Photochemical α Cleavage and Free-Radical Reactions of Some Deoxybenzoins[1a,b]

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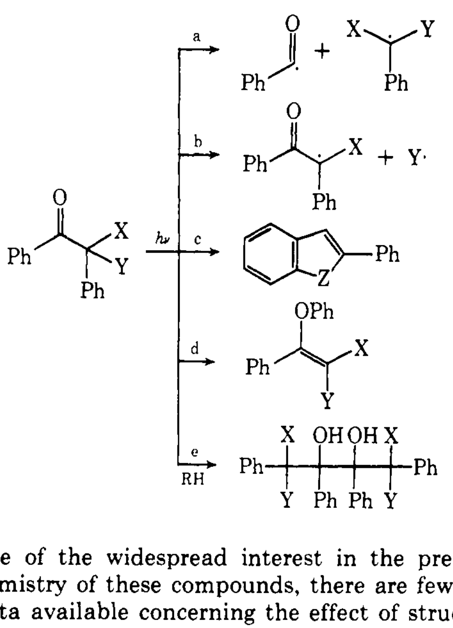
The effect of α-methyl and α-phenyl substituents on the photochemical α-cleavage reactions of alkyl phenyl ketones has been investigated. α cleavage is the only primary process observed upon irradiation of the deoxybenzoins 1-4 in degassed benzene solution. Photoreduction competes with α cleavage of deoxybenzoin in 2-propanol-benzene solution. The reactions of the benzoyl and benzyl free radicals formed upon α cleavage have been studied in some detail. Spectroscopic and energy transfer data indicate that α cleavage occurs exclusively from the lowest $^3n,\pi^*$ excited state. Triplet lifetimes were measured by Stern-Volmer analysis of product quenching by naphthalene and, for deoxybenzoin, by quenching of room temperature phosphorescence. The effects of substituents upon triplet lifetimes indicate that the rate constants do not depend on the stability of the resulting radicals. From a comparison of the rate constants for photochemical α cleavage of the deoxybenzoins studied and the rate constants for thermolysis of corresponding peresters it is concluded that the transition state for α cleavage resembles the excited ketone rather than the radical pair.

The photochemical reactions of benzoin, deoxybenzoin, and their derivatives have received sporadic attention since the early days of organic photochemistry.[2-17] Particularly intriguing are the reports that these compounds undergo a wide variety of reactions (Scheme I), the nature of which depends on both substituents and solvent. For example, benzoin,[3,4] benzoin ethers,[5,6] deoxybenzoin,[7-9] α-alkyl- and α-phenyldeoxybenzoin,[9-11] and 2-phenyl-1-indanone[12] undergo photochemical α cleavage (path a) whereas desyl chloride[13] and sulfides[10,14] undergo β cleavage (path b). Some benzoin esters and desyl amine salts yield 2-phenylbenzofuran,[13,15] and desyl sulfides yield 2-phenylbenzo[*b*]thiophene when irradiated in hydrogen-donor solvents (path c).[14] α,α-Diphenyldeoxybenzoin undergoes a unique 1,3-phenyl shift to give a vinyl ether (path d) along with lesser amounts of α cleavage products (path a).[16] Deoxybenzoin forms a mixture of diastereomeric pinacols when irradiated in hydrogen-donor solvents (path e).[17-20]

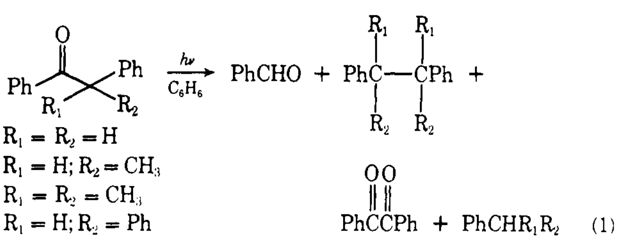
Scheme I
Photochemical Reactions of Deoxybenzoins



In spite of the widespread interest in the preparative photochemistry of these compounds, there are few quantitative data available concerning the effect of structure on photochemical reactivity. Thus the ability to predict which of the primary photochemical processes shown in Scheme I will be the most efficient for a given compound is rather limited. In view of our interest in the photochemical α cleavage reactions of aryl alkyl ketones,[5,9,16,21-24] we have undertaken a detailed investigation of the photochemical behavior of deoxybenzoins. In the present paper the effect of α-methyl and α-phenyl substituents on the reactivity of deoxybenzoin is described. Subsequent papers in this series will deal with the effects of aromatic substituents on the reactivity of deoxybenzoin and the photochemistry of benzoin ethers.

Results

Product Studies and Quantum Yields. Irradiation of deoxybenzoin (1) in degassed benzene solution results in the formation of benzaldehyde, benzil, bibenzyl, and toluene (eq 1). Ketones 2-4 give analogous products along with styrene and α-methylstyrene in the case of 2 and 3, respectively. The products were identified by comparison of spectral properties and vpc retention times with those of authentic samples. No attempt was made to identify the higher molecular weight products which result from prolonged irradiation or irradiation in the presence of oxygen.[7]



1, $R_1 = R_2 = H$
2, $R_1 = H; R_2 = CH_3$
3, $R_1 = R_2 = CH_3$
4, $R_1 = H; R_2 = Ph$ (1)

Bibenzyl is the major product formed upon irradiation of a 0.03 *M* benzene solution of ketone 1 at low conversions. Quantum yields for bibenzyl formation are dependent on light intensity, per cent conversion, and the presence or absence of oxygen. The variation in quantum yield (313-nm irradiation) with conversion at two different light intensities is shown in Figure 1.[25] The quantum yields decrease to half their extrapolated initial values at <5% conversion. The extrapolated quantum yields are 0.18 for $I = 1.7 \times 10^{-6}$ einstein $l.^{-1}$ sec^{-1} and 0.13 for $I = 1.0 \times 10^{-6}$ einstein $l.^{-1}$ sec^{-1}. At the former light intensity and 1% conversion the benzaldehyde quantum yield is 0.050.

In view of the low quantum yields for bibenzyl and benzaldehyde formation from ketone 1, it appeared likely that cage[24] and/or noncage recombination of benzyl and

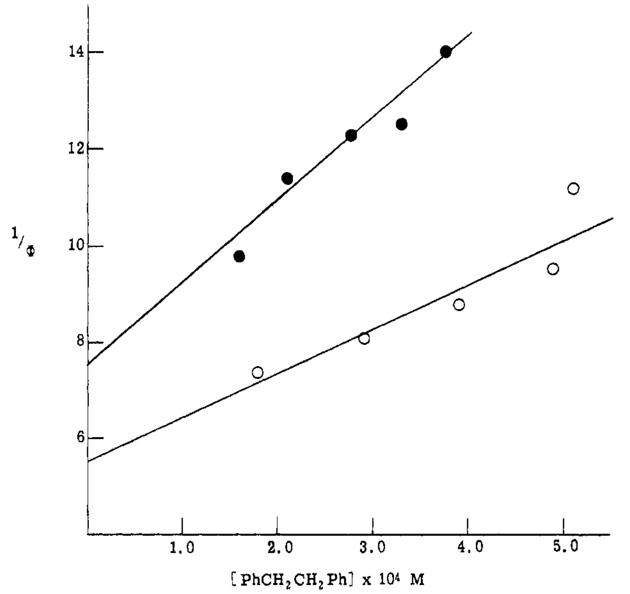
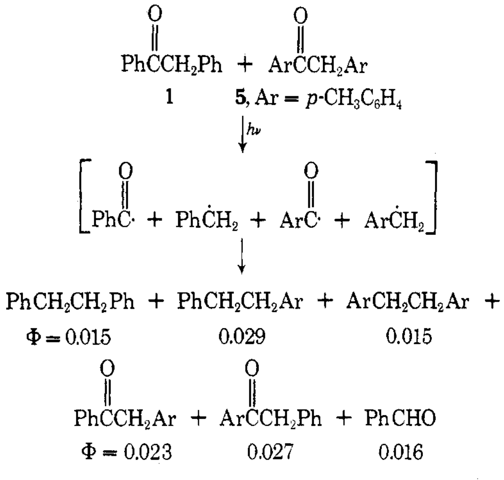


Figure 1. Variation in quantum yield for bibenzyl formation from deoxybenzoin with conversion: ●, I = 1.7 × 10^{-6} einstein $l.^{-1}$ sec^{-1}; ○, I = 1.0 × 10^{-6} einstein $l.^{-1}$ sec^{-1}.

benzoyl radicals occurs. In order to assess the extent of noncage recombination, an equiabsorbing mixture of ketone 1 and 4,4′-dimethyldeoxybenzoin (5) was irradiated to ~5% conversion (313 nm, 3.8 × 10^{-6} einstein $l.^{-1}$ sec^{-1}). Fortuitously, 1 and 5 have similar quantum yields for bibenzyl formation under these conditions (0.058 and 0.048, respectively). The results shown in Scheme II indicate that the efficiency of crossover ketone formation (Φ = 0.050) is comparable to that for bibenzyl formation (Φ = 0.059) and greater than that for benzaldehyde formation.

Scheme II



$$\underset{\mathbf{1}}{\mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2Ph}} + \underset{\mathbf{5},\ \mathrm{Ar} = p\text{-}\mathrm{CH_3C_6H_4}}{\mathrm{Ar\overset{O}{\overset{\|}{C}}CH_2Ar}} \xrightarrow{h\nu} \left[\mathrm{Ph\overset{O}{\overset{\|}{C}}\cdot} + \mathrm{Ph\dot{C}H_2} + \mathrm{Ar\overset{O}{\overset{\|}{C}}\cdot} + \mathrm{Ar\dot{C}H_2}\right] \longrightarrow$$

$$\underset{\Phi = 0.015}{\mathrm{PhCH_2CH_2Ph}} + \underset{0.029}{\mathrm{PhCH_2CH_2Ar}} + \underset{0.015}{\mathrm{ArCH_2CH_2Ar}} + \underset{\Phi = 0.023}{\mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2Ar}} + \underset{0.027}{\mathrm{Ar\overset{O}{\overset{\|}{C}}CH_2Ph}} + \underset{0.016}{\mathrm{PhCHO}}$$

In order to simplify the product mixtures resulting from irradiation of ketones 1-4, low concentrations of 1-dodecanethiol (RSH) were added to the solutions. Figures 2 and 3 show the dependence of product quantum yields on thiol concentration for ketones 1 and 3 (~2% conversion). The benzaldehyde quantum yields increase to a maximum value at 2 × 10^{-3} M RSH. The quantum yield for benzaldehyde formation from ketone 1 appears to decrease at higher thiol concentration; however, no decrease is observed for ketone 2 up to 0.05 M thiol[24] and for ketone 3 up to 0.10 M thiol. The decrease in bibenzyl quantum yield[25] from ketone 1 with added thiol (Figure 2) is accompanied by increased toluene formation. The quantum yields for cumene formation from ketone 3 increases with added thiol whereas the values for bicumyl- and α-methylstyrene remain constant (Figure 3). Addition of 0.03 M thiol to a mixture of ketones 1 and 5 completely suppresses the formation of crossover ketones.

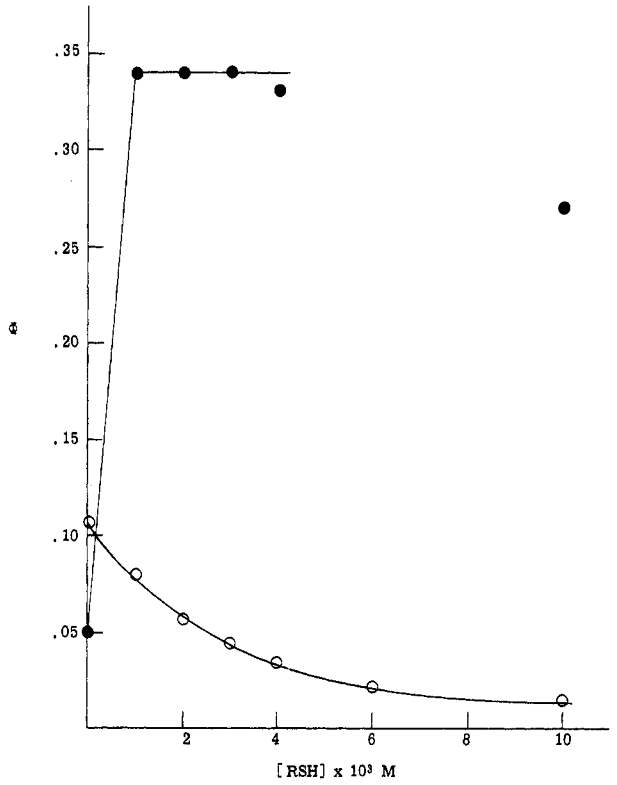


Figure 2. Effect of added dodecanethiol on quantum yields for benzaldehyde (●) and bibenzyl (○) formation from deoxybenzoin.

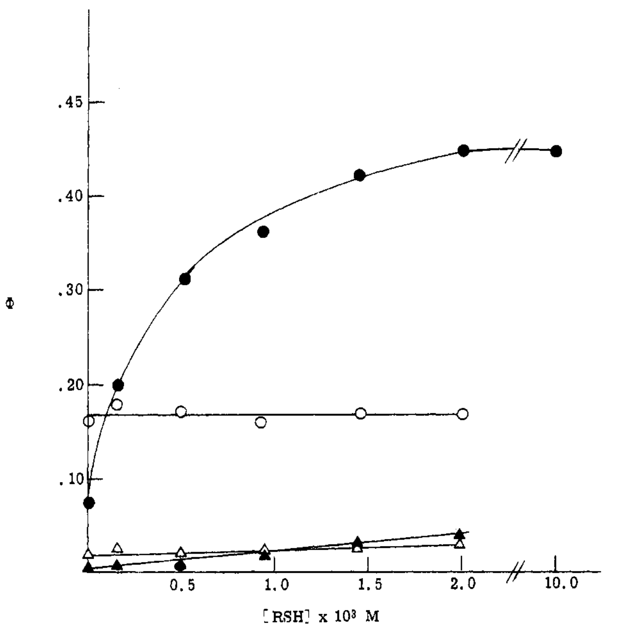


Figure 3. Effect of added dodecanethiol on quantum yields for benzaldehyde (●), bicumyl (○), cumene (▲), and α-methylstyrene (△) formation from α,α-dimethyldeoxybenzoin.

Maximum quantum yields for benzaldehyde formation from ketones 1-3 were determined by irradiating 3 × 10^{-2} M benzene solutions containing 3 × 10^{-3} M thiol to varying conversions. The dependence of $1/\Phi$ with conversion (expressed in terms of benzaldehyde concentration) for ketones 1 and 2 is shown in Figure 4. The decrease in quantum yield for ketone 2 is more gradual than for ke-

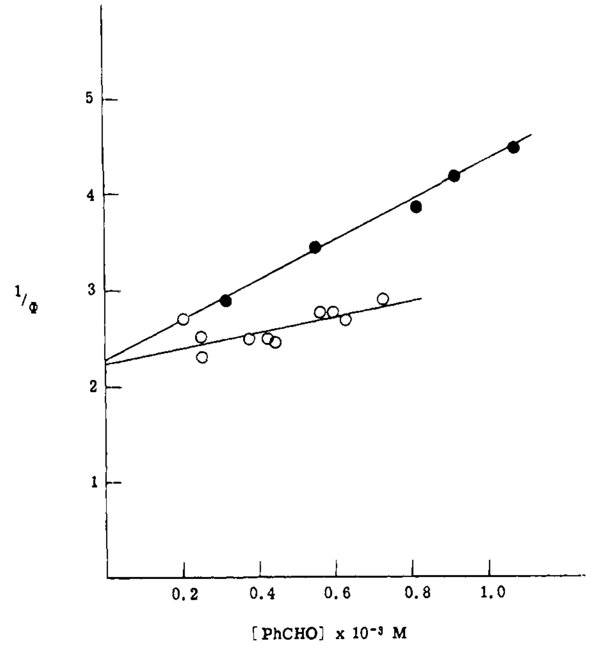


Figure 4. Variation in quantum yield for benzaldehyde formation from deoxybenzoin (●), and α-methyldeoxybenzoin (O) with conversion.

tone **1**, and the value for ketone **3** is invariant up to several per cent conversion. Quantum yields extrapolated to zero conversion are given in Table I.

Table I
Quantum Yields and Kinetic Data

Ketone	Solvent	Φ^a	$k_q\tau$, $M^{-1\,b}$	$1/\tau$ $\times 10^{-7}$, sec^{-1}
$PhCOCH_2Ph$ (**1**)	C_6H_6		2100	0.24
	C_6H_6–RSH	0.44	3100	0.16
$PhCOCH(CH_3)Ph$ (**2**)	C_6H_6		170	2.9
	C_6H_6–RSH	0.44	240	2.1
$PhCOC(CH_3)_2Ph$ (**3**)	C_6H_6		33	15
	C_6H_6–RSH	0.45	42	12
$PhCOCHPh_2$ (**4**)	C_6H_6		50	10

[a] Quantum yield for benzaldehyde formation in 3×10^{-3} M dodecanethiol–benzene extrapolated to zero conversion, ±5%. [b] Slopes of linear Stern–Volmer plots for naphthalene quenching, ±35% for ketone **1**, ±15% for ketones **2–4**.

Kinetics. Irradiation of ketones **1–4** in the presence of conjugated dienes, biphenyl, or naphthalene diminishes the quantum yields for product formation. Curved Stern–Volmer quenching plots were obtained for diene quenchers, presumably due to reaction of the free radical products with the diene. Biphenyl (313-nm irradiation) and naphthalene (365-nm irradiation) both gave linear Stern–Volmer plots; however, the slope ($k_q\tau$) for the biphenyl quenching plot is two to three times less than that for naphthalene quenching. This is indicative of quenching at less than the diffusion-controlled rate by biphenyl.[26a] Thus naphthalene proved to be the most satisfactory quencher in spite of the necessity of irradiating at wavelengths >330 nm to avoid competitive absorption by quencher. Sufficient naphthalene was used to quench between 30 and 60% of product formation. This required naphthalene concentrations of $\sim 10^{-4}$ M for ketone **1** and $\sim 10^{-2}$ M for ketones **3** and **4**. The slopes of individual Stern–Volmer plots were determined by the method of least squares and had correlation coefficients of 0.98 or better. The slopes of linear Stern–Volmer plots for naphthalene quenching of benzaldehyde formation decrease with increasing conversions. As is the case for the benzaldehyde quantum yields (Figure 4), the effect is greatest for ketone **1**. This results in a larger error in the value of $k_q\tau$ for ketone **1** than for ketones **2–4**.

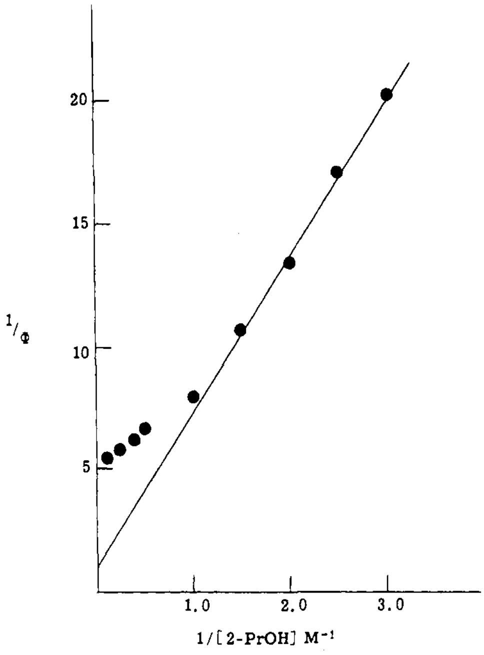


Figure 5. Dependence of quantum yield for deoxybenzoin photoreduction with 2-propanol concentration.

Table II
Absorption Spectral Data for Phenyl Ketones PhCO–R

Compd	R	Cyclohexane λ_{max}, nm	Cyclohexane (ϵ)	Ethanol λ_{max}, nm	Ethanol (ϵ)
6	CH_3	323	(40)	316	(63)
7	$C(CH_3)_3$	321	(89)	317	(130)
1	CH_2Ph	323	(126)	321	(160)
2	$CH(CH_3)Ph$	323	(168)	321	(210)
3	$C(CH_3)_2Ph$	325	(140)	320	(170)
4	$CHPh_2$	327	(200)	324	(196)

The $k_q\tau$ values given in Table I are the slopes of Stern–Volmer quenching plots obtained at <1% conversion both with and without added thiol. The data obtained without added thiol are the average of four or more Stern–Volmer plots. The data for ketone **1** with added thiol are the average of six Stern–Volmer plots with a standard deviation of 35%. The error limits for ketones **2–4** are considerably smaller (±15%). The $1/\tau$ values in Table I are calculated assuming $k_q = 5 \times 10^9$ M^{-1} sec^{-1} for naphthalene quenching. By analogy to the results of Wagner[26b] for quenching of valerophenone and α,α-dimethylvalerophenone, we assume that there is no steric effect on the rate constant for energy transfer.

Irradiation of ketone **1** in 2-propanol–benzene solution results in the formation of acetone and a mixture of stereoisomeric pinacols[17-20] in addition to the products of α cleavage. The variation in the quantum yield for acetone formation with 2-propanol concentration is shown in Figure 5. The linear portion of the line obtained for 2-propanol concentrations <1 M has a slope of 6.4 ± 0.1 M and an intercept of 1.0 ± 0.2. The deviation from linearity at higher 2-propanol concentrations is similar to that observed for acetophenone photoreduction.[27,28]

Spectroscopic Data. The ultraviolet absorption data for ketones **1–4** in cyclohexane and ethanol solvent are given in Table II along with values for acetophenone (**6**) and pivalophenone (**7**). Emission spectra were recorded at 77°K in both polar and nonpolar glasses. Structured emis-

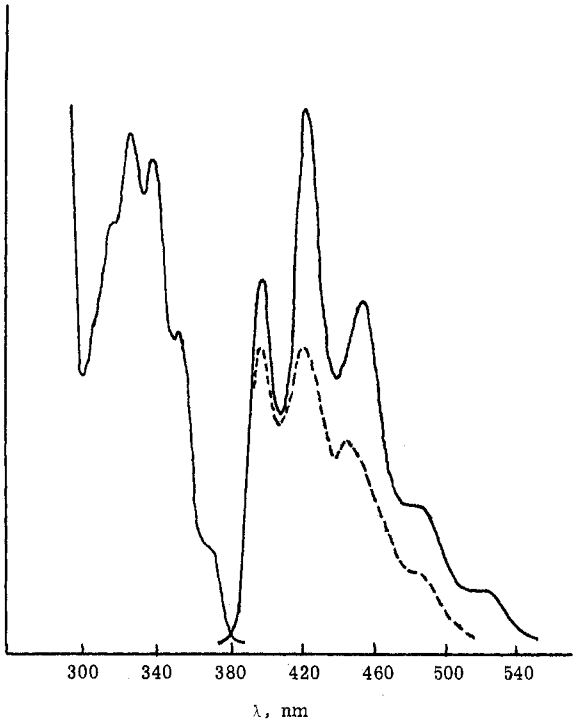


Figure 6. Room temperature absorption (——), emission (- - -), and 77°K emission (——) spectra of deoxybenzoin (arbitrary intensities).

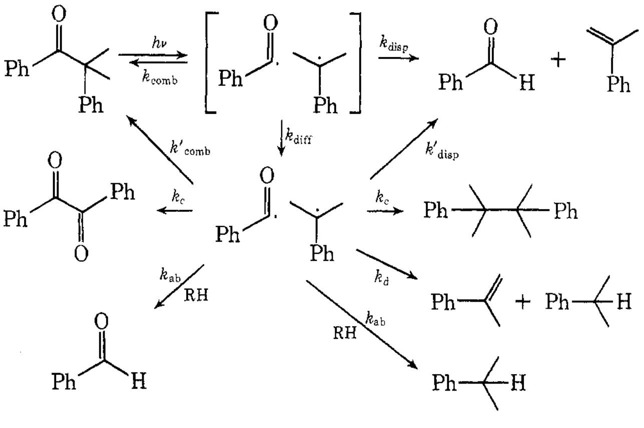
sion similar to that for acetophenone or pivalophenone was observed for ketones 2-4. The positions of the emission maxima for ketone 1 in EPA agree with a previous report.[29] Triplet energies are estimated from the position of the highest energy emission maxima and are the same in MC and MP glasses. Triplet lifetimes were determined by flash-emission studies at 77°K. Emission from ketones 2-4 and 7 occurs predominantly from a single short-lived excited state (τ < 10 msec) in both polar and nonpolar solvents. Intersystem crossing quantum yields for ketones 2-4 and 7 were determined by the method of Lamola and Hammond.[30] Comparison of the extent of trans → cis piperylene isomerization to that for benzophenone ($\Phi = 1.0$) gave values of 1.0 ± 0.05 for all of the ketones studied.

Room temperature emission was observed from highly degassed carbon tetrachloride or benzene solutions of ketones 1 and 6. Room temperature emission of ketone 6 has previously been observed[31] and is considerably more intense than that for ketone 1. The room temperature and 77°K emission spectra and absorption spectrum of ketone 1 are shown in Figure 6. The position of the emission maxima at 77°K and at room temperature are quite similar. Quenching of the room temperature emission in benzene by 2,5-dimethyl-2,4-hexadiene yields a value of $1/\tau = 1.2 \pm 0.2 \times 10^6$ sec^{-1}, in excellent agreement with the values obtained by product quenching (Table I). The room temperature emission of ketone 1 was also quenched by 1-dodecanethiol. From the slope of the phosphorescence quenching plot ($k_q\tau = 37\ M^{-1}$) and the triplet lifetime, a value of $k_q = 4.4 \pm 1.5 \times 10^7\ M^{-1}$ sec^{-1} for thiol quenching is obtained.

Discussion

Free Radical Reactions. The products observed upon irradiation of ketones 1-4 in benzene solution (eq 1) can be accounted for in terms of a general mechanism shown in Scheme III for ketone 3. There is no evidence for products arising from any photochemical process other than α cleavage and the subsequent free radical reactions. We will concern ourselves first with the cage and noncage reactions of the benzoyl radical and subsequently with the nature of the excited state and α cleavage process.

Scheme III
Reactions of the Photochemically Generated Radical Pair



Possible cage reactions of the initially formed radical pair include recombination to give ground state ketone (k_{comb}), diffusion to give separated free radicals (k_{diff}), and, in the case of ketones 2 and 3, disproportionation to benzaldehyde and styrene or α-methylstyrene (k_{disp}). Since α cleavage occurs from a triplet state (*vide infra*) cage recombination and disproportionation require spin inversion prior to bond formation. Salem[32] has recently shown that a triplet diradical state is nearly degenerate with the singlet diradical. Thus there should be no spin-correlation effect[33] on the radical pair cage reactions. In accord with Salem's theory we have found cage recombination of optically active ketone 2 to account for at least one-third of the initially excited molecules.[24] Cage disproportionation may be responsible for some of the benzaldehyde from 2 and 3 and the excess of α-methylstyrene over cumene from 3 in the absence of thiol scavenger (Figure 3, $\Phi_{\mathrm{disp}} \leq 0.02$).

Noncage radical reactions include recombination of benzoyl and benzyl radicals to give ground state ketone (k'_{comb}). The formation of crossover ketones upon irradiation of a mixture of ketones 1 and 5 (Scheme II) indicates the importance of this reaction in the absence of added thiol. Since the quantum yields for crossover ketone and bibenzyl formation are comparable, the rate constant for benzoyl-benzyl combination must be comparable to the known rate constant for benzyl-benzyl combination ($4.1 \times 10^9\ M^{-1}$ sec^{-1}).[34] Noncage disproportionation (k'_{disp}) of benzoyl-cumyl radical pairs from ketone 3 cannot be very important in view of the low α-methylstyrene quantum yield and its insensitivity to added thiol (Figure 3).

In addition to reactions with benzyl radicals, benzoyl radicals can combine to form trace amounts of benzil (k_c) or abstract hydrogen to form benzaldehyde (k_{ab}). Similarly, benzyl radicals can combine or abstract hydrogen, and the 1-phenylethyl and cumyl radicals can disproportionate. The quantum yields for cumene and bicumyl formation from ketone 3 provide a value of 0.059 for the disproportion/combination ratio of the cumyl radical. This result is in excellent agreement with the value 0.054 reported by Nelsen and Bartlett.[35]

Addition of low concentrations of dodecanethiol (RSH) to the benzene solvent greatly increases the quantum yields for benzaldehyde formation (Figures 2 and 3) and thereby simplifies quantitative study of the α cleavage reaction.[22-24,36] The ability of thiol to scavenge all of the noncage benzoyl radicals (eq 2) is indicated by the total supression of crossover ketone formation from ketones 1

$$\mathrm{Ph\dot{C}O + RSH \longrightarrow PhCHO + RS\cdot} \qquad (2)$$

Table III
Phosphorescence Data for Phenyl Ketones

Compd	R	Solvent	E_T, kcal/mol	τ, msec
6	CH_3[a]	MC[b]	73.5	4
		EtOH	74.0	8.0
		CCl_4[c]	72.0	
7	$C(CH_3)_3$	MC	71.5	3.7
		EPA[d]	72.2	4.9
1	CH_2Ph	MC	72.0	1.9
		EPA	73.3	2.8
		C_6H_6[c]	72.0	
2	$CH(CH_3)Ph$	MC	73.0	2.9
		EPA	73.3	4.6
3	$C(CH_3)_2Ph$	MC	73.0	4.1
		EPA	73.0	6.1
4	$CHPh_2$	MP[e]	72.4	

[a] Data from ref 44. [b] Methylcyclohexane. [c] Room temperature emission. [d] Ether–isopentane–ethanol. [e] Methylcyclohexane–isopentane.

and **5** (Scheme II) by 3×10^{-2} *M* RSH and by the maximization of benzaldehyde quantum yields with $\sim 10^{-3}$ *M* RSH (Figures 2 and 3). Possible complications arising from the use of thiols include reactions of the thiyl radical and quenching of the excited state by thiol. The abstraction reaction (eq 2) is known to be approximately thermoneutral.[37] The thiyl radicals formed do not initiate the decarbonylation of benzaldehyde as they do for aliphatic aldehydes.[38] Zepp and Wagner[39] have reported that thiols quench the $^3n,\pi^*$ state of acetophenone with a rate constant of 1.4×10^7 M^{-1} sec^{-1}. The rate constant for dodecanethiol quenching of ketone **1** obtained by quenching of room temperature phosphorescence is 4.4×10^7 M^{-1} sec^{-1}. Since we typically used thiol concentrations of 10^{-3} *M*, quenching of ketones with lifetimes shorter than 10^{-6} sec should be insignificant.

The thiol scavenging results shown in Figures 2 and 3 can also be used in conjunction with the known rate constants for benzyl[34] and cumyl[40] radical combination (eq 3 and 4) to provide rate constants for the reaction of benzyl and cumyl radicals with dodecanethiol. A steady-state assumption for benzyl radical gives eq 5, where Φ is the quantum yield for noncage radical formation, *I* is the light intensity, and k_c and k_{SH} are the rate constants for reactions 3 and 4. From the light intensity and a value of $\Phi \approx 0.5$ (Table I), the steady-state concentration of benzyl radicals in the absence of thiol is 1.1×10^{-8} *M*. Estimation of k_{SH} by successive approximation gives a best fit to the experimental data for bibenzyl formation (Figure 2) for a value of $k_{SH} = 3.5 \times 10^4$ M^{-1} sec^{-1}. This value is in good agreement with the rate constant for benzyl radical hydrogen abstraction from α-toluenethiol ($k_{SH} = 5.1 \times 10^4$ M^{-1} sec^{-1}) reported by Burkhart.[34] Similar analysis of the data for cumene formation from ketone **3** gives a value of $k_{SH} = 8.3 \times 10^3$ M^{-1} sec^{-1} for the abstraction reaction of cumyl radical. The smaller rate constant for cumyl *vs.* benzyl radical is expected on the basis of radical stability.

$$2PhCH_2\cdot \xrightarrow{k_c} PhCH_2CH_2Ph \tag{3}$$

$$PhCH_2\cdot + RSH \xrightarrow{k_{SH}} PhCH_3 + RS\cdot \tag{4}$$

$$\Phi I = \frac{-d[PhCH_2\cdot]}{dt} = 2k_c[PhCH_2\cdot]^2 + k_{SH}[PhCH_2\cdot][RSH] \tag{5}$$

Identity of the Reactive Excited State. The nature of the reactive excited state is of considerable importance in photochemical α cleavage reactions. For example, the lowest triplet state of dialkyl ketones is much more reactive toward α cleavage than the singlet state.[41] The configuration of the lowest triplet state is also important, since it is known that a lowest $^3n,\pi^*$ state is more reactive than a $^3\pi,\pi^*$ state in the case of substituted pivalophenones[23] and 2-phenyl-1-indanones.[12] The ability of naphthalene, biphenyl, and dienes to quench the formation of products from ketones **1**–**4** indicates that α cleavage occurs from a triplet state. High intersystem crossing quantum yields establish that triplet formation occurs with unit efficiency. The n,π^* absorption spectra of ketones **2**–**4** and pivalophenone (**7**) are much more intense than that of acetophenone (**6**) (Table II). The exhalted n,π^* absorption of α-phenyl ketones has been attributed to interaction of the n,π^* state with the adjacent π electrons.[42,43] This interaction could lead to a lowest n,π^* triplet with substantial π,π^* character or a lowest π,π^* triplet. In either case a decrease in reactivity compared to pivalophenone would be expected.

The low temperature emission spectra of ketones **1**–**4** are highly structured (Figure 6) and similar in appearance to those of ketones **6** and **7**. Ketones **1**–**4** and **7** display predominantly short-lived emission in both polar and nonpolar glasses (Table III). Such emission is characteristic of phenyl ketone $^3n,\pi^*$ states.[44] The weak room temperature emission of ketone **1** in benzene is less well resolved than the low temperature emission (Figure 6); however, the emission maxima occur at similar wavelengths. Thus the lowest energy triplet state both at room temperature and at 77°K is the $^3n,\pi^*$ state.

Transition State for α Cleavage. The formation of benzaldehyde from ketones **1**–**4** can be described by the abbreviated mechanism given in eq 6–9

$$D \xrightarrow{h\nu} {}^1D \xrightarrow{k_{ST}} {}^3D \tag{6}$$

$$^3D \xrightarrow{k_d} D \tag{7}$$

$$^3D + Q \xrightarrow{k_q} D + {}^3Q \tag{8}$$

$$^3D \xrightarrow{k_\alpha} Ph\dot{C}O + Ph\dot{C}R_1R_2 \xrightarrow{RSH} PhCHO \tag{9}$$

where D is the deoxybenzoin and Q is the quencher naphthalene. Since the $^3n,\pi^*$ state is formed with unit efficiency, the quantum yield for benzaldehyde formation is determined by the efficiency of α cleavage and the probability (β) that the benzoyl radical will form benzaldehyde. The ratio of the quantum yield expressions with and without added quencher (eq 10 and 11) gives the Stern-Volmer equation (eq 12). The probability factor β should not change upon addition of quencher and thus will not affect lifetimes determined by Stern–Volmer kinetics. Evidence has recently been presented that cage recombination of benzoyl and benzyl radicals rather than nonradiative decay of the $^3n,\pi^*$ state is responsible for the inefficiency in product formation from ketone **2**.[24] Thus the triplet lifetimes obtained from Stern–Volmer quenching experiments (Table I) are determined by the rate constant for α cleavage ($k_\alpha = 1/\tau$).

$$\Phi^0 = \left(\frac{k_\alpha}{k_\alpha + k_d}\right)\beta \tag{10}$$

$$\Phi = \left(\frac{k_\alpha}{k_\alpha + k_d + k_q[Q]}\right)\beta \tag{11}$$

$$\frac{\Phi^0}{\Phi} = 1 + \frac{k_q[Q]}{k_\alpha + k_d} = 1 + k_q\tau[Q] \tag{12}$$

The kinetic data in Table I show that the triplet lifetimes decrease with substitution of either methyl or phenyl groups at the α carbon. Such a trend would be expected if the rate constant for α cleavage is determined by the stability of the radical pair. It has been commonly assumed that reactivity toward α cleavage is determined by the stability of the radicals produced;[45] however, evidence concerning the free radical character of the transition

Table IV
Rate Constants for Photochemical α Cleavage and Perester Thermolysis[a]

R	PhC(=O)R, $k_\alpha^{22°} \times 10^{-7}$ sec^{-1}	Registry no.	RC(=O)OO-t-Bu, $k_{therm}^{60°} \times 10^3$, sec^{-1}	Registry no.
$-CH(CH_3)_2$	0.034[b,c]	611-70-1	0.069	109-13-7
$-C(CH_3)_3$	1.1[b]		2.3	927-07-1
$-CH_2Ph$	0.16		0.41	3377-89-7
$-CH(CH_3)Ph$	2.1		5.8	3377-90-0
$-C(CH_3)_2Ph$	12		58	24161-29-3
$-CHPh_2$	10		27	13144-32-6

[a] Values from ref 48. [b] Values from ref 23. [c] See ref 49.

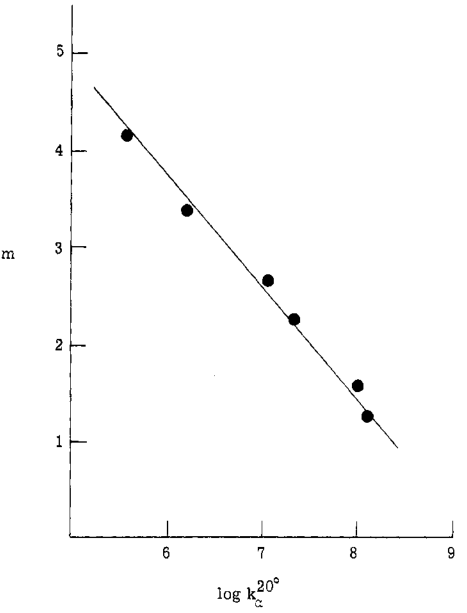
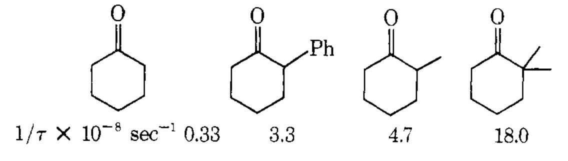
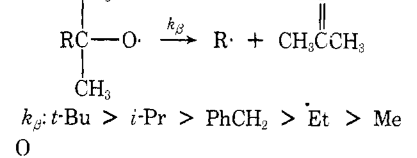


Figure 7. Linear free-energy relationship of photochemical α cleavage [PhC(=O)R] and perester thermolysis [RC(=O)OO-t-Bu].

state is lacking. Consideration of bond dissociation energies[22] indicates that α cleavage of ketones 1-4 is exothermic. Thus, according to the Hammond principle,[46] the transition state should more nearly resemble the ketone excited state than the radical pair. The faster α cleavage rate constant for pivalophenone (7) *vs.* deoxybenzoin is clearly contrary to predictions based on radical stability. There are several previous reports of homolytic cleavage reactions in which *tert*-alkyl compounds are more reactive than benzyl compounds. Among these are the photochemical α cleavage reactions of cyclohexanones (eq 13),[45b] the β-scission reaction of alkoxy radicals (eq 14),[47] and perester thermolysis (eq 15 and Table IV).[48]

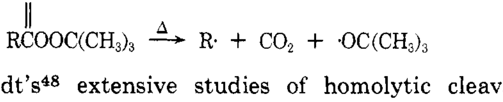


(13)



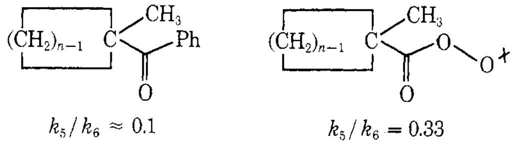
$$RC(CH_3)_2-O\cdot \xrightarrow{k_\beta} R\cdot + CH_3C(=O)CH_3 \quad (14)$$

k_β: t-Bu > i-Pr > $PhCH_2$ > Et > Me



$$RC(=O)OC(CH_3)_3 \xrightarrow{\Delta} R\cdot + CO_2 + \cdot OC(CH_3)_3 \quad (15)$$

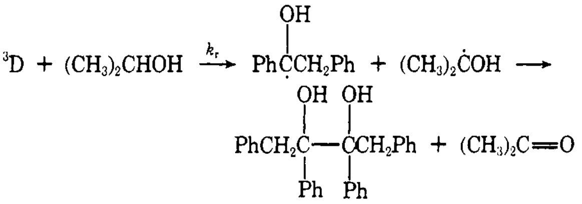
Rüchardt's[48] extensive studies of homolytic cleavage reactions have resulted in several criteria for determining the position of the transition state along the reaction coordinate. One criterion involves the relative effects of α-methyl and α-phenyl substituents upon reaction rate. Tertiary alkyl radicals are always formed more rapidly than secondary or primary, even when bond breaking is not far advanced in the transition state. However, substantial rate acceleration upon α-phenyl substitution requires a radical-like transition state. Rüchardt has presented convincing evidence that the perester C_α-CO bond is only insignificantly lengthened in the transition state (eq 15). Since radical character is not highly developed, the stability of the benzyl radical is not reflected in the rate of thermolysis. Thus comparison of our results for α cleavage of phenyl ketones with Rüchardt's studies of perester decomposition should be particularly informative. The free energy relationship for the data given in Table IV is shown in Figure 7. The linearity of this relationship (correlation coefficient = 0.996) indicates that substituents have similar effects on the transition states for both reactions. A second criterion for the position of the transition state along the reaction coordinate is the effect of ring size on reaction rate. Both photochemical α cleavage of α-methyl cycloalkyl ketones[50] and the corresponding peresters[48c] have larger rate constants for six-membered than for five-membered rings. Since the introduction of an sp^2 center in a cycloalkane ring produces a larger decrease in conformational strain for five-membered than for six-membered rings, a value of $k_5/k_6 > 1$ would be expected if the transition states had substantial free radical character.



From the preceding analogies with perester thermolysis, we conclude that *the transition states for α cleavage of phenyl ketones* 1-4 *and* 7 *lie early on the reaction coordinate.* It should be emphasized that increased reactivity toward α cleavage with increasing substitution at the α carbon is due mainly to ground state steric effects[48] rather than increased stability of the product radical pair.[45] The results of Wagner[45b] for α cleavage of cyclohexanones indicate that this conclusion may apply to photochemical α cleavage reactions in general.

As previously mentioned, an alternative explanation of the decreased reactivity of ketone 1 *vs.* 7 is that the α-phenyl group alters the triplet energy or the configuration of the lowest triplet state. Although the spectroscopic data do not support such an explanation, it was further explored by studying the photoreduction of ketone 1. Photoreduction rate constants for aryl ketones are known to be sensitive to the configuration of the lowest triplet state.[23,51] Incorporation of photoreduction (eq 16) into the previous kinetic scheme (eq 6-9) gives the relationship between the quantum yield for acetone formation and 2-propanol (RH) concentration in eq 17. A plot Φ^{-1} *vs.*

$[RH]^{-1}$ is linear for 2-propanol concentrations less than 1.0 M and has an intercept of 1.0 (Figure 5). The nonlinearity at higher 2-propanol concentrations is similar to that observed for photoreduction of acetophenone.[52] From the slope of the linear portion of Figure 5 and the triplet lifetime from Table I, a value of $k_r = 2.5 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ is obtained. This value is similar to that for propiophenone ($4.4 \times 10^5\ M^{-1}\ \text{sec}^{-1}$) and distinctly faster than those for isobutyrophenone ($0.9 \times 10^5\ M^{-1}\ \text{sec}^{-1}$) and pivalophenone ($0.24 \times 10^5\ M^{-1}\ \text{sec}^{-1}$).[23] Thus it seems highly unlikely that the lowest triplet of deoxybenzoin has more $^3\pi,\pi^*$ character than the lowest triplet of pivalophenone.



$$^3\mathrm{D} + (\mathrm{CH_3})_2\mathrm{CHOH} \xrightarrow{k_r} \mathrm{Ph\dot{C}(OH)CH_2Ph} + (\mathrm{CH_3})_2\mathrm{\dot{C}OH} \longrightarrow \mathrm{PhCH_2C(OH)(Ph){-}C(OH)(Ph)CH_2Ph} + (\mathrm{CH_3})_2\mathrm{C{=}O} \tag{16}$$

$$\frac{1}{\Phi} = 1 + \frac{k_\alpha + k_d}{k_r[\mathrm{RH}]} = 1 + \frac{1}{k_r\tau[\mathrm{RH}]} \tag{17}$$

One final aspect of our results that warrants discussion is the unusually marked decrease in product quantum yields with increasing conversion (Figures 1 and 4).[53] This behavior provides one of the few examples of efficient quenching by a photoproduct.[54,55] Incorporation of benzaldehyde (B) quenching (eq 18) into the previous kinetic scheme (eq 6–9) gives eq 19.[55b]

$$^3\mathrm{D} + \mathrm{B} \xrightarrow{k_{qp}} \mathrm{D} + {}^3\mathrm{B} \tag{18}$$

$$\frac{1}{\Phi_B} = \frac{1}{\Phi_B{}^0}\left(1 + \frac{k_{qp}\tau[\mathrm{B}]}{2}\right) \tag{19}$$

The slope/intercept ratios from Figure 4 give $k_{qp}\tau$ values of 1700 and 72 M^{-1} for ketones **1** and **2**. Using the triplet lifetimes in Table I, the apparent rate constants[55b] for quenching of ketones **1** and **2** by benzaldehyde are both $\sim 2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. Owing to its relatively long triplet lifetime, ketone **1** is more sensitive to product quenching than are ketones **2**–**4**. Product quenching decreases lifetimes measured by Stern-Volmer quenching as well as quantum yields. This problem was minimized by conducting quenching studies at <1% conversion. The excellent agreement of the lifetimes measured by naphthalene quenching of product formation and 2,5-dimethyl-2,4-hexadiene quenching of room temperature phosphorescence for ketone **1** indicates that the product quenching data in Table I are reliable. However, it should be borne in mind that quantum yield and kinetic data for reactions in which a product quenches the excited state precursor must be extrapolated to zero conversion.

Experimental Section

Ketones and Solvents. Deoxybenzoin (**1**) was either a commercial sample (Aldrich) or prepared *via* Friedel-Crafts acylation of benzene with phenylacetyl chloride, mp 55–56°. α-Methyldeoxybenzoin (**2**) was prepared by the method of Meyer and Oelkers,[56] mp 51° (lit.[56] 53°). α,α-Dimethyldeoxybenzoin (**3**) was prepared by alkylation of deoxybenzoin with sodium hydride and methyl iodide or by the reaction of α,α-dimethylbenzyl cyanide with phenylmagnesium bromide,[57] mp 45–46° (lit.[57] mp 46–47°). α-Phenyldeoxybenzoin (**4**) was prepared by Friedel-Crafts alkylation of benzene with desyl chloride, mp 136–137° (lit.[58] 135–136°). 4,4′-Dimethyldeoxybenzoin (**5**), 4-methyldeoxybenzoin, and 4′-methyldeoxybenzoin were all synthesized by Grignard reactions of benzylmagnesium chloride or 4-methylbenzylmagnesium chloride with benzaldehyde or *p*-tolualdehyde, mp 101° (lit.[59] 102°), mp 96° (lit.[60] 97°), and mp 108° (lit.[60] 110°), respectively. All ketones were extensively purified by recrystallization, chromatography on silica gel, or vacuum sublimation. Purity was >99% by vpc in all cases. Naphthalene was purified by sublimation or zone refining. Benzene (thiophene-free or spectrograde) was distilled from sodium wire or phosphorus pentoxide prior to use. Dodecanethiol (Aldrich) was distilled prior to use.

Quantum Yields and Kinetics. For quantum yield measurements, benzene solutions containing $3 \times 10^{-2}\ M$ ketone and $10^{-3}\ M$ tetradecane internal standard were degassed and sealed under vacuum in 13-mm-o.d. Pyrex tubes. The tubes were irradiated on a merry-go-round apparatus at 23 ± 2° using a Hanovia 450-W lamp and a potassium chromate filter solution to isolate the 313-nm mercury line. Light intensities were measured by simultaneous irradiation of benzophenone-benzhydrol[61] and/or potassium ferroxalate[62] actinometers. Both actinometer systems gave the same measured intensities. Product yields were determined by vpc analysis on either a 7 ft × 0.125 in. column of 10% FFAP on DMSC-treated Chromosorb G or a 6 ft × 0.125 in. column of 4% QF1 and 1% Carbowax 20M on Chromosorb G using a Hewlett-Packard 5750 gas chromatograph. Naphthalene quenching studies were conducted both with and without added dodecanethiol. The studies with added thiol were conducted on 0.1 M ketone solutions containing $3 \times 10^{-3}\ M$ thiol in degassed benzene. Corning filters 7-54 and 0-52 were used to isolate 365-nm irradiation. Quenching studies without added thiol were conducted on $5 \times 10^{-2}\ M$ ketone solutions contained in quartz tubes and bubbled with oxygen-free nitrogen for 5 min. Light from a Philips 125-W high pressure mercury lamp was filtered to prevent irradiation at wavelengths shorter than 330 nm. The tubes were analyzed for benzaldehyde and bibenzyl formation on a 2 m × 0.4 cm column of 5% SE-30 on DMSC treated Chromosorb G using a Perkin-Elmer F 20 gas chromatograph. Quantum yields for acetone formation from irradiation of ketone **1** in degassed 2-propanol–benzene were determined as previously described.[28]

Spectroscopic Data. Absorption spectra were recorded on a Cary 14 spectrophotometer. Emission spectra were recorded at 77°K in a 4:1 methylcyclohexane-isopentane (MP) glass using an Aminco-Bowman spectrophotometer and in methylcyclohexane (MC) and 5:5:2 ether-isopentane-ethanol (EPA) using a Perkin-Elmer MPF-2A spectrophotometer. The results obtained in MP and MC with the two different spectrophotometers were identical. Room temperature emission spectra of acetophenone and deoxybenzoin ($10^{-2}\ M$) were recorded on highly degassed samples in sealed Pyrex ampoules at 22° using the Perkin-Elmer spectrophotometer. Quenching of room temperature emission was investigated by adding increasing amounts of 2,5-dimethyl-2,4-hexadiene.

Flash-Emission Kinetics. Phosphorescence lifetimes were measured by a fully computerized, signal averaging approach. The exciting source was a Xenon Corp. micropulse flashtube (pulse width ~5 μsec) with a Model 457 power supply. Light from the flash tubes was filtered by a Corning 7-54 glass filter to reduce scattered light with wavelengths >370 nm. Degassed samples contained in sealed 4-mm-o.d. Pyrex tubes were cooled to 77°K in a quartz dewar. Emitted light was viewed at 90° to the excitation through a 0.25-m Bausch and Lomb grating monochrometer by an EMI Model 6256 photomultiplier. The photomultiplier output was amplified by a series of three Philbrick-Nexus Model 1011 operational amplifiers interfaced to the 40-kHz analog-to-digital converter of a Raytheon 704 on-line digital computer. The computer is programmed to fire the flashtube, acquire the phosphorescence decay data, and compute the lifetime from a least-squares fix of the data. The results in Table III are the average of three or more lifetimes determined at the 0–0 emission band.

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Registry No.—**1**, 451-40-1; **2**, 2042-85-5; **3**, 13740-70-0; **4**, 1733-63-7; **6**, 98-86-2; **7**, 938-16-9.

References and Notes

(1) (a) Part V: Photochemical α Cleavage of Ketones in Solution. (b) Part IV: H.-G. Heine, *Tetrahedron Lett.*, 4755 (1972). (c) Bayer AG. (d) Northwestern University. (e) Northwestern University Fellow, 1969–1973.

(2) (a) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag New York, New York, N. Y., 1968, Chapters 22 and 23; (b)

H.-G. Heine, H.-J. Rosenkranz, and H. Rudolph, *Angew. Chem., Int. Ed. Engl.*, **11**, 974 (1972).
(3) G. Ciamician and P. Silber, *Ber.*, **34**, 1530 (1901).
(4) G. Kornis and P. de Mayo, *Can. J. Chem.*, **42**, 2822 (1964).
(5) Part IV, ref 1b.
(6) T. Dominh, *Ind. Chim. Belg.*, **36**, 1080 (1971).
(7) J. Kenyon, A. R. A. A. Rassoul, and G. Soliman, *J. Chem. Soc.*, 1774 (1956).
(8) G. L. Closs and D. R. Paulson, *J. Amer. Chem. Soc.*, **92**, 7229 (1970).
(9) H.-G. Heine, *Tetrahedron Lett.*, 3411 (1972).
(10) A. Schönberg, A. K. Fateen, and S. M. A. R. Omran, *J. Amer. Chem. Soc.*, **78**, 1224 (1956).
(11) K. Müller and G. L. Closs, *J. Amer. Chem. Soc.*, **94**, 1002 (1972).
(12) A. A. Baum, *J. Amer. Chem. Soc.*, **94**, 6866 (1972).
(13) J. C. Sheehan and R. M. Wilson, *J. Amer. Chem. Soc.*, **86**, 5277 (1964).
(14) J. R. Collier and J. Hill, *Chem. Commun.*, 640 (1969).
(15) J. C. Sheehan, R. M. Wilson, and A. W. Oxford, *J. Amer. Chem. Soc.*, **93**, 7222 (1971).
(16) H.-G. Heine, *Tetrahedron Lett.*, 1473 (1971).
(17) A. Paterno, G. Chieffi, and G. Perret, *Gazz. Chim. Ital.*, **44** I, 151 (1914).
(18) W. D. Cohen, *Chem. Weekbl.*, **13**, 902 (1916).
(19) F. Bergmann and Y. Hirshberg, *J. Amer. Chem. Soc.*, **65**, 1429 (1943).
(20) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33**, 1271 (1968).
(21) H.-G. Heine, *Justus Liebigs Ann. Chem.*, **732**, 165 (1970).
(22) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852 (1972).
(23) F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, **37**, 2102 (1972).
(24) F. D. Lewis and J. G. Magyar, *J. Amer. Chem. Soc.*, **95**, 5973 (1973).
(25) Bibenzyl quantum yields are corrected for the requirement of two photons per molecule of product.
(26) (a) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2820 (1967); (b) P. J. Wagner, J. M. McGrath, and R. G. Zepp, *ibid.*, **94**, 6883 (1972).
(27) S. G. Cohen and B. Green, *J. Amer. Chem. Soc.*, **91**, 6824 (1969).
(28) F. D. Lewis, *J. Phys. Chem.*, **74**, 3332 (1970).
(29) A. Heller and E. Wasserman, *J. Chem. Phys.*, **42**, 949 (1965).
(30) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
(31) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).
(32) L. Salem, W. G. Dauben, and N. J. Turro, *J. Chim. Phys.*, **70**, 694 (1973).
(33) P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).
(34) R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).
(35) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).
(36) P. J. Wagner and J. M. McGrath, *J. Amer. Chem. Soc.*, **94**, 3849 (1972).
(37) R. M. Kellog in "Methods in Free Radical Chemistry," Vol. 2, E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 1.
(38) K. E. J. Barrett and W. A. Waters, *Discuss. Faraday Soc.*, **No. 14**, 221 (1953).
(39) R. G. Zepp and P. J. Wagner, *J. Chem. Soc., Chem. Commun.*, 167 (1972).
(40) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969).
(41) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Shore, *Accounts Chem. Res.*, **5**, 92 (1972).
(42) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).
(43) M. E. Scanlan and S. MacKenzie, *J. Org. Chem.*, **37**, 1579 (1972).
(44) P. J. Wagner, M. J. May, A. Haug, and D. R. Graber, *J. Amer. Chem. Soc.*, **92**, 5269 (1970), and references therein.
(45) (a) J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, **21**, 499 (1970); (b) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969); (c) O. L. Chapman and D. S. Weiss, *Org. Photochem.*, **3**, 197 (1973); (d) H. Paul and H. Fisher, *Helv. Chim. Acta*, **56**, 1575 (1973).
(46) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).
(47) C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1593 (1963).
(48) (a) C. Rüchardt, *Fortschr. Chem. Forsch.*, **6**, 251 (1966); (b) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970); (c) C. Rüchardt, H.-D. Beckhaus, J. Bonnekessel, H. Böck, E. Dempewolf, F. A. Groeger, V. Golzke, G. Hamprecht, K. Herwig, J. Hinz, P. Lorenz, I. Mayer-Ruthardt, J. Müller, A. Oberlinner, and E. Schacht, XXIII International Congress of Pure and Applied Chemistry, Special Lectures, Vol. 4, Butterworths, London, 1971, p 223.
(49) The quantum yield for the formation of benzaldehyde from isobutyrophenone in 3 × 10^{-3} *M* RSH-benzene is 0.006. Thus unlike ketones **1-4** and **7**, its lifetime is primarily determined by the rate of radiationless decay and not the rate of α cleavage.
(50) F. D. Lewis and R. W. Johnson, *J. Amer. Chem. Soc.*, **94**, 8914 (1972).
(51) (a) N. C. Yang and R. L. Dusenbery, *J. Amer. Chem. Soc.*, **90**, 5899 (1968); (b) N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).
(52) Possible explanations for the nonlinearity of such plots include competitive absorption by a strongly absorbing intermediate[27] and a solvent effect on the reactivity of the lowest triplet state.[28]
(53) k_α values for **1-4** given in our preliminary communication[9] were obtained before we made these observations.
(54) Competitive absorption by products cannot account for the decrease in quantum yield as the absorbance at 313 nm does not increase at <5% conversion. Benzaldehyde (E_T = 72 kcal/mol) is the only product with low enough triplet energy which is present in high enough concentration to be responsible for product quenching.
(55) (a) K. R. Huffman, C. E. Kuhn, and A. Zweig, *J. Amer. Chem. Soc.*, **92**, 599 (1970); (b) P. J. Wagner, I. E. Kochevar, and A. E. Kemppainen, *ibid.*, **94**, 7489 (1972).
(56) V. Meyer and L. Oelkers, *Ber.*, **21**, 1295 (1888).
(57) A. Brodhag and C. R. Hauser, *J. Amer. Chem. Soc.*, **77**, 3024 (1955).
(58) C. F. Koelsch, *J. Amer. Chem. Soc.*, **54**, 2049 (1932).
(59) R. Stierlin, *Ber.*, **22**, 376 (1889).
(60) H. Strassmann, *Ber.*, **22**, 1229 (1889).
(61) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).
(62) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1965).

Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. VII. Reaction of 5-Indanol with Methanol[1a]

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The alumina-catalyzed reaction of 5-indanol (1) with excess methanol was investigated as a function of temperature (330-520°) and catalyst acidity. 4,5,6,7-Tetramethylindan (3), 4,5,6,7-tetramethylindene (4), and 2,4,5,6,7-pentamethylindene (5) are the major products formed at 390-520° over a catalyst (B) containing sodium ion. Compound 4 is the main component (37-50 mol % yield, based on converted 1) at 390-420°, whereas 3 is favored (44-54 mol %) at 470-520°. At 470°, methanol serves as a hydrogen donor (for the forward reaction) in the quasi-equilibrium system $4 + 2H \rightleftharpoons 3$. With a sodium-free catalyst (A), 3 is the main product from 1 at 390-420° (61 mol %), whereas 4 is a minor component. With A, the yield of 5 decreases (from 27 to 13 mol %) with increasing temperature in the range of 330-390°. Compound 5 was also synthesized by a noncatalytic method.

It was shown previously[2-4] that phenol and naphthols react with methanol at 400-550° in the presence of alumina catalysts to form polymethylarenes. At milder temperatures the formation of oxygen-containing intermediates, *i.e.*, methylated hydroxyarenes and hydroaromatic ketones, was observed. As an extension of these studies the alumina-catalyzed reaction of 5-indanol (1) with methanol, and its dependence on temperature (330-520°) and