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# Photolysis of 2-Alkoxy-1,4-naphthoquinones

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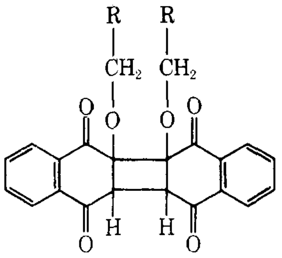
The photolysis of 2-methoxy- and 2-ethoxy-1,4-naphthoquinones in acetic anhydride solution caused dimerization and subsequent cyclization of the alkoxy group to spiro-3-oxetanols in high yield. Similar photolysis of the 2-isopropoxy derivative produced no dimer but a product in which ring closure *via* the keto group adjacent to the alkoxy group formed the acetate of 3,4-isopropylidenedioxy-1-naphthol. Photolyses of film coatings of various 2-alkoxy- and 2-aralkoxy-1,4-naphthoquinones produced reducing species that are believed to be the 3,4-alkylidenedioxy-1-naphthols.

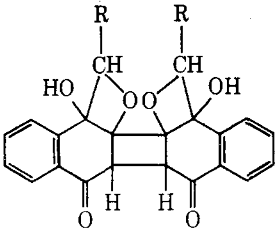
It is well known that certain alkoxy- and alkylamino-substituted quinones are photolyzed by intramolecular hydrogen abstraction and ring closure to produce substituted hydroquinones.[1-6] An interest in the photochemistry of quinones led us to investigate the photolysis of naphthoquinones containing alkoxy groups with more easily extractable H atoms, with the expectation that the cyclization reaction might occur more readily.

## Results

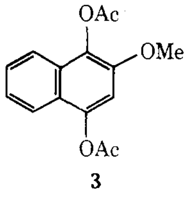
Photolysis of 2-methoxy-1,4-naphthoquinone in acetic anhydride solution produced mainly two dimers (1 and 2), neither of which was reported by Baldwin and Brown.[1] One (1) crystallized from the solvent in yellow prisms during photolysis, and the other (2) was recovered from the filtrate. Small quantities of the acetylated hydroquinone (3) and its rearrangement product (4) obtained by Baldwin and Brown may have been formed, but no attempt was made to isolate them.



1, R = H
5, R = $CH_3$



2, R = H
6, R = $CH_3$



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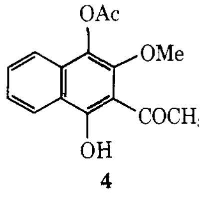

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Prolonged photolysis resulted in lower yields of 1 and larger quantities of **2**, suggesting that the ring closure to the oxetanol structure occurred from irradiation of **1**. The structure of 1 was assigned by analogy to the photooxidation of 2-methyl-[7] and 2-hydroxynaphthoquinone,[8] whose dimeric products are the result of head-to-head coupling. No attempt was made to determine the steric arrangement about the cyclobutane ring.

Upon being melted at a normal rate, the dimer (**1**) cleaved to the monomer, but when immersed in a preheated apparatus, the dimer melted rapidly only at temperatures above 210°. It was insoluble in all common solvents, and an nmr spectrum was unobtainable. It was cleaved when heated with solvents such as acetic anhydride or acetic acid during attempts at recrystallization. Although the dimer was detectable as a trace by mass spectrography, it was cleaved during analysis, giving relatively large quantities of the monomer; a fragmentation pattern characteristic of the monomer was observed. Its ir spectrum (KBr pressing) was different from that of the starting material.

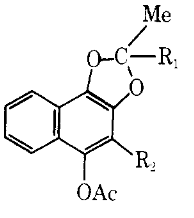
The structure of **2** was assigned on the basis of its ir spectrum, which showed a very sharp OH band at 3500 $cm^{-1}$ and a carbonyl band at 1680 $cm^{-1}$, its proton nmr spectrum, which showed two doublets characteristic of an AB system involving the $-CH_2-$group of a 3-aryl-substituted 3-oxetanol,[9,10] and its $C^{13}$ nmr spectrum.

The compound lost two molecules of formaldehyde in the determination of the mass spectrum. The major component was mass 316 and the fragmentation pattern was nearly identical with that of the dimer of 1,4-naphthoquinone. The silated compound also lost formaldehyde thermally; the heaviest fragment observed was the tetrasilated dimer of 1,4-naphthoquinone.

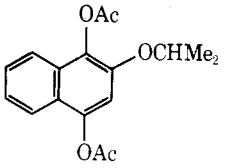
Photolysis of an acetic anhydride solution of 2-ethoxy-1,4-naphthoquinone with narrow-band irradiation centered at 436 nm produced the simple dimer **5** in 90% yield. This dimer, whose absorption tailed out weakly to 400 nm, was converted to the spirooxetanol **6** upon being irradiated at 365 nm. Photolysis of the quinone with light of wavelengths longer than 370 nm produced **6** in 70% yield.

Other evidence consistent with structure **6** for the photolysis product of the quinone is its failure to be acetylated by acetic anhydride and its stability toward mild acid hydrolytic conditions. Both **2** and **6** were readily oxidized by air or oxidizing agents such as 2-*p*-iodophenyl)-3-(*p*-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride in alkaline solutions. Bubbling air through the alkaline solution of **6** caused its oxidative decomposition with liberation of acetaldehyde.

The 3-methyl derivative of 2-ethoxy-1,4-naphthoquinone produced no dimeric products. The major product was the ring-closed acetate **7a.** Other products isolated in much smaller yields were the 2-hydroxy-1,4-naphthoquinone and its acetate.



7a, $R_1$ = H; $R_2$ = Me
b, $R_1$ = Me; $R_2$ = H



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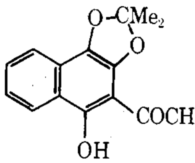
Photoreduction of 2-isopropoxy-1,4-naphthoquinone in acetic anhydride solution at room temperature produced no easily separable products. Gas chromatography of the residue remaining after removal of the acetic anhydride indicated the presence of small amounts of **7b** and **8** in about equal quantities, along with other products not easily identifiable. Only **7b** and its photo-Fries rearrangement product **9** were isolated in pure form. There was no evidence for the formation of dimeric products analogous to **1** or **2.**



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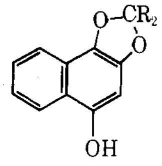
The structure of **7b** was established from ir, nmr, and mass spectra along with certain chemical evidence. The ir spectrum showed a maximum at 1645 $cm^{-1}$, consistent with the enediol ether,[11] as well as a maximum at 1755 $cm^{-1}$, associated with the acetoxycarbonyl group.

Saponification of **7b** in ethanol under $N_2$ by addition of NaOH occurred within a few seconds. Acidification by HCl produced the free hydroxy compound, which was extremely sensitive to aerial oxidation and was not isolated in a crystalline state. Bubbling air through the alkaline solution liberated acetone quantitatively and formed 2-hydroxy-1,4-naphthoquinone. The compound was not hydrolyzed by acid.[12]

Photolysis of film coatings of alkoxy or aralkoxy naphthoquinones for short times produced 2-hydroxy-1,4-naphthoquinone[7] and prolonged photolysis converted the hydroxyquinone into dimeric products.[13] Either solutions or film coatings of the alkoxyquinones were nonemissive at the onset of photolysis, but as irradiation proceeded an emission characteristic of **10** (R = Me) (maximum 420 nm in film or 440 nm in methanol solution) developed. The initial products were very labile in the presence of air and the intensity of emission decreased rapidly either in the dark or during prolonged irradiation.

Since oxidation of the hydroquinone **11** (R = isopropoxy) produced mainly the quinone and oxidation of **10** (R = Me) produced the 2-hydroxy compound, it is proposed that the initial products of the photolysis of 2-alkoxy or aralkoxy naphthoquinones under these conditions most likely have structures of the form of **10.**



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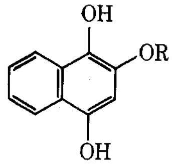
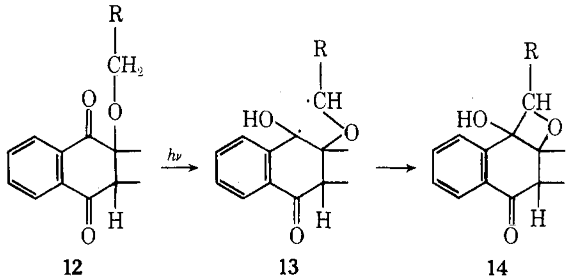


11

## Discussion

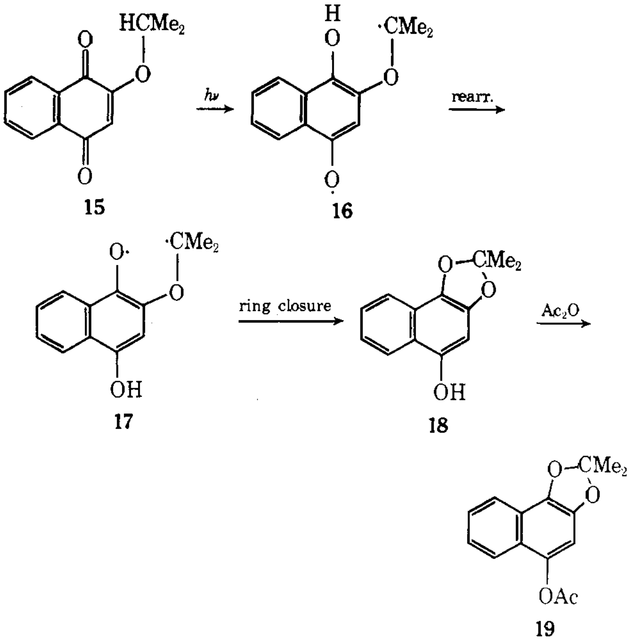
Any discussion of mechanism to account for the different behavior of the isopropoxy derivative is admittedly speculative. The difference may lie in its failure to dimerize, the reason for which is not readily apparent.

The methoxy and ethoxy derivatives most likely photodimerize to **12** as the first step. Excitation of the dimer, involving the carbonyl group adjacent to the alkoxy group (presumably $n\pi^*$), produces the diradical **13** following the H-transfer reaction. Ring closure of the diradical produces the oxetanol **14.**



Support for the stepwise process comes from the dimerization of the 2-ethoxy quinone and subsequent photolysis to produce the oxetanol. A similar cyclization and dimerization of a 3-methoxychromone reported by Gupta and Mukerjee most likely also involved two photolytic steps.[14]

The failure of the isopropoxy compound **15** to dimerize allows the reaction from the excited state to proceed differently. The $n\pi^*$ excitation of the isopropoxy derivative and H abstraction might produce an intermediate shown as **16.**



Rearrangement and ring closure between the alkyl radical and the electron-deficient oxygen atom produces the substituted naphthol (**18**) which, by nucleophilic displacement on the acetic anhydride, produces the product (**19**). The aromatization following H transfer is impossible with the excited dimer (**13**).

## Experimental Section

**Photolysis of 2-Methoxy-1,4-naphthoquinone in Acetic Anhydride.** A solution of 2.0 g of the quinone in 175 ml of acetic anhydride was photolyzed at room temperature in a Rayonet reactor equipped with mercury arc lamps rich in 365-nm radiation for 60 hr. During this time pale yellow prisms of **1** (0.88 g, 44%) separated from the solution: mp > 210° dec; uv max ($CH_3CN$) 205 ($\epsilon$ $5.3 \times 10^4$), 251 ($\epsilon$ $2.6 \times 10^4$), 278 nm ($\epsilon$ $2.8 \times 10^3$); ir (KBr) 1690 $cm^{-1}$ ($C{=}O$) different from the monomer; mass spectrum (70 eV) *m/e* (major peaks underlined) 376, 346, $\underline{188}$, $\underline{173}$, 159, $\underline{158}$, $\underline{102}$, 89, 76.

*Anal.* Calcd for $C_{22}H_{16}O_6$: C, 70.23; H, 4.26. Found: C, 69.9; H, 4.6.

Evaporation of the filtrate to dryness *in vacuo* and triturating the residue with acetonitrile produced 0.4 g (20%) of a yellow crystalline solid (**2**), which crystallized from acetic anhydride in pale yellow needles: mp 230–240° dec; ir (KBr) 3500 (OH), 1680 $cm^{-1}$ ($C{=}O$) appreciably different from **1** at lower frequencies; nmr (DMSO) $\delta$ 3.12 (s, 1), AB pair 4.46, 5.06 (AB, 2, $J$ = 7 Hz), 6.42 (s, 1, OH), 7.73 ppm (m, 4, aromatic); $^{13}C$ nmr (DMSO) $\delta$ 192.3 (s, 1, $C{=}O$), 146.4 (s, 1, aromatic), 136.2 (d, 1, aromatic), 129.7 (d, 1, aromatic), 128.6 (d, 1, aromatic), 127.3 (s, d, 2, aromatic), 84.5 (2t, 2, $-OCH_2$),[15] 91.1 (s, 1, –C-O–), 73.7 (s, 1, –C-O–), 46.5 ppm (d, 1, $O{=}C{-}CH$); mass spectrum (70 eV) *m/e* (major peaks underlined) 376, 346, $\underline{316}$, 299, 298, 288, 287, $\underline{271}$, 231, 215, 202, 130, 128, 104, 102, $\underline{76}$; mass spectrum after silation (70 eV) *m/e* (major peaks underlined) $\underline{604}$, 562, 561, 489, 462, 147, $\underline{75}$, $\underline{73}$.

*Anal.* Calcd for $C_{22}H_{16}O_6$: C, 70.23; H, 4.26. Found: C, 70.1; H, 4.4.

1,4-Naphthoquinone dimer: mass spectrum (70 eV) *m/e* (major peaks underlined) $\underline{316}$, 299, 298, 288, 287, $\underline{271}$, 270, $\underline{231}$, 215, 202, 130, 128, $\underline{104}$, 102, $\underline{76}$.

A dilute alkaline methanol solution of **2** yellowed rapidly in air and reduced instantaneously a solution of 2-(*p*-iodophenyl)-3-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride.

**Photolysis of 2-Ethoxy-1,4-naphthoquinone in Acetic Anhydride. 1. Dimerization.** A solution of 0.15 g of the quinone in 10 ml of acetic anhydride was photolyzed using the 436 line of a mercury source. Removal of the acetic anhydride *in vacuo* produced the dimer (**5**), which crystallized from ethanol in colorless needles (0.135 g, 90%): mp 125–126°; uv max ($CH_3CN$) 233 ($\epsilon$ $5.25 \times 10^4$), 302 nm ($\epsilon$ $2.49 \times 10^3$); ir (KBr) 1710 $cm^{-1}$ ($C{=}O$); nmr ($CDCl_3$) $\delta$ 0.04 (t, 3, $J$ = 12 Hz, $CH\mathbf{CH_3}$), 2.96 (q, 2, $J$ = 11 Hz, $\mathbf{CH_2}CH_3$), 3.56 (s, 1, $C\mathbf{H}$), 7.45 (m, 2, aromatic), 7.75 ppm (m, 2, aromatic); mass spectrum (70 eV) *m/e* (major peaks underlined) 404, 387, 386, 360, 316, 314, $\underline{202}$, $\underline{158}$, $\underline{146}$, $\underline{105}$, 102, $\underline{89}$. The nmr quartet at 2.96 ppm showed a splitting of 3 Hz.

**2. Spirooxetanol Formation.** A solution of 2.0 g of the quinone in 175 ml of acetic anhydride was photolyzed using a high-pressure mercury arc filtered to pass only light of wavelengths longer than 370 nm. Removal of the acetic anhydride *in vacuo* gave a solid **6** (1.5 g), which crystallized from acetonitrile as nearly colorless prisms (1.4 g, 70%): mp 206–207°; uv max ($CH_3OH$) 255 ($\epsilon$ $2.18 \times 10^4$), 292 nm ($\epsilon$ 3050); ir (KBr) 3640 (OH), 1690 $cm^{-1}$ ($C{=}O$); nmr ($CDCl_3$) $\delta$ 1.74 (d, 3, $J$ = 12 Hz, $CH\mathbf{CH_3}$), 3.14 (s, 1, $C\mathbf{H}$), 4.92 (q, 1, $J$ = 10 Hz, $C\mathbf{H}CH_3$), 5.34 (s, 1, $O\mathbf{H}$), 7.62 (s, 1, aromatic), 8.23 ppm (m, 3, aromatic); $^{13}C$ nmr ($CDCl_3$ + DMSO) $\delta$ 191.2 (s, 1, $C{=}O$), 145.5 (s, 1, aromatic), 135.0 (d, 1, aromatic), 128.5 (d, 1, aromatic), 127.5 (s, d, 2, aromatic), 126.8 (d, 1, aromatic), 89.6 (d, 1, OCHR), 87.7 (s, 1, C-O), 73.6 (s, 1, –C-O–), 45.7 (d, 1, $O{=}C{-}CH$), 16.3 ppm (q, 1, $CH_3$); mass spectrum (70 eV) *m/e* (major peaks underlined) $\underline{202}$, 187, 173, $\underline{158}$, 146, $\underline{105}$, 102, $\underline{89}$.

*Anal.* Calcd for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 71.3; H, 5.0.

Photolysis in the Rayonet reactor produced the same results.

**3. Spirooxetanol from Dimer.** A solution of 0.1 g of the dimer **5** in 10 ml of acetic anhydride was photolyzed using the 365-nm line of a mercury source. Removal of the acetic anhydride *in vacuo* and trituration with ethanol gave nearly colorless needles of **6** (0.06 g, 60%). The product was identified by mp and nmr.

Upon acidification of an alkaline ethanolic solution of **6** which had been held under $N_2$, **6** was recovered unchanged. Bubbling air through the alkaline solution caused oxidative decomposition of **6** with 90% recovery of acetaldehyde as its dinitrophenylhydrazone. Alkaline solutions of the spirooxetanol reduced tetrazolium salts instantaneously.

**Photolysis of 2-Ethoxy-3-methyl-1,4-naphthoquinone in Acetic Anhydride.** A solution of 1.5 g of the quinone in 175 ml of acetic anhydride was photolyzed for 60 hr in the Rayonet reactor. Acetic anhydride was removed *in vacuo* and the residual oil was chromatographed on a silica column eluted with benzene.

Compound **7a** was obtained as a pale red oil: 0.5 g (33%): ir (KBr) 1660 (–$OC{=}CO$–), 1760 $cm^{-1}$ ($C{=}O$); nmr ($CDCl_3$) $\delta$ 1.65 (d, 3, $CH\mathbf{CH_3}$), 2.15 (s, 3, $CH_3$), 2.27 (s, 3, $CO\mathbf{CH_3}$), 6.26 (q, 1, $J$ = 8 Hz, $C\mathbf{H}CH_3$), 6.38 (m, 2, aromatic) 7.6 ppm (m, 2, aromatic); mass spectrum (70 eV) *m/e* (major peaks underlined) 258, $\underline{216}$, 201, 171, 115, 43.

**Photolysis of 2-Isopropoxy-1,4-naphthoquinone in Acetic Anhydride.** A solution of 5.0 g of the quinone in 175 ml of acetic anhydride was photolyzed for 60 hr in the Rayonet reactor. Acetic anhydride was removed *in vacuo* and the residual oil was triturated with 15 $cm^3$ of methanol. The solid that separated (1.7 g) was nearly pure starting material.

Alcoholic filtrates from three photolyses were evaporated to dryness and the residual oil was dissolved in benzene. Chromatography on a silica column eluted with benzene (or methylene chloride) produced two crystalline products.

Compound **7b** was obtained as pale yellow prisms from hexane (1.4 g, 11.7%): mp 84–86°; uv max ($CH_3OH$) 300 ($\epsilon$ 3800), 312 ($\epsilon$ 4300), 350 nm ($\epsilon$ 4100); ir (KBr) 1645 (–$OC{=}CO$–), 1755 $cm^{-1}$ ($C{=}O$); nmr ($CDCl_3$) $\delta$ 1.72 (s, 6, $C(\mathbf{CH_3})_2$), 2.32 (s, 3, $CO\mathbf{CH_3}$), 6.92 (s, 1, $={\mathbf{CH}}-$), 7.32 (m, 2, aromatic), 7.72 ppm (m, 2, aromatic); mass spectrum (70 eV) *m/e* (major peaks underlined) $\underline{258}$, $\underline{216}$, $\underline{201}$, $\underline{176}$, $\underline{175}$, 102, 101, 43.

*Anal.* Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.6; H, 5.6.

The Fries-rearranged product **9** crystallized from hexane as orange needles (1.1 g, 9.2%): mp 138–139°; uv ($CH_3OH$) 332 ($\epsilon$ 3150), 450 nm ($\epsilon$ 3640); uv ($CH_3OH$ + $NMe_3$) 360 ($\epsilon$ 6200), 460 nm ($\epsilon$ 5100); ir (KBr) 1655 (–$OC{=}CO$–), 1640 $cm^{-1}$ (acetyl $C{=}O$); nmr ($CDCl_3$) $\delta$ 1.76 (s, 6, $C(\mathbf{CH_3})_2$), 2.63 (s, 3, $CO\mathbf{CH_3}$), 7.30 (m, 3, aromatic), 8.18 ppm (m, 1, aromatic); mass spectrum (70 eV) *m/e* (major peaks underlined) $\underline{258}$, 240, 218, 217, 200, 199, 172, 144, 129, 115, 101, 43, 41.

*Anal.* Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.9; H, 5.6.

**$C^{13}$ Nmr Spectra.** The spectra were obtained by T. Regan on a Brucker HX-90 spectrometer equipped with a Digilab NMR-3 Pulse-Fourier transform system. Spectra under both broad-band and off-resonance continuous wave decoupling were obtained. The multiplicities were observed during partial decoupling. Chemical shifts are relative to tetramethylsilane.

**Film Coatings.** To 1 mmol of the compound was added 10 g of a 10% solution of Eastman cellulose acetate butyrate in acetone–methanol (10:7). The mixture was stirred until the solid dissolved. It was coated at a wet thickness of 200 $\mu$m on a film support and dried and cured at 40° to remove the solvents.

**Acknowledgment.** The authors are indebted to J. C. Fleming for supplies of quinones, to S. Farid for many helpful discussions, and to T. H. Regan for the $^{13}C$ nmr spectra and their interpretation.

**Registry No.**—**1**, 53626-42-9; **2**, 53626-43-0; **5**, 53626-44-1; **6**, 53626-45-2; **7a**, 53626-46-3; **7b**, 53626-47-4; **9**, 53626-48-5; **15**, 53626-49-6; 2-methoxy-1,4-naphthoquinone, 2348-82-5; 2-ethoxy-1,4-naphthoquinone, 7473-18-9; 2-ethoxy-3-methyl-1,4-naphthoquinone, 53626-50-9.

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# Substituent Effects on the Photochemical α Cleavage of Deoxybenzoin[1]

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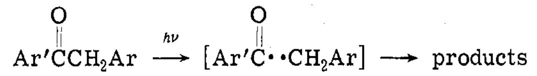
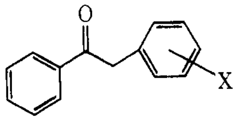
The effects of aromatic substituents which are not conjugated with the carbonyl on the photochemical behavior of deoxybenzoin have been investigated. Photochemical α cleavage is the exclusive primary photoprocess observed in benzene solution. Room temperature phosphorescence is observed for several deoxybenzoins and provides a convenient method of measuring triplet lifetimes. Substituents affect the rate constant for α cleavage without altering the triplet energy or radiative lifetime. The rate constants for α cleavage fit the Hammett equation with the use of $\sigma^+$ ($\rho = -1.1$). It is concluded that the transition state for α cleavage lies early on the reaction coordinate and has moderate ionic character.

Deoxybenzoin and several of its aryl-substituted derivatives undergo photochemical α cleavage (Norrish type I) to give a benzoyl–benzyl radical pair (eq 1).[3–6] The preceeding



$$\mathrm{Ar'\overset{\overset{O}{\|}}{C}CH_2Ar} \xrightarrow{h\nu} [\mathrm{Ar'\overset{\overset{O}{\|}}{C}\cdot \, \cdot CH_2Ar}] \longrightarrow \text{products} \qquad (1)$$

paper in this series[5] describes the effects of α-methyl and α-phenyl substituents on the photochemical reactivity of deoxybenzoin. From a comparison of the rate constants for photochemical α cleavage of the deoxybenzoins studied and the rate constants for thermolysis of the corresponding peresters,[7] we concluded that the transition state for α cleavage resembles the excited ketone rather than the radical pair. This conclusion is contrary to the common assumption that the rate of α cleavage is determined by the stability of the radical pair or biradical intermediate.[8] In order to provide further information about the mechanism of photochemical α cleavage and the possible influence of polar effects in the transition state, we have investigated the photochemical and photophysical reactions of a number of substituted deoxybenzoins (1).[9] Polar effects, *e.g.*, partial charge formation in the transition state, have often been used in interpreting the influence of substituents on free radical abstraction[11] and decomposition[12–14] reactions which result in the formation of benzyl radicals. For example, substituent effects on phenyl-substituted *tert*-butylperoxyphenylacetate thermolysis have been successfully explained in terms of different partial charge formation in the transition state.[12,13] In view of the previously observed similarity of the structure–reactivity relationships for photochemical α cleavage of deoxybenzoins and perester thermolysis,[5] we expected to observe polar contributions to the transition state for α cleavage.



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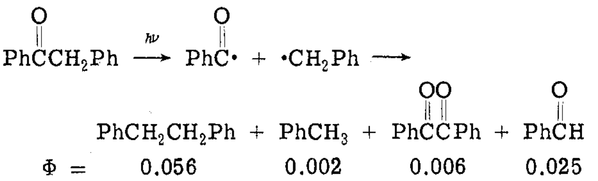
## Results

**Quantum Yields and Kinetics.** Irradiation of deoxybenzoin and a number of aryl-substituted deoxybenzoins in degassed benzene solution results in the formation of bibenzyls, toluenes, benzils, and benzaldehyde (eq 2). Quantum yields for product formation at 3% conversion from deoxybenzoin (0.03 *M*) are given in eq 2. The quantum yields for bibenzyl and benzil formation are corrected for the requirement of two benzyl or benzoyl radicals for the formation of one product molecule. Bibenzyls are the major products formed upon irradiation in degassed benzene solution for all of the deoxybenzoins in Table I. Toluene quantum yields are 2–5% of the bibenzyl quantum yields.



$$\begin{aligned} &\mathrm{Ph\overset{\overset{O}{\|}}{C}CH_2Ph} \xrightarrow{h\nu} \mathrm{Ph\overset{\overset{O}{\|}}{C}\cdot} + \cdot\mathrm{CH_2Ph} \longrightarrow \\ &\qquad \mathrm{PhCH_2CH_2Ph} + \mathrm{PhCH_3} + \mathrm{Ph\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Ph} + \mathrm{Ph\overset{\overset{O}{\|}}{C}H} \qquad (2) \\ &\Phi = \quad 0.056 \qquad 0.002 \qquad 0.006 \qquad 0.025 \end{aligned}$$

Irradiation of deoxybenzoin in the presence of either biphenyl (313-nm irradiation) or naphthalene (365 nm irradiation) gave linear Stern–Volmer plots for quenching of bibenzyl formation (Table I). The slope of the quenching plot ($k_q\tau$) for naphthalene quenching is twice as large as that for biphenyl quenching. Wagner[15] has previously reported that biphenyl quenches aryl ketone type II photoelimination with a rate constant ($\sim 2 \times 10^{-9}\ M^{-1}\ \mathrm{sec}^{-1}$) which is slightly less than the diffusion-controlled limit. Since the triplet energies of all the deoxybenzoins in Table I are similar (*vide infra*), it is assumed that the rate of triplet quenching by biphenyl will also be similar.

Quantum yields for benzaldehyde formation (Table II) were determined for degassed 0.03 *M* benzene solutions containing low concentrations of dodecanethiol. We have previously described the use of alkane thiols as efficient scavengers for benzoyl radicals.[5,16] Benzaldehyde quantum yields decrease rapidly with increasing conversion due to quenching by photoproduct.[5] The values given in Table II