7.1–8.8 (m, 9 H, aromatic), 7.10 (d, 1 H, aromatic), 6.91 (q, 1 H, aromatic), 3.95 (t, 2 H, CH₂O), 1.25 (2 OH, CH₂), and 0.87 (t, 3 H, CH₃). The mass spectrum had a parent ion peak at *m/e* 452 (*M* – 20).

Anal. Calcd for C₃₂H₃₈O₂: C, 85.00; H, 8.41. Found: C, 85.00; H, 8.29.

The combined hexane fractions from the above precipitation were evaporated to dryness, and the residue was then dissolved in a small volume of ethanol, cooled to –70°, and filtered. A second recrystallization furnished 1.9 g (63.5%) of a white, crystalline material identified as 6-(dodecyloxy)-2,3-diphenylbenzofuran (**6b**): mp 62–64°; nmr (CDCl₃) δ 7.0–7.8 (m, 11 H, aromatic), 6.96 (d, 1 H, aromatic), 6.75 (q, 1 H, aromatic), 3.95 (t, 2 H, CH₂O), 1.25 (2 OH, CH₂), and 0.90 (t, 3 H, CH₃). The mass spectrum had a parent ion peak at *m/e* 454 (*M* – 18, loss of water).

Anal. Calcd for C₃₂H₃₈O₂: C, 84.50; H, 8.37. Found: C, 84.38; H, 8.56.

Photolysis of 2-Isopropoxy-4-methoxybenzophenone (9).—A solution of 500 mg of **9** in 100 ml of benzene was irradiated for 7 hr. The yellow solution was evaporated to a paste, which was taken up in a small quantity of acetone and chromatographed on two 20 cm × 20 cm × 2 mm silica gel thin layer plates with 1:1.5 isooctane–methylene chloride. The plates were divided into three bands, top, center, and bottom, and eluted with acetone.

The top band (140 mg, 28%) was recrystallized from ethanol at –70°. The white, crystalline material obtained, mp 104–107°, was identified as 7-methoxy-2,2-dimethyl-4-phenyl-1,3-benzodioxane (**13**). The mass spectrum included, in addition to the parent ion peak at *m/e* 270, a predominant peak at *m/e* 212 (*M* – 58, loss of acetone); nmr spectrum (CDCl₃) δ 7.29 (s, 5 H, aromatic), 7.1 (m, 1 H, aromatic), 6.25–6.6 (m, 2 H, aromatic), 5.74 (s, 1 H, benzylic), 3.70 (s, 3 H, OCH₃), and 1.61 (s, 6 H, geminal dimethyl).

Anal. Calcd for C₁₇H₁₈O₃: C, 75.59; H, 6.67. Found: C, 75.70; H, 6.81.

The center band (70 mg, 14%) was recrystallized from ethanol, mp 62–64°. Mixture melting point and ir spectrum were identical with those of an authentic sample of 2-hydroxy-4-methoxybenzophenone.

The bottom band (220 mg, 44%) was recrystallized from ethanol at –70°, to yield a white, crystalline material, mp 122–123°, identified as 2,3-dihydro-6-methoxy-2,2-dimethyl-3-phenyl-3-benzofuranol (**12**): nmr (CDCl₃) δ 7.1–7.6 (m, 5 H, aromatic), 6.96 (d, 1 H, aromatic), 6.35–6.39 (m, 2 H, aromatic), 3.69 (s, 3 H, OCH₃), 2.25 (s, 1 H, CH₃), 1.53 (s, 3 H, CH₃), and 0.82 (s, 3 H, CH₃).

Anal. Calcd for C₁₇H₁₈O₃: C, 75.59; H, 6.67. Found: C, 75.60; H, 6.77.

Photolysis of 2,3-Dihydro-6-methoxy-2,2-dimethyl-3-phenyl-3-benzofuranol (12).—A solution of 0.200 g of **12** in 50 ml of benzene was irradiated for 29 hr. The solution was concentrated and chromatographed as in the photolysis of **1b** to yield 0.106 g of starting material (53%) and 0.032 g (38%) of 2-hydroxy-4-methoxybenzophenone.

Registry No.—**1b**, 28856-48-6; **4b**, 28856-49-7; **5**, 28856-50-0; **6b**, 28856-51-1; **9**, 28856-52-2; **12**, 28856-53-3; **13**, 28856-54-4.

Acknowledgment.—The authors gratefully acknowledge the help of Professor David Whitten, of the University of North Carolina, with whom many fruitful discussions of this work were held.

(12) We have found that hydrogen abstraction from the carbon β to the ether function occurs in the photolysis of 4-methoxy-2-(2-phenylethoxy)benzophenone, but the complex reaction mixture has not yet been resolved. The possibility that **13** was formed *via* reduction of **9** to the benzhydrol was also considered; however, when **9** was photolyzed in isopropyl alcohol, the major products appeared to be the benzhydrol and the pinacol. The reaction mixture could not be satisfactorily separated, but the nmr spectrum of the photolysis product showed that no **13** was present.

(13) The reliability of this method for oxygen removal was confirmed by comparison with the more tedious freeze-pump-thaw method. Quenching data from the two degassing procedures fell on the same line in the Stern-Volmer plot.

(14) C. R. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Catalytic, Photochemical, Electrolytic Reactions (Techniques of Organic Chemistry)," 2nd ed, Vol. II, A. Weissberger, Ed., Interscience, New York N. Y., 1965, pp 294–298.