by a Vidar 6210 digital integrator when possible and by Disc or Triangulation.

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(1) Taken in part from the Ph.D. theses of C. N. Shih and A. Yeshurun, Indiana University, January 1972 and January 1973, respectively. Supported in part by the National Science Foundation Grant No. GP 27621 and the Alfred P. Sloan Foundation.
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Photochemical α Cleavage of Benzoin Derivatives. Polar Transition States for Free-Radical Formation[1]

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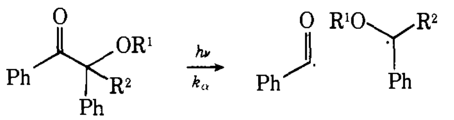
Abstract: The photochemical α cleavage reactions of benzoin, benzoin ethers, benzoin acetate, and several related phenyl ketones have been investigated. α cleavage is the only primary process observed for benzoin and the benzoin alkyl ethers in benzene solution. β cleavage is a minor competing reaction for benzoin phenyl ether. Substituents at the α carbon have little effect on the efficiency (quantum yield) of cleavage; however, they have a pronounced effect on the rate constant for cleavage. Benzoin alkyl ethers are about 10^5 times more reactive toward α cleavage than deoxybenzoin. Substituents capable of stabilizing an adjacent positive charge are far more effective in accelerating α cleavage than are substituents capable of stabilizing free radical centers. It is concluded that the transition state for α cleavage has considerable ionic character and does not resemble the free radical products.

Benzoin,[3-5] benzoin ethers,[5-9] and benzoin esters[10] undergo photochemical α cleavage to form a benzoyl-substituted benzyl radical pair (eq 1). The photochemical α cleavage of benzoin acetate is a relatively slow triplet-state reaction[10] as is the α cleavage of deoxybenzoin ($k_\alpha = 1.6 \times 10^6$ sec^{-1}).[11] In contrast, the α cleavage of benzoin ethers cannot be quenched by standard triplet quenchers[7-9] and must be either an exceptionally rapid triplet process ($k_\alpha > 10^{10}$ sec^{-1}) or a singlet process which competes efficiently with intersystem crossing.[12] γ-Hydrogen abstraction (eq 2), which is the predominant photochemical reaction for α-alkoxyacetophenones ($k_\gamma > 10^9$ sec^{-1}),[13] does not compete with the α-cleavage reaction of benzoin ethers.[7,9] Benzoin and benzoin ethers are widely used as initiators for photopolymerization.[14] Therefore elucidation of structure-reactivity relationships for the α cleavage of benzoin and its derivatives has practical as well as mechanistic consequences.



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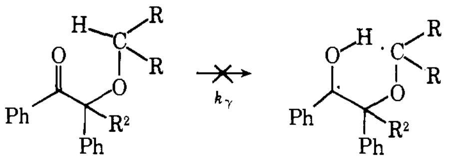

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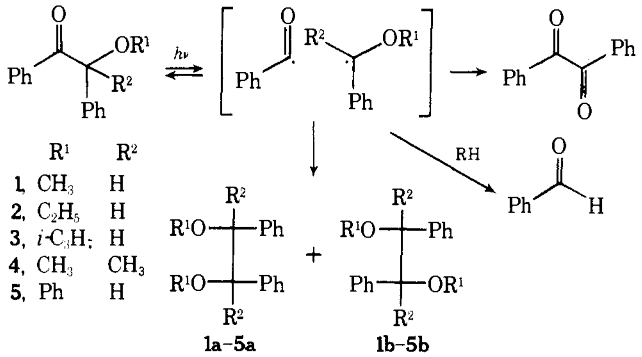
Results and Discussion

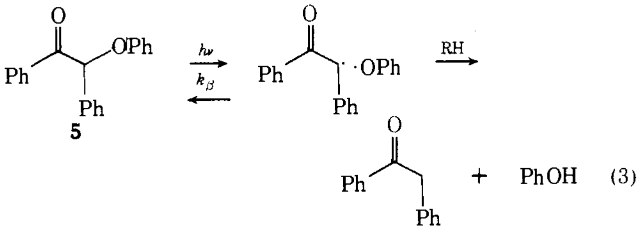
Benzoin Ethers. Irradiation of the benzoin ethers **1–4** in benzene solution results in the formation of benzaldehyde, benzil, and an equimolar mixture of diastereomeric pinacol ethers. Isolated yields of the pinacol ethers are 60–70%. All of the products can be accounted for by photochemical α cleavage followed by free-radical reactions of the benzoyl-alkoxybenzyl radical pair (Scheme I). There is no evidence for free-radical cage[1b,15] processes other than cage recombination. Addition of low concentrations (0.01 *M*) of dodecanethiol (RSH), an efficient scavenger of benzoyl radicals,[11] results in an increased yield of benzaldehyde and complete suppression of benzil formation. Dienes and styrene (1 *M*) reduce the yields of benzaldehyde and benzil but do not affect pinacol ether formation. Thus 1 *M* diene does not appreciably quench the reactive excited state but does scavenge benzoyl radicals. Attempts to quench the formation of pinacol ethers or benzaldehyde with naphthalene (0.1 *M*) were also unsuccessful. Naphthalene is known to quench the reactive[3] (n,π*) excited state of other alkyl phenyl ketones which undergo α cleavage.[1b,11,15] The absence of quenching indicates that α cleavage of benzoin ethers **1–4** is either an exceedingly rapid triplet process or occurs prior to intersystem crossing (vide infra).

Scheme I



Quantum yields for pinacol ether formation in benzene and benzaldehyde formation in 0.01 *M* RSH-benzene are given in Table I for benzoin ethers **1** and **3**. For benzoin ether **3**, the quantum yields determined using 313 and 365 nm irradiation of comparable intensity are the same, within the experimental error.[16] The benzaldehyde quantum yields are similar to those for other alkyl phenyl ketones which undergo α cleavage with unit efficiency.[11,15] The quantum yields for pinacol ether formation are lower than those for benzaldehyde formation, even after correction for the requirement of two alkoxybenzyl radicals per pinacol ether molecule. Noncage recombination of benzoyl and alkoxybenzyl radicals[13] accounts for part of this difference. Alkoxybenzyl radicals must also undergo termination reactions other than combination, in view of the 60–70% maximum isolated yields of pinacol ethers.

Benzoin phenyl ether (**5**) forms small amounts of phenol and deoxybenzoin in addition to benzaldehyde, benzil, and pinacol ethers **5a** and **5b**. Phenol and deoxybenzoin are formed via photochemical β cleavage[17] followed by hydrogen abstraction (eq 3). The quantum yields for benzaldehyde and phenol formation in 0.01 *M* RSH-benzene are 0.39 and 0.12, respectively.[19] The benzaldehyde quantum yield is nearly as large as those for the benzoin alkyl ethers **1** and **3** (Table I). Thus α cleavage is the major primary process for benzoin phenyl ether. Both benzaldehyde (0.01 *M* RSH-benzene) and pinacol ether (benzene) formation can be quenched by added naphthalene. The slopes of linear Stern–Volmer plots ($\Phi^\circ/\Phi = 1 + k_q\tau[\mathrm{Q}]$) are given in Table I. Assumption of diffusion-controlled quenching by naphthalene gives a value of $1/\tau = 5 \pm 1 \times 10^9$ sec^{-1}. Since the triplet lifetime is determined by the rate constants for both α cleavage and β cleavage ($1/\tau = k_\alpha + k_\beta$), the value of $1/\tau$ in Table I provides an upper limit for the rate constant for α cleavage.



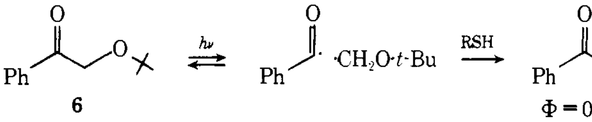
(3)

Table I. Quantum Yield and Kinetic Data for α Cleavage of PhCOCRHPh

	R	Φ_{BA}[a]	Φ	$k_q\tau$, M^{-1}[f]	$1/\tau$, sec^{-1}[i]
1	OCH_3	0.44	0.24[d]	<0.5[g]	$>10^{10}$
3	$OCH(CH_3)_2$	0.44	0.13[d]	<0.5[g]	$>10^{10}$
		0.47[b]	0.13[b,d]		
5	OPh	0.39	0.12[e]	0.88	6×10^9
				1.3[h]	4×10^9
7	$OCOCH_3$	0.33		95	5.3×10^7
8	OH	0.41[c]		4.0	1.2×10^9
		0.87			
9	OD	0.37[c]		4.1	1.2×10^9
13	CN	0.07		230	2.2×10^7
14	$N(CH_3)_2$	0.04		<0.5[g]	

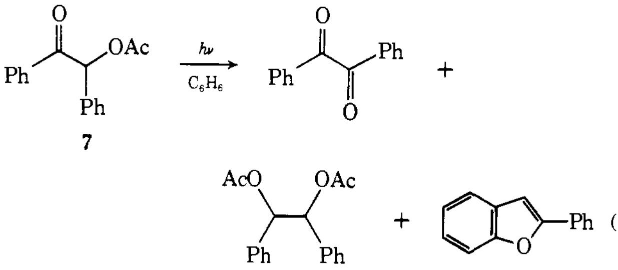
[a] Quantum yield for benzaldehyde formation in 0.01 *M* RSH–benzene with 313 nm irradiation, except as noted. [b] 365 nm irradiation. [c] Quantum yield in benzene solution. [d] Quantum yield for pinacol ether formation. [e] Quantum yield for phenol formation. [f] Slope of linear Stern–Volmer plot for quenching of benzaldehyde formation in 0.01 *M* RSH–benzene solution by naphthalene (365 nm irradiation), except as noted. [g] No quenching observed. [h] Quenching of pinacol ether formation in benzene solution. [i] Calculated assuming $k_q = 5 \times 10^9 M^{-1}$ sec^{-1}.

In order to separate the effects of α-alkoxy and α-phenyl substituents on the rate constant for α cleavage, the photochemistry of α-*tert*-butoxyacetophenone (**6**) was reinvestigated. Ketone **6** cannot undergo type II photoelimination because of the absence of a γ hydrogen and was previously reported to be photostable in benzene solution.[13] The quantum yield for benzaldehyde formation in 0.01 *M* RSH-benzene is 0.39, indicating that α cleavage is the major excited-state reaction (eq 4). Quenching of benzaldehyde formation by naphthalene gave a value of $1/\tau = 6.7 \times 10^6$ sec^{-1}, in good agreement with the value previously obtained by quenching the photoreduction of ketone **6**.[13] Irradiation of α-phenoxyacetophenone in 0.01 *M* RSH-benzene did not lead to detectable α-cleavage product formation. Inefficient β cleavage is the only process observed for α-phenoxyacetophenone.[18c]



(4)

Benzoin Acetate. The preparative photochemistry of benzoin esters has been extensively investigated by Sheehan and coworkers.[10] Benzoin acetate (**7**) is reported to yield the α-cleavage products benzil and pinacol acetate along with 10–20% of a cyclization product 2-phenylbenzofuran (eq 5). Both the cyclization and cleavage processes are completely quenched by 1 *M* diene. Irradiation of benzoin acetate in 0.01 *M* RSH-benzene results in the formation of benzaldehyde ($\Phi = 0.33$) as the major volatile product. The benzaldehyde quantum yield is ~20% lower than the values for the benzoin ethers (Table I), in accord with the cleavage-cyclization ratio observed in the preparative photolysis.[10] The formation of benzaldehyde from benzoin acetate can also be quenched by naphthalene. From the slope of the Stern–Volmer plot, a value of $1/\tau = 5.3 \times 10^7$ sec^{-1} is ob-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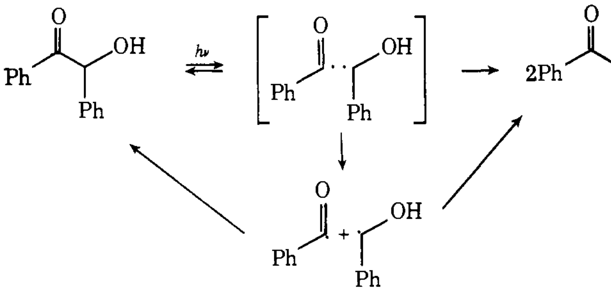
(5)

tained. The actual rate constant for α cleavage is somewhat smaller than this value because of the competing cyclization reaction.

Benzoin. Irradiation of benzoin (**8**) in benzene solution leads to the formation of benzaldehyde as the major product. The only other product isolated upon chromatography of the photolysis mixture is benzoin benzoate (15%). Irradiation in 0.01 M RSH-benzene results in an increased yield of benzaldehyde and total suppression of benzoin benzoate formation. The quantum yield for benzaldehyde formation from benzoin in benzene solution ($\Phi_{BA} = 0.41$) in the absence of thiol scavenger is substantially higher than for deoxybenzoin[1b,11] and the benzoin ethers ($\Phi_{BA} \leq 0.05$). Kornis and deMayo[3] attributed the efficient formation of benzaldehyde from benzoin to hydrogen transfer of the hydroxyl proton of the hydroxybenzyl radical to the benzoyl radical (eq 6). Benzaldehyde could also be formed via an intramolecular O-H abstraction, such as that reported by Pitts and coworkers[20] for vapor-phase photolysis of acetoin (eq 7). Several lines of evidence indicate that at least part of the benzaldehyde is formed via an α-cleavage mechanism (eq 6). Polarized NMR spectra (CIDNP) have been observed for benzaldehyde formation from benzil.[4] Both the benzoyl and hydroxybenzyl radical have been trapped by N-oxides and nitroso compounds.[5] The increase in benzaldehyde quantum yield with added thiol (Table I) also indicates that benzoyl free radicals are formed. None of these observations rules out benzaldehyde formation by both α-cleavage and hydrogen-transfer mechanisms. If hydrogen transfer is involved in the rate-determining step, a positive kinetic isotope effect should be observed. The triplet lifetime of benzoin-O-d (**9**) is identical with that for benzoin (Table I). Thus it seems unlikely that concerted fragmentation competes with α cleavage. The smaller quantum yield for benzaldehyde formation from benzoin-O-d vs. benzoin probably is due to an isotope effect on the rate of cage disproportionation vs. recombination.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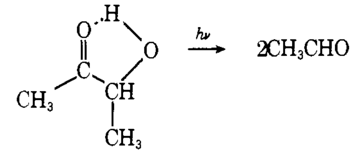
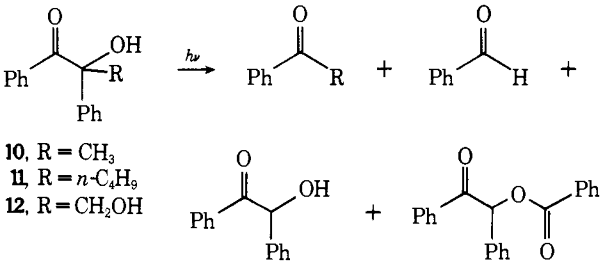
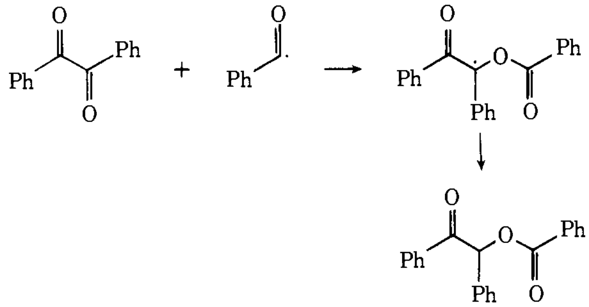

(7)

Irradiation of α-methylbenzoin (**10**) in benzene solution results in a quantitative yield of acetophenone along with lesser amounts of benzaldehyde, benzoin, and benzoin benzoate (eq 8). α-n-Butylbenzoin (**11**) and α-hydroxymethylbenzoin (**12**) form products analogous to those observed for α-methylbenzoin.[21] The valerophenone formed upon irradiation of **11** undergoes type II photoelimination to give acetophenone[22] upon prolonged irradiation. None of the benzoins investigated formed detectable quantities of pinacol product. Apparently the hydroxybenzyl radicals terminate by hydrogen transfer rather than combination.[5] The formation of alkyl phenones via free-radical intermediate has been confirmed by CIDNP studies.[23] The formation of benzoin in the preparative irradiation of **10–12** results from a secondary photoreaction of benzaldehyde.[4,24] Benzoin benzoate could be formed by attack of a benzoyl radical either on benzil (eq 9) or benzaldehyde (eq 10). Benzil is formed by combination of two benzoyl radicals[11,25] and is known to yield benzoin benzoate as the major photolysis product in cumene solution.[25] Formation of benzoin benzoate via eq 10 appears less likely since the intermediate benzoyloxybenzyl radical is reported to yield hydrobenzoin dibenzoate.[26]


10, R = CH_3
11, R = n-C_4H_9
12, R = CH_2OH

(8)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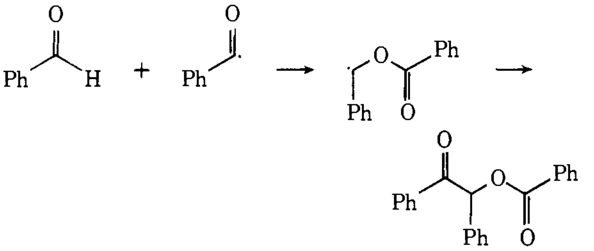

(10)

The formation of benzaldehyde from benzoins **8–12** can be quenched by naphthalene. The value of $1/\tau = 1.2 \times 10^9$ sec^{-1} for benzoin is somewhat smaller than that for benzoin phenyl ether (Table I). Introduction of α-alkyl substituents causes a decrease in the triplet lifetime, as is the case for the deoxybenzoins.[11] The α-substituted benzoins **10–12** have values of $1/\tau \sim 10^{10}$ sec^{-1}.

Other Deoxybenzoin Derivatives. α-Cyanodeoxybenzoin (**13**) yields benzaldehyde, benzil, and benzylcyanide upon irradiation in benzene solution. The quantum yield for benzaldehyde formation in 0.01 M RSH-benzene is 0.07, significantly lower than that for the benzoin derivatives in Table I. Assuming 50% cage recombination[15] of benzoyl and cyanobenzyl radicals, the quantum yield for α cleavage is ~0.15. No evidence was obtained for other photochemical processes; however, photoenolization[27] followed by rapid thermal ketonization[28] would have gone undetected. Quenching of benzaldehyde formation by naphthalene gives a value of $1/\tau = 2.2 \times 10^7$ sec^{-1}. An approximate value for the rate constant of α cleavage can be calculated from the triplet lifetime and α-cleavage quantum yield ($k_\alpha = \Phi_\alpha\tau^{-1}$

Table II. Relative Reactivities for Homolytic Reactions

	$\mathrm{Ph\overset{\overset{O}{\|}}{C}{-}\overset{\overset{R}{|}}{C}HPh}$	$\mathrm{RCH_2\overset{\overset{O}{\|}}{C}OO\text{-}\mathit{t}\text{-}Bu}$[a]	$\mathrm{R\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}N{=}N\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}R}$[b]	$\mathrm{PhCOCH_2CH_2CH_2R}$[c]
$\mathrm{CH_3}$	1[d]	1	1	1
$\mathrm{OCOCH_3}$	2.5	3.4[e]	0.36	0.1
OH	57			3.1
OPh	2.4×10^2	2.4×10^3	50	1.8
$\mathrm{OCH_3}$	$>10^3$	5.0×10^4	10	5.0
CN	0.14	3.5×10^{-4}	3.0×10^5	0.031
Ph	4.8[d]	1.3×10^2	3.9×10^6	3.1

[a] Data from ref 32 for thermolysis at 60° except as noted. [b] Data from ref 33. [c] Data from ref 36. [d] Data from ref 11. [e] Value at 91°.

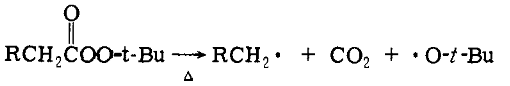
$= 3 \times 10^6$ sec^{-1}).

α-Amino ketones undergo very rapid type II photoelimination via a singlet charge-transfer process.[29] The photochemistry of α-dimethylaminodeoxybenzoin (**14**) was investigated in order to determine whether α cleavage could compete with photoelimination. The major product formed upon irradiation of ketone **14** in benzene is the photoelimination product deoxybenzoin; however, small amounts of benzaldehyde, benzil, and benzyldimethylamine were also observed. The quantum yield for benzaldehyde formation in 0.01 *M* RSH is 0.04. Since the formation of benzaldehyde and deoxybenzoin cannot be quenched, there is no basis for estimation of the rate constant for α cleavage.

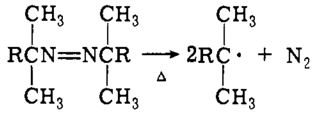
Structure–Reactivity Relationships for α Cleavage. α cleavage is the predominant photochemical reaction for benzoin and a number of its derivatives (**1–12**), as it is for deoxybenzoin.[11] Thus α hydroxy, acetoxy, and alkoxy substituents do not alter the primary photoprocess. Neither do these substituents significantly alter the maximum quantum yields for benzaldehyde formation in 0.01 *M* RSH–benzene solution (Table I). The quantum yields for the benzoin ethers **1** and **3** are identical with those for deoxybenzoin and its α-methyl derivatives.[11] The quantum yield for benzoin is approximately twice as large, in line with the possibility of forming two molecules of benzaldehyde from one excited state. The quantum yields for benzoin phenyl ether (**5**) and benzoin acetate (**6**) are somewhat smaller because of the competition of β cleavage (eq 3) and cyclization (eq 5), respectively. Since α cleavage is the major photochemical process for benzoin and its derivatives, the excited-state lifetime is determined by the rate of α cleavage ($1/\tau \sim k_\alpha$).[30]

While α-oxygen substituents do not affect the quantum yields or nature of the primary photoprocess, they have a marked effect on α-cleavage rate constants. Benzoin phenyl ether is $>10^3$ times more reactive than deoxybenzoin ($k_\alpha = 1.6 \times 10^6$ sec^{-1}), and the benzoin alkyl ethers, which cannot be quenched, are even more reactive. Triplet quenching and CIDNP[4,23] studies establish that α cleavage occurs from a triplet state for benzoin and benzoin acetate. There is no direct evidence concerning the reactive excited state of the benzoin ethers. In view of the very rapid intersystem-crossing rate constants of aryl ketones,[12] singlet cleavage would require a value of $k_\alpha > 10^{11}$ sec^{-1}. Dialkyl ketones are known to undergo α cleavage from both singlet and triplet n, π* excited states; however, the triplet state is usually far more reactive.[31] Thus it seems unlikely that singlet cleavage is rapid enough to compete with intersystem crossing in the benzoin ethers. The effect of a paramagnetic quencher on the product yields from 2,2-dimethoxydeoxybenzoin has recently been interpreted as evidence for a triplet cleavage.[9a] In view of the failure to observe triplet quenching, rate constants for triplet cleavage must be $\geq 10^{10}$ sec^{-1}.

The α-oxygen substituents do not alter the n,π* triplet energies or triplet lifetimes at 77 K (see Experimental Section). Thus their effect on α-cleavage reactivity must reflect their ability to stabilize the transition state for α cleavage. Information about the transition state for α cleavage can be obtained by comparing the effects of α substituents on photochemical cleavage with those for ground-state homolytic reactions (Table II). The transition state for perester decomposition (eq 11)[32] is thought to be polarized, whereas the transition state for azoalkane decomposition (eq 12) is void of polarization.[32c,33] The effects of substituents on photochemical α cleavage and perester thermolysis are similar. The acetoxy group is weakly activating, in contrast to its deactivating effect on azoalkane thermolysis. Alkoxy and phenoxy substituents also have a much larger rate-enhancing effect for α cleavage and perester thermolysis than for azoalkane decomposition. Alkoxy substituents are known to stabilize adjacent carbonium ion centers. For example, chloromethyl ethyl ether undergoes solvolysis in aqueous dioxane 10^9 times more rapidly than *n*-butyl chloride.[34] Alkoxy groups have a much smaller effect on free-radical stabilities.[33a] The effect of an α-cyano group on α cleavage and azoalkane thermolysis also is in accord with ionic and free-radical transition states, respectively, for these reactions.[35] The effect of an α-phenyl substituent on α cleavage may be underestimated by comparing α-phenyl and α-methyldeoxybenzoin.[11] However, a comparison of the rate constants for α cleavage of α-*tert*-butoxyacetophenone (**6**) and deoxybenzoin[11] reveals that an α phenyl is less effective than an α alkoxyl in stabilizing the transition state for α cleavage. Once again, this result is the same as that for perester thermolysis. The analogous effects of substituents on photochemical α cleavage and perester thermolysis can be used to provide an estimate of the rate constant for benzoin ether triplet α cleavage. The linear free-energy relationship for the two reactions is shown in Figure 1. Extrapolation of the available data using $k_\alpha = 2.1 \times 10^7$ sec^{-1} for α-methyldeoxybenzoin[11] provides a value of $k_\alpha \sim 10^{10}$ sec^{-1} for benzoin methyl ether.



$$\mathrm{RCH_2\overset{\overset{O}{\|}}{C}OO\text{-}t\text{-}Bu \xrightarrow[\Delta]{} RCH_2\cdot + CO_2 + \cdot O\text{-}\mathit{t}\text{-}Bu} \qquad (11)$$



$$\mathrm{R\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}N{=}N\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}R \xrightarrow[\Delta]{} 2R\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot + N_2} \qquad (12)$$

The effects of substituents on photochemical γ-hydrogen abstraction of γ-substituted butyrophenones (eq 13) have been investigated by Wagner and Kemppainen[36] (Table II). Their results are similar to those previously observed by

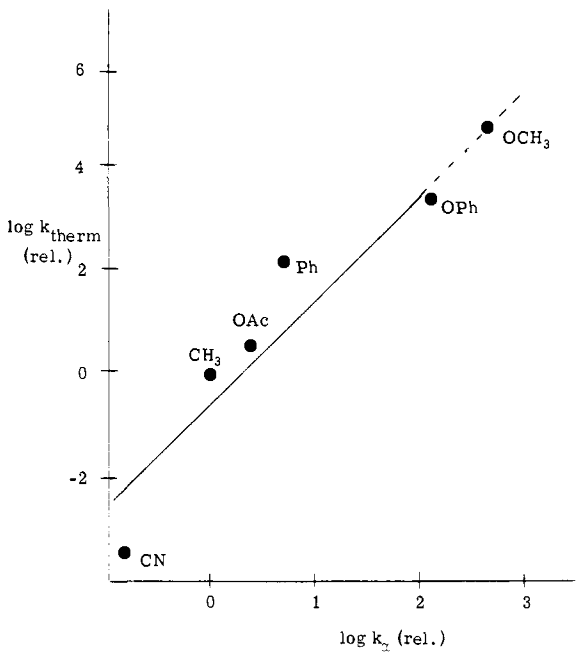
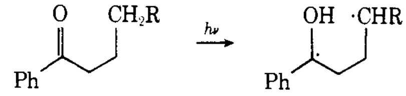


Figure 1. Linear free-energy relationship for photochemical α cleavage and perester thermolysis (Table II).

Walling and coworkers[37] for intermolecular hydrogen abstraction by *tert*-butoxy radical (eq 14). The effects of α-oxygen substituents upon photochemical α cleavage and γ-hydrogen abstraction are similar ($OCH_3 > OH \sim OPh \gg OAc$). This trend reflects the availability of the nonbonded electrons on oxygen.[36,37] The two reactions differ in that acetoxy is rate enhancing for α cleavage and rate retarding for γ-hydrogen abstraction. In addition, the magnitude of the substituent effects for α cleavage or perester thermolysis is much greater than for hydrogen abstraction. We conclude that there is considerably more ionic character in the transition state for photochemical α cleavage than for γ-hydrogen abstraction.



(13)

$$t\text{-BuO}\cdot + \text{H}\overset{|}{\underset{|}{\text{C}}}\text{R} \longrightarrow t\text{-BuOH} + \cdot\overset{|}{\underset{|}{\text{C}}}\text{R} \qquad (14)$$

Benzoin and its derivatives are commercially important as initiators for photopolymerizations.[14] Free-radical polymerization is initiated by the radicals formed upon α cleavage. The effects of α substituents upon reactivity of benzoin derivatives in the light-induced curing of unsaturated polyester resins[14] parallel α-cleavage reactivities ($OCH_3 > OPh > OH \gg OAc$). In degassed benzene solution, all of the benzoin derivatives form free radicals with comparable efficiency and might be expected to initiate polymerization equally well. However, under the conditions used for photopolymerization quenching by the high concentrations of vinyl monomer becomes important. Thus the benzoin derivatives with the shortest triplet lifetimes are the most efficient initiators.

Conclusions

Prior to our investigation of the α-cleavage reactions of aryl alkyl ketones,[1b,11] it was assumed that photochemical reactivity was determined by the stability of the radical-pair produced.[38] The effects of α-methyl and α-phenyl substituents on the rate constants for α cleavage of alkyl phenyl ketones[11] and cycloalkanones[38b] demonstrate that rate constants do not depend upon the stability of the radical pair. *tert*-Alkyl ketones undergo α cleavage at least an order of magnitude faster than the corresponding benzyl ketones. Evidence for a transition state with a moderate amount of ionic character was provided by the effect of nonconjugated aromatic substituents on the rate constants for deoxybenzoin α cleavage.[1b] The rate constants give an excellent fit to the Hammett equation with the use of σ^+, indicative of the development of partial positive charge at the α carbon (eq 15). Further evidence for the importance of polar effects on photochemical α cleavage is provided by the present study. Substituents capable of stabilizing an adjacent positive charge are the most effective in accelerating α cleavage. Finally, the effects of substituents upon photochemical α cleavage are readily understood using ground-state concepts. Photochemical α cleavage and perester thermolysis (eq 11)[32] display remarkably similar structure-reactivity relationships.[1b,11] Since α cleavage of a $^3n,\pi^*$ state to form a triplet diradical intermediate is an adiabatic process,[39] a transition-state model for the reaction seems justified.

$$\text{PhCOCH}_2\text{Ar} \xrightarrow{h\nu} [\overset{\delta-}{\text{PhCO}}\cdots\cdot\overset{\delta+}{\text{CH}_2\text{Ar}}] \longrightarrow \text{Ph}\dot{\text{C}}\text{O} + \cdot\text{CH}_2\text{Ar} \qquad (15)$$

Experimental Section

Ketones. Benzoin alkyl ethers **1-3** were prepared by the method of Fischer[40] and purified by crystallization from hexane-ether: **1**, mp 49-51° (lit.[40] mp 49-50°); **2**, mp 62-63° (lit.[40] mp 62°); **3**, mp 78-79° (lit.[41] mp 72-75°). α-Methylbenzoin methyl ether (**4**), α-methylbenzoin (**10**), and α-*n*-butylbenzoin (**11**) were prepared and purified as previously described.[42] Benzoin phenyl ether (**5**) was synthesized from desyl chloride and phenol[43] and recrystallized from ethanol, mp 87° (lit.[43] mp 85°). α-*tert*-Butoxyacetophenone (**6**) was synthesized from α-diazoacetophenone and *tert*-butyl alcohol[44] and purified by chromatography on silica gel and distillation, bp 80-85° (2 mm). Benzoin acetate was prepared by the method of Corson and Saliani,[45a] mp 82° (lit.[45a] mp 81.5-82.5°). α-Hydroxymethylbenzoin (**12**) was synthesized by aldol condensation of benzoin (**8**) with formaldehyde and recrystallized from carbon tetrachloride, mp 84-85° (lit.[45b] mp 85-86°). α-Cyanodeoxybenzoin (**13**) was synthesized by the method of Chase and Walker[46] and recrystallized from ethanol, mp 98-99° (lit.[46] mp 94-95°). α-Dimethylaminodeoxybenzoin (**14**) was prepared from desyl chloride and dimethylamine and isolated as the hydrochloride, mp 230° (lit.[47] mp 232-234°). The free amine **14** was liberated with aqueous sodium hydroxide and extracted into benzene prior to spectroscopic and photochemical studies. Absorption and emission spectral data for ketones **1-14** are given in Table III.[48] No room temperature emission was observed for the benzoin alkyl ethers.[8]

Photolysis of Benzoin Methyl Ether (1). A solution of 3.4 g of ketone in 300 ml of benzene was irradiated for 6 hr under nitrogen in a water-cooled Pyrex apparatus with a Philips 125-W high-pressure mercury lamp. Solvent and benzaldehyde were removed by distillation, and the residue was separated by chromatography on silica gel (benzene) to yield 0.15 g of benzil (10%) and 1.3 g of a 1:1 mixture of pinacol ethers **1a** and **1b** (72%). Rechromatography of the pinacol ethers gave the meso pinacol ether **1a**, mp 140-141° (lit.[49] mp 139-140°), and the *d,l* pinacol ether **1b**, mp 92-93° (lit.[49] 90-91°), both of which were identical with authentic samples.[49]

Photolysis of Benzoin Ethyl Ether (2). Irradiation of 3.6 g of ketone in 300 ml of benzene for 6 hr followed by work-up similar to that described for **1** afforded 0.2 g of benzil (13%), 0.65 g of **2a** (32%), mp 62-63°, and 0.6 g of **2b** (30%), mp 69-70°. Meso pinacol ether **2a** was identical with an authentic sample prepared by alkylation of *meso*-hydrobenzoin.[50] NMR ($CDCl_3$) for **2a**: δ 0.94 (t, 6 H, J = 7 Hz), 2.83-3.65 (m, 4 H), 4.30 (s, 2 H), 7.09-7.58 (m, 10 H). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20; O, 11.84. Found: C, 79.80; H, 8.30; O, 12.20. *d,l* pinacol ether **2b** was identical with an authentic sample prepared by alkylation of *d,l*-hydro-

Table III. Spectral Data for Ketones **1–14**

Ketone	λ_{max}, nm[a]	ϵ	E_T, kcal/mol[b]	τ, msec[c]
1	345	(220)	71.5	
2	345	(230)	71.5	
3	345	(235)	71.5	
4	344	(185)	71.5	
5	342	(275)	72.5	3.0
6	340 (sh)			
7	329	(242)		
8	340 (sh)	(120)	73.4	9.1
9	345 (sh)	(167)		
10	344	(167)	72.4	2[d]
11	340 (sh)	(110)	72.2	1[d]
12	340	(150)	71.1	2.8
14	336	(131)		

[a] Wavelength of n,π^* absorption maximum in cyclohexane at room temperature. [b] Estimated from the wavelength of the highest energy-emission maximum at 77 K in ether–ethanol. [c] Lifetime of 77 K emission in methylcyclohexane for **5** and in ether–isopentane for **8–11**. [d] Approximate values from low-intensity emission.

benzoin.[51] NMR ($CDCl_3$) for **2b:** δ 1.13 (t, 6 H, J = 7 Hz), 3.43 (q, 4 H, J = 7 Hz), 4.42 (s, 2 H), 6.92–7.33 (m, 10 H). Anal. Found for $C_{18}H_{22}O_2$: C, 80.05; H, 8.09; O, 11.90.

Photolysis of Benzoin Isopropyl Ether (3). Irradiation of 3.81 g of **3** in 300 ml of benzene for 5 hr gave after work-up 0.1 g of benzil (7%), 0.8 g of meso pinacol ether **3a** (36%), mp 82–83°, and 0.7 g of *d,l* pinacol ether **3b** (32%), mp 37–38°. Pinacol ether **3a** was characterized by its NMR spectrum and elemental analysis. NMR ($CDCl_3$) for **3a:** δ 0.73 (d, 6 H, J = 6 Hz), 0.90 (d, 6 H, J = 6 Hz), 3.30 (sept, 2 H, J = 6 Hz), 4.25 (s, 2 H), 7.08–7.60 (m, J = 10 Hz). Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78; O, 10.72. Found: C, 80.50; H, 8.97; O, 10.75. *d,l* pinacol ether **3b**: NMR ($CDCl_3$), δ 1.02 (d, 6 H, J = 6 Hz), 1.08 (d, 6 H, J = 6 Hz), 3.55 (sept, 2 H, J = 6 Hz), 4.43 (s, 2 H), 7.10 (s, 10 H). Anal. Found for $C_{20}H_{26}O_2$: C, 80.55; H, 8.78; O, 10.85.

Photolysis of α-Methylbenzoin Methyl Ether (4). Irradiation of 3.6 of **4** in 300 ml of benzene for 6.5 hr followed by repeated chromatography on silica gel (hexane) afforded 2.5 g of a 1:1 mixture of **4a** and **4b** (62%). Fractional crystallization from acetone yielded pure **4a**, mp 170–171° (lit.[52] 171–173°), identified by comparison with an authentic sample. NMR ($CDCl_3$) for **4a:** δ 1.42 (s, 6 H), 3.01 (s, 6 H), 7.25 (s, 10 H). The isomeric pinacol ether **4b** was obtained after tedious fractional crystallization from ether–hexane, mp 114–116°. NMR ($CDCl_3$) for **4b:** δ 1.65 (s, 6 H), 3.10 (s, 6 H), 6.70–7.40 (m, 10 H). Anal. Found for $C_{18}H_{22}O_2$: C, 80.00; H, 8.28; O, 11.97.

Photolysis of Benzoin Phenyl Ether (5). Irradiation of 3.4 g of **5** in 300 ml of benzene for 6 hr resulted in the formation of benzaldehyde, benzil, phenol, and a 1:1 mixture of pinacol ethers **5a** and **5b.** Chromatography on silica gel (hexane–benzene) afforded 1.4 g of **5a** and **5b** (65%) and 0.11 g of benzil (9%). Fractional crystallization from acetone yielded a pure sample of **5a,** mp 172–173°. NMR ($CDCl_3$) for **5a:** δ 5.41 (s, 2 H). 6.70–7.45 (m, 20 H). Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05; O, 8.73. Found: C, 84.95; H, 5.95; O, 8.53. Pure **5b** could not be obtained by fractional crystallization; however, slow chromatography using a high excess of silica gel afforded a pure sample of **5b,** mp 150–152°. NMR ($CDCl_3$) for **5b:** δ 5.48 (s, 2 H), 7.15 (s, 10 H), 6.70–7.35 (m, 10 H). Anal. Found for $C_{26}H_{22}O_2$: C, 84.99; H, 6.25; O, 8.86.

Photolysis of Benzoin (8). Irradiation of 3.18 g of **8** in 300 ml of benzene for 6 hr resulted in only 28% conversion. VPC showed benzaldehyde and benzoin benzoate were the only volatile products formed. Column chromatography on silica gel afforded 2.1 g of unreacted **8** (66%) and 0.21 g of benzoin benzoate (13% based on benzoyl radical, eq 9).

Photolysis of α-Alkylbenzoins 10–12. Irradiation of 3.4 g of **10** in 300 ml of benzene followed by distillation of solvent, benzaldehyde, and acetophenone and chromatography on silica gel afforded 0.23 g of benzoin benzoate (15%) and 0.15 g of benzoin (9%). No 1-phenylethanol or acetophenone pinacol could be detected by VPC, TLC, or NMR analysis. Analogous results were obtained for **11** and **12.**

General Procedures for purification of materials, quantum yield measurements, and Stern–Volmer kinetics have been previously described.[11]

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Skeletal Rearrangement of the Methylcyclopentane Ion. Field-Ionization Kinetic Measurements

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Abstract: Field-ionization kinetic (FIK) measurements of the rates of loss of CH_3 and CH_4 from the molecular ion of methylcyclopentane show that at 10^{-11} to 10^{-10} sec after field ionization, the loss of CH_3 is predominant, while at 10^{-9} to 10^{-8} sec, loss of CH_4 is preferred. However, at parent-ion lifetimes $>10^{-8}$ sec, elimination of CH_3 again becomes dominant. No such reversal is observed in methylcyclohexane. These results are accounted for on the basis of two competing processes for the formation of $C_5H_9^+$ $(M - CH_3)$. At short times, direct cleavage of the side chain is most important, but at longer lifetimes, opening of the five-membered ring increasingly precedes loss of CH_3. FIK measurements of methylcyclopentane-α-^{13}C reveal that at times $<10^{-9}$ sec, at least 95% of the $C_5H_9^+$ ions formed does not contain the labeled C atom. At longer times, a progressively larger fraction of the $C_5H_9^+$ ions does contain the tagged atom, approaching statistical randomization at $\sim 10^{-5}$ sec. This result confirms the hypothesis above and suggests that the ionized alkene resulting from ring opening can undergo further skeletal isomerization prior to elimination of CH_3. The $C_4H_8^+$ fragment ions formed by loss of C_2H_4 from the labeled molecular ion were found to contain the labeled side chain to an extent >95% at 10^{-10} to 10^{-11} sec, but only 75% at 10^{-5} to 10^{-6} sec. It is suggested that there is a rapid, specific pathway for elimination of C_2H_4 at short times, while at longer times, an ionized alkene intermediate has sufficient time to undergo intramolecular rearrangement prior to elimination of C_2H_4.

The gaseous ion chemistry of cycloalkanes presents many complexities. One of the more interesting of these arises in the mass spectra of alkyl cycloalkanes, which often (but not always) show a significant peak corresponding to the loss of the alkyl side chain from the molecular ion.[2] In 1958, Stevenson[3] showed by means of isotopic labeling experiments that when methylcyclopentane undergoes loss of a methyl radical following electron-impact (EI) ionization, about half of the original methyl carbon atoms are retained by the remaining $C_5H_9^+$ ions. Further detailed studies with both ^{13}C- and D-labeled compounds by Meyerson et al.[4,5] demonstrated that the loss of the alkyl side chain in both methyl- and ethylcyclopentane proceeds by (at least) two competing pathways. One of these pathways apparently corresponds to the expected simple bond cleavage, but a significant fraction of the molecular ions must decompose by means of an intramolecular rearrangement followed by (or in concert with) bond scission.[4,5]

The convincing evidence for the presence of competing modes of unimolecular decomposition strongly suggested to us that a kinetic study of the reactions involved would shed important new light on the details of these processes. The field-ionization kinetic (FIK) method[6,7] which has been employed in the work reported here permits the study of unimolecular decomposition reactions of (radical) ions over a range of molecular-ion lifetimes extending from 10^{-11} to 10^{-5} sec. Molecular ions produced by field ionization have relatively low internal energies[8] as compared with the molecular ions formed by standard electron-impact (EI) techniques. The resulting reduction in the number of available competing decomposition-reaction channels can greatly simplify the interpretation of the results in terms of gas-phase reaction mechanisms. The results of previous FIK studies[9,10] have shown that these data can offer a more detailed and complementary view of essentially the same gas-phase unimolecular decomposition phenomena which are observed following other ionization processes, particularly those which impart a relatively low energy to the molecular ion.

Experimental Section

The experimental results reported here were obtained with a modified double-focusing mass spectrometer of Mattauch–Herzog geometry[11] (Du Pont/CEC 21-110B) equipped with a modified[7] combination FI–EI ion source and an electrical detection system. Commercial uncoated stainless steel razor blades were used as FI emitters. Curves of ion current vs. blade voltage were recorded on an X-Y recorder, by setting the magnetic analyzer for a particular fragment ion and varying blade voltage in increments of 10 V.

Detailed descriptions of the FIK technique employed here[7] and the theory behind it[6,7] have been published, as have the details of the calculations required to convert the curves of ion current vs. blade voltage to curves of reaction rate as a function of time.[7,12] In brief, ions formed at or very near the emitter edge (either by ionization or fragmentation) are fully accelerated when leaving the source and have the correct amount of translational energy to be transmitted by the electric sector analyzer (ESA); they are then momentum analyzed by the magnetic sector and detected in the usual fashion. These ions constitute the "normal FI spectrum". Fragment ions formed by gas-phase unimolecular decompositions occurring at some distance from the emitter are energy deficient and are therefore rejected by the ESA. These ions can, however, be