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

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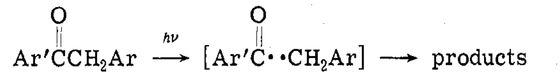
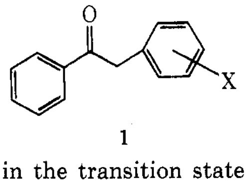
The effects of aromatic substituents which are not conjugated with the carbonyl on the photochemical behavior of deoxybenzoin have been investigated. Photochemical α cleavage is the exclusive primary photoprocess observed in benzene solution. Room temperature phosphorescence is observed for several deoxybenzoins 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 σ^+ ($\rho = -1.1$). 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



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

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



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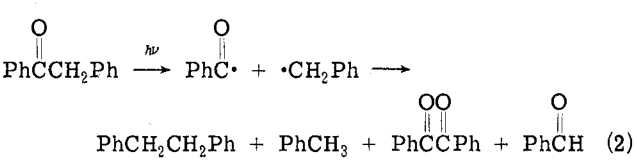
charge formation in the transition state, have often been used in interpreting the influence of substituents on free radical abstraction[11] and decomposition[12–14] reactions which result in the formation of benzyl radicals. For example, substituent effects on phenyl-substituted *tert*-butylperoxyphenylacetate 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.

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). Quan-



$$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2Ph} \xrightarrow{h\nu} \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot + \cdot\mathrm{CH_2Ph} \longrightarrow$$

$$\mathrm{PhCH_2CH_2Ph} + \mathrm{PhCH_3} + \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} + \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} \qquad (2)$$

$$\Phi = \quad 0.056 \qquad 0.002 \qquad 0.006 \qquad 0.025$$

tum 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.

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 (~2×10^{-9} M^{-1} 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

Table I
Quantum Yields for Bibenzyl Formation and Kinetic Data for Biphenyl Quenching

$PhCOCH_2C_6H_4$-X X	Φ[a]	$k_q\tau$, M^{-1} [b]	$1/\tau \times 10^{-6}$,[d] sec^{-1}
H	0.056	1040	1.9
		2100[c]	2.4
p-OCH_3	0.13	294	6.8
p-CH_3	0.10	375	5.3
m-CH_3	0.048	412	4.9
p-F	0.070	842	2.4
p-Cl	0.052	1020	2.0
m-Cl	0.046	2160	0.93

[a] Quantum yields for bibenzyl formation in degassed benzene (~3% conversion). Corrected for requirement of two benzyl radicals per bibenzyl. [b] Least-squares slope of Stern–Volmer plot for qunehing of bibenzyl formation by biphenyl. [c] Naphthalene quenching value from ref 5. [d] Calculated assuming $k_q = 2 \times 10^9$ M^{-1} sec^{-1} for biphenyl quenching and $k_q = 5 \times 10^9$ M^{-1} sec^{-1} for naphthalene quenching.

Table II
Quantum Yields for Benzaldehyde Formation and Kinetic Data for Naphthalene Quenching

$PhCOCH_2$-C_6H_4-X X	Registry No.	Φ[a]	$k_q\tau$, M^{-1} [c]	$1/\tau \times 10^{-6}$, sec^{-1} [d]
H	451-40-1	0.44[b]	3100	1.6
p-OCH_3	24845-40-7	0.23	270	19
p-CH_3	2430-99-1	0.18	1400	3.6
m-CH_3	34403-03-7	0.14	1100	4.5
p-F	347-91-1	0.17	1800	2.8
m-F	347-90-0	0.14	4900	1.0
p-Cl	6332-83-8	0.33	2700	1.9
m-Cl	27798-43-2	0.10[b]	3700	1.4
m-CF_3	30934-66-8	0.10[b]		

[a] Quantum yield for benzaldehyde formation in degassed 0.01 *M* dodecanethiol–benzene solution except as noted. Extrapolated to zero conversion. [b] Quantum yield in 3×10^{-3} *M* dodecanethiol-benzene. [c] Least-squares slope of Stern–Volmer plot for naphthalene quenching of benzaldehyde formation. [d] Calculated assuming $k_q = 5 \times 10^9$ M^{-1} sec^{-1}.

Table III
Absorption and Low-Temperature Emission Spectral Data for Deoxybenzoins

$PhCOCH_2C_6H_4$-X X	λ_{max}, nm[a] (ϵ)	E_T,[b] kcal/mol	τ, msec
H	325 (129)	72.0	1.9
p-OCH_3	325 (256)	71.6	2.2
p-CH_3	325 (162)	71.0	1.9
m-CH_3	324 (156)		
p-F	325 (121)	72.2	2.5
m-F	323 (110)		
p-Cl	324 (128)	72.6	
m-Cl	323 (111)		
m-CF_3	323 (100)		

[a] Long wavelength absorption maximum in benzene solution at room temperature. [b] Estimated from the position of the highest energy emission maximum at 77°K in methylcyclohexane.

Table IV
Room-Temperature Phosphorescence Quantum Yield and Kinetic Data

$PhCOCH_2$-C_6H_4-X X	Φ_p[a]	τ, μsec	τ_R, msec	$k_\alpha \times 10^{-6}$, sec^{-1}
H	0.0034	1.8[b]	0.53	0.56
		2.1[c]		
		0.83[d]		
p-OCH_3	<0.0001			
p-CH_3	0.0004	0.67[b]	1.6	1.5
p-F	0.0026	1.5[b]	0.59	0.67
		0.83[d]		
m-F	0.0028	3.6[b]	1.3	0.28
p-Cl	0.0035	2.6[b]	0.71	0.39
m-CF_3	0.0061	5.3[b]	0.86	0.19
$PhCOCH_3$	0.015	56[e]	3.7	
Ph_2CO	0.015	150[e]	10	

[a] Values in carbon tetrachloride, limits of error ± 0.0005. [b] Calculated from the slopes of linear Stern–Volmer plots for diene quenching in carbon tetrachloride. Limits of reproducibility ~20%. [c] Measured by single photon counting. [d] Diene quenching in benzene solution. [e] Measured by flash emission.

are extrapolated to zero conversion. Quenching of benzaldehyde formation by added naphthalene (365-nm irradiation) gave linear Stern–Volmer plots when maximum conversions were <1%. The estimated error in the kinetic data (±50%) is large due to the relatively long triplet lifetimes and the experimental difficulties associated with measuring quantum yields at very low conversion. The kinetic data in Tables I and II are in reasonable agreement except for the values for *p*-methoxydeoxybenzoin.

Spectroscopic Data. Ultraviolet absorption data for the n,π* absorption band in benzene solution are given in Table III. Neither the position nor the intensity of the n,π* absorption is significantly different in cyclohexane or carbon tetrachloride solution. Aryl substitution affects the intensity, but not the wavelength, of the n,π* absorption, as previously observed for benzyl ketones[17] and aldehydes.[18] The absorption intensities give a moderately good fit to a Hammett equation using σ^+ substituent constants (eq 3).

$$\epsilon = 143 \pm 6 + (-166 \pm 17)\sigma^+ \qquad (3)$$

$$r = 0.937$$

Emission spectra for several deoxybenzoins were recorded at 77°K in methylcyclohexane and EPA (ether–isopentane–ethanol). Structured emission similar to that for acetophenone was observed in both solvents. Triplet energies estimated from the position of the highest energy emission band in methylcyclohexane are given in Table III. Triplet lifetimes were determined by the flash emission method[5] at 77°K. Only short-lived (τ < 5 msec), single-component emission was observed in either methylcyclohexane or EPA.

Room temperature phosphorescence was observed for a number of deoxybenzoins, acetophenone, and benzophenone in highly degassed benzene or carbon tetrachloride solution (Table IV). The room-temperature spectra were broader than the 77°K spectra, but showed the same vibrational structure. The spectra disappeared completely upon exposing the solutions to air. The position of the highest energy emission maximum is 400 ± 2 nm (71.5 kcal/mol) for all the ketones in Table IV. Phosphorescence quantum yields were measured by comparing the integrated emission intensity to that of quinine sulfate.[19] The value obtained for benzophenone in carbon tetrachloride is identical with that reported by Saltiel and coworkers.[20]

Triplet lifetimes (τ) for the deoxybenzoins were determined by quenching of room temperature phosphorescence intensity by naphthalene or 2,5-dimethyl-2,4-hexadiene. Linear Stern–Volmer plots (eq 4) were obtained with both

$$\Phi_p°/\Phi_p = 1 + k_q\tau[Q] \quad (4)$$

quenchers; however, the diene is the quencher of choice due to the absence of competitive absorption and emission. Assumption of diffusion-controlled quenching by diene in carbon tetrachloride (k_q = 6.7 × 10^9 M^{-1} sec^{-1})[21a] and benzene (k_q = 5.0 × 10^9 M^{-1} sec^{-1})[21b] leads to the estimated lifetimes given in Table IV. The lifetime of deoxybenzoin in carbon tetrachloride was also directly measured using time-correlated single photon counting. The value is similar to that obtained by phosphorescence quenching (Table IV). The lifetimes of acetophenone and benzophenone in degassed carbon tetrachloride are sufficiently long to allow measurement by a signal averaged flash emission technique (see Experimental Section). Larger phosphorescence quantum yields and longer lifetimes were observed in carbon tetrachloride than in benzene solution.[20,22] These parameters are highly dependent upon the purity of the solvent and ketone and the extent of degassing. A single batch of purified carbon tetrachloride[22] was used for all the measurements reported in Table IV.

Discussion

Photochemical α cleavage is the only primary photochemical process observed for the deoxybenzoins in Tables I and II. Weak room-temperature phosphorescence is observed for several deoxybenzoins (Table IV) and provides an invaluable probe of excited state behavior (*vide infra*).[5,23] Both α cleavage and phosphorescence occur from the lowest triplet excited state. The slopes of Stern–Volmer plots for naphthalene quenching of benzaldehyde formation (Table II) and the phosphorescence (Table IV) of deoxybenzoin in benzene are the same, within the experimental error. A simplified kinetic scheme which accounts for α cleavage and phosphorescence is given in eq 5–9.

$$\mathrm{PhCOCH_2Ar} \xrightarrow[(2)\,\mathrm{ST}]{(1)\,h\nu} \mathrm{T_1} \quad (5)$$

$$\mathrm{T_1} \xrightarrow{k_p} \mathrm{S_0} + h\nu \quad (6)$$

$$\mathrm{T_1} \xrightarrow{k_d} \mathrm{S_0} \quad (7)$$

$$\mathrm{T_1} \xrightarrow{k_\alpha} \mathrm{PhCO\cdot} + \mathrm{\cdot CH_2Ar} \quad (8)$$

$$\mathrm{T_1} + \mathrm{Q} \xrightarrow{k_q} \mathrm{S_0} + \mathrm{Q^*} \quad (9)$$

Since the triplet state of deoxybenzoin is formed with unit efficiency,[5] the quantum yields for phosphorescence and product formation (benzaldehyde or bibenzyl) in the absence of added quencher are as given in eq 10 and 11. The

$$\Phi_p° = k_p/(k_p + k_d + k_\alpha) = k_p\tau \quad (10)$$

product quantum yields are determined by the efficiency of α cleavage ($k_\alpha\tau$) and the probability that the initially formed radical pair will give products (β). Assuming that added quencher does not alter β,[24] the same Stern–Volmer expression (eq 12) is obtained for quenching of phosphorescence or product formation.

$$\Phi_{BA}° = \left(\frac{k_\alpha}{k_p + k_d + k_\alpha}\right)\beta = (k_\alpha\tau)\beta \quad (11)$$

$$\Phi_p°/\Phi_p = \Phi_{BA}°/\Phi_{BA} = 1 + k_q\tau[Q] \quad (12)$$

The results in Table I show that electron donating benzyl substituents give modest increases in the quantum yield for bibenzyl formation, whereas electron-withdrawing substituents have little or no effect. In view of the low bibenzyl quantum yields, the variation in triplet lifetime with aromatic substituents could be due to changes in the rates of α cleavage, radiative, and/or nonradiative decay. Since the values of $1/\tau$ are not significantly larger than rate constants for nonradiative decay of aryl ketones in benzene solution ($k_d \sim 3 \times 10^5$ sec^{-1}),[10a,25] nonradiative decay may compete with α cleavage to a significant extent. The low quantum yields for bibenzyl formation (Table I) result in part from cage and noncage recombination of benzoyl and benzyl radicals as well as other free radical processes which compete with benzyl radical combination.[5,16] The quantum yields for benzaldehyde formation (Table II) are significantly larger due to the ability of alkane thiols to efficiently scavenge noncage benzoyl radicals.[5] The benzaldehyde quantum yields in Table II represent minimum values for the α cleavage quantum yield. Cage recombination of benzoyl and benzyl radicals can account for approximately one-half of the initially excited molecules.[16] For those deoxybenzoins with long triplet lifetimes, the alkane thiol scavenger decreases the quantum yield by quenching the ^{3}n,π* excited state. Since the rate constant for thiol quenching of deoxybenzoin phosphorescence is 4.4 × 10^7 M^{-1} sec^{-1},[5] the rate of quenching by 0.01 *M* thiol is 0.44 × 10^6 sec^{-1}. Thus quenching by thiol may influence the lifetimes and quantum yields in Table II.

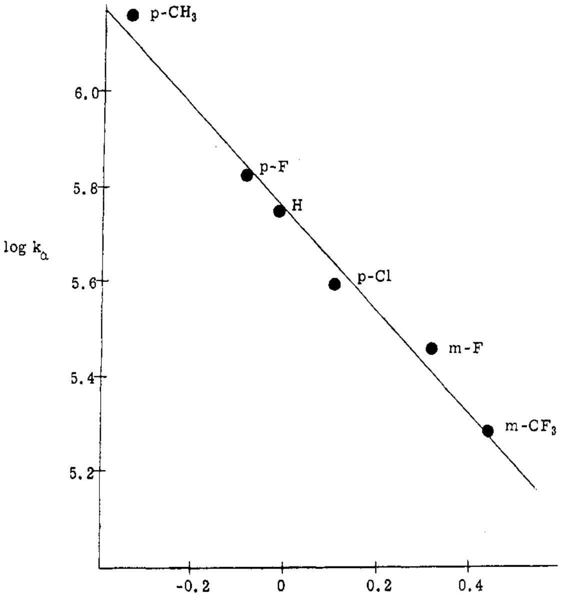


Figure 1. Hammett plot for photochemical α cleavage of deoxybenzoins.

The observation of weak room-temperature phosphorescence from deoxybenzoin and its benzyl-substituted derivatives (Table IV) provides a useful probe of photochemical reactivity. Room-temperature phosphorescence has previously been observed for several aromatic ketones in solution and phosphorescence quenching has been used to study the intermolecular reactions of aromatic ketones with a variety of solvents and other substrates.[19,21,25,26] The deoxybenzoins provide only the second example[27] of room-temperature phosphorescence from an aromatic ketone which undergoes an efficient intramolecular reaction. The triplet lifetimes in Table IV are determined by quenching of room-temperature phosphorescence with added diene. The value for deoxybenzoin has been confirmed by single photon counting. Not only is phosphorescence quenching far simpler than product quenching, but it eliminates the major sources of error in the product quenching studies, including quenching by products and by thiol scavenger. The triplet lifetimes for deoxybenzoin and *p*-fluorodeoxybenzoin determined by phosphorescence quenching are somewhat longer than those determined by product quenching and are considered to be more reliable. Triplet lifetimes are also 2–3 times longer in carbon tetrachloride than in benzene. High apparent rate constants for nonradiative decay of aryl ketone triplets in benzene are due to quenching by benzene.[26c] A solvent effect on the rate constant for α cleavage seems much less likely.

Phosphorescence quantum yields for the deoxybenzoins decrease with decreasing triplet lifetime (Table IV). For p-methoxydeoxybenzoin the emission is too weak to allow accurate measurement with our spectrophotometer. Radiative lifetimes can be determined from the triplet lifetimes and phosphorescence quantum yields ($\tau_R = \tau/\Phi_p$). Values for acetophenone and benzophenone are in good accord with previous reports,[25,26a] The radiative lifetimes of the deoxybenzoins are somewhat shorter than that of acetophenone, perhaps as a result of a weak interaction of the carbonyl n,π* triplet with the α-aryl group. No significance should be attached to the variation in τ_R with substituent, in view of the substantial errors in Φ_p and τ.

The triplet lifetimes of the deoxybenzoins are all substantially shorter than those of acetophenone and benzophenone (Table IV). Photochemical α cleavage is responsible for at least part of the decrease in lifetime. The quantum yields for benzaldehyde formation (Table II) suggest that α cleavage is not the exclusive pathway for nonradiative decay of the deoxybenzoins in dodecanethiol–benzene solution. However, quenching by both thiol[5] and benzene[26c] results in triplet lifetimes 3 to 5 times shorter than those in carbon tetrachloride. Thus we assume that α cleavage is the predominant mode of deoxybenzoin nonradiative decay in carbon tetrachloride solution ($k_\alpha \sim 1/\tau$).

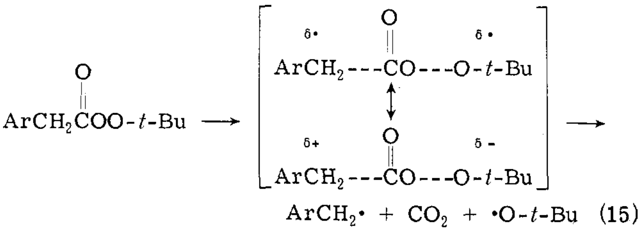
The rate constants for α cleavage in Table IV give a better fit to the Hammett equation[28] with the use of σ^+ (eq 13) than with σ (eq 14). The good fit of the k_α values to the

$$\log k_\alpha = 5.77 - (1.13 \pm 0.08)\sigma^+ \qquad r = 0.989 \quad (13)$$

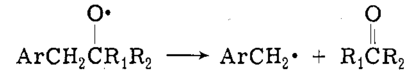
$$\log k_\alpha = 5.88 - (1.35 \pm 0.15)\sigma \qquad r = 0.976 \quad (14)$$

Hammett equation corroborates our assumption that the triplet lifetimes are largely determined by k_α. The Hammett relationships (eq 13 and 14) can be used to estimate values of k_α for p-methoxydeoxybenzoin; $k_\alpha = 4.5 \times 10^6(\sigma^+)$ and $k_\alpha = 9.9 \times 10^5(\sigma)$. The σ^+ value is in better agreement with both the kinetic data in Tables I and II and the low phosphorescence quantum yield (Table IV). It should be noted that neither the product quantum yields nor the triplet lifetimes in Tables I and II give satisfactory linear free energy relationships with any substituent parameters. This is a result of the fact that substituents affect both excited state reactivity and subsequent free radical reactions. There have been several previous attempts to correlate quantum yields or relative yields for photochemical abstraction[29] and cleavage[28,30] reactions with Hammett substituent constants. Since there is no necessary relationship between quantum yield and photochemical reactivity,[31] the results of these previous investigations must be interpreted with caution.

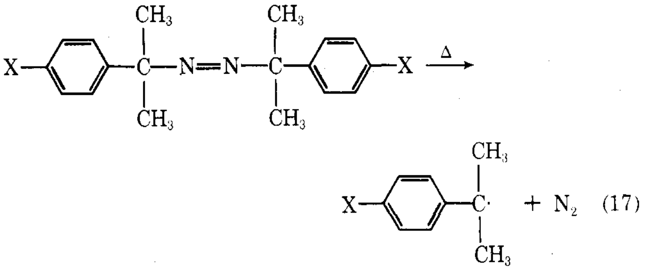
Correlations of free radical abstraction[11] and decomposition[12,13,32] reactions with σ^+ have frequently been interpreted as evidence for a transition state with ionic character. Bartlett and Rüchardt[12a] found that the rates of thermal decomposition of *tert*-butyl aryl peracetates (eq 15) correlate with σ^+ rather than σ ($\rho = -1.2$ at 65°). Walling and Clark[32] have recently reported that relative rates of alkoxy radical β scission (eq 16) also correlate with σ^+ ($\rho = -1.04$ at 30°). Thermolysis of azopropanes is cited as an example of a free radical reaction for which the transition state resembles the free radical.[7,14] The limited data for azocumene decomposition[14] (eq 17) show that substituent effects are substantially different than those for α cleavage.



$$\mathrm{ArCH_2\overset{O}{\overset{\|}{C}}OO\text{-}\mathit{t}\text{-}Bu} \longrightarrow \left[\begin{array}{c} \overset{\delta\cdot}{\mathrm{ArCH_2}}\text{---}\overset{O}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{---}\overset{\delta\cdot}{\mathrm{O}}\text{-}t\text{-Bu} \\ \updownarrow \\ \overset{\delta+}{\mathrm{ArCH_2}}\text{---}\overset{O}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{---}\overset{\delta-}{\mathrm{O}}\text{-}t\text{-Bu} \end{array}\right] \longrightarrow \mathrm{ArCH_2\cdot + CO_2 + \cdot O\text{-}\mathit{t}\text{-}Bu} \quad (15)$$



$$\mathrm{ArCH_2\overset{O\cdot}{\overset{|}{C}}R_1R_2 \longrightarrow ArCH_2\cdot + R_1\overset{O}{\overset{\|}{C}}R_2} \quad (16)$$

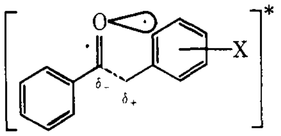


(17)

$k_{\rm rel}$: Cl > OCH$_3$ > CH$_3$ > F > H

The similar values of ρ for perester decomposition and photochemical α cleavage of deoxybenzoins illustrate once again[5] the remarkable similarity of the effects of substituents on the rates of these reactions and provide a possible insight into the nature of the transition state for α cleavage. Rüchardt[7] has conclusively demonstrated that the transition state for perester thermolysis lies early on the reaction coordinate and has little free radical character. Walling[32] appears to argue for radical character in the transition state for β scission (eq 16); however, he attributes benzyl substituent effects to the contribution of polar structures to the transition state and proposes similar transition states for β scission and perester thermolysis.

We conclude that the preponderance of evidence favors an early transition state with a moderate degree of ionic character for photochemical α cleavage[5] and perester thermolysis.[7] The transition state for α cleavage can be depicted as follows:



The partial negative charge can be stabilized by the electrophilic half-vacant nonbonding orbital on oxygen and the partial positive charge by electron-donating aromatic substituents. α substituents which are capable of stabilizing an adjacent positive charge should effectively accelerate photochemical α cleavage. The high photochemical reactivity of benzoin ethers indicates that this is indeed the case.[33]

Experimental Section

Materials. All deoxybenzoins were prepared by standard literature procedures and had physical and spectral properties in agreement with literature values.[34] Several deoxybenzoins were the gift of Dr. R. Scriven. All deoxybenzoins were extensively purified by recrystallization and vacuum sublimation to >99% purity by vpc. Naphthalene (Baker Photograde) and biphenyl (Aldrich zone refined) were used as received and 2,5-dimethyl-2,4-hexadiene was distilled prior to use. Benzene (spectrograde) was distilled from phosphorus pentoxide prior to use and carbon tetrachloride was purified by the method of Schuster and Weil.[22]

Quantum Yields and Lifetimes. Quantum yields for product formation, Stern–Volmer kinetic data, and 77°K triplet lifetimes were obtained as previously described.[5] Phosphorescence quantum yields were determined for highly degassed samples sealed in Pyrex ampoules using a Perkin-Elmer MPF-2A spectrophotometer. Lifetimes for acetophenone and benzophenone were measured by pulsing the sample with the filtered output (Corning CS 7-60) of a Xenon Corp. 437A nanopulser and monitoring the transient emission at right angles with an RCA 1P28 photomultiplier through a Corning CS 3-74 filter. A Princeton Applied Research TDH-9 waveform eductor was used to average 100 or more decay transients and the output was recorded on an X–Y recorder. The single photon counting apparatus is similar to that described by Ware.[35]

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Registry No.—Acetophenone, 98-86-2; benzophenone, 119-61-9.

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Thermal Isomerizations of Dimethyl 3,4-Diphenylmuconates

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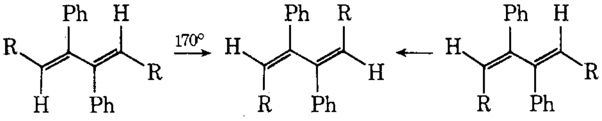
The isomerization of dimethyl (*E,E*)-3,4-diphenylmuconate to its *Z,Z* stereoisomer is shown to proceed through an isolable cyclobutene intermediate with the stereochemistry predicted by orbital symmetry rules. Rate constants and activation parameters have been obtained for the individual steps in the reversible isomerizations.

Several years ago one of us was led to a reinvestigation of the structure and reactivity of the diastereomeric dimethyl 1,3-diphenylbicyclobutane-2,4-dicarboxylates by the violations of orbital symmetry control suggested by the initial study of these compounds.[1] The major discrepancies have been resolved by subsequent work,[2,3] but the thermal interconversions of the dimethyl 3,4-diphenylmuconates **1**, **2**, and **3** which were reported[1,3] still invited explanation (eq 1, R = CO_2Me).



1 (*E,E*) **2** (*Z,Z*) **3**(*E,Z*) (1)

The thermal isomerization of **1** to **2** was originally observed by D'yakonov and coworkers,[1] and the conversion of **3** to **2** was postulated by them[3] to account for the observation that the thermolysis of the exo,exo- and endo,endo-substituted bicyclobutanes produced **2**, rather than **3** as predicted by orbital symmetry theory. The conversion of **1** to **2** could be accomplished by successive double-bond isomerizations involving **3** as an intermediate or by a conrotatory ring closure of **1** to cyclobutene **4** and subsequent conrotatory opening to **2** (eq 2, R = CO_2Me). The former pathway is consistent with the postulated conversion of **3** to **2**, while the latter has ample precedent in the work of Doorakian and Freedman.[4] The isomerization of **3** to **2** might proceed by a double-bond isomerization or by way of a disrotatory ("forbidden") opening of the cis isomer of **4**.