

Photochemistry of α -Cycloalkoxyacetophenones. Type II and Vibronic Pathways for Radiationless Triplet Decay

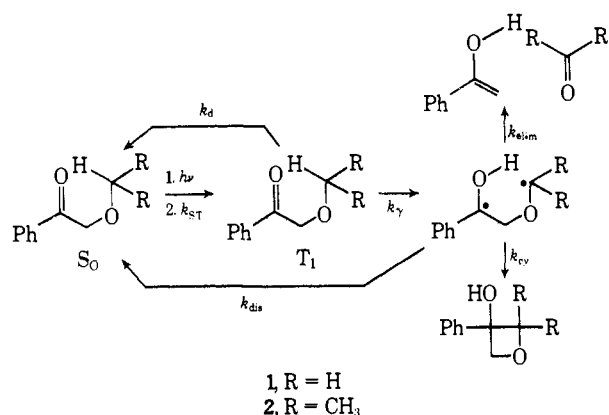
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Abstract: Medium and small ring α -cycloalkoxyacetophenones other than α -cyclopropoxyacetophenones undergo normal photochemical type II reactions with high efficiency. The products obtained are a novel family of 1-oxaspiro[3.*n*]alkanes as well as the corresponding cycloalkanones. The photochemical behavior of α -cyclopropoxyacetophenones deviates markedly from that of their higher homologs and is characterized by: (1) low efficiency of product formation, (2) unprecedented cis-trans isomerization of the cyclopropane ring for the α -(2,3-dimethylcyclopropoxy)acetophenones, and (3) triplet lifetimes which are shortened by remote ring methyl substitution. Replacement of the γ hydrogen with deuterium increases the triplet lifetime and the quantum yields for the type II and ring isomerization processes. Both the ring isomerization and the rapid radiationless decay of the triplet state are attributed to vibronic energy transfer between the excited carbonyl chromophore and the γ hydrogen-cyclopropyl unit.

Several years ago we reported on the Norrish type II reactions of several α -alkoxyacetophenones.² At that time the general mechanism shown in Scheme I

Scheme I



appeared adequate to explain the photochemical behavior of the α -alkoxyacetophenones and most alkyl phenyl ketones.^{3,4} Additional evidence has accumulated to the point where the type II process is among the best understood of photochemical reactions. In nearly all cases both the n, π^* triplet state and the 1,4-biradical intermediate are formed with unit efficiency. Thus the quantum yield for product formation is determined only by the partitioning of the biradical intermediate between cyclization and elimination product formation and disproportionation to ground state ketone (eq 1).³ Considerable progress has also been

$$\Phi_0 = \Phi_{ST} \left(\frac{k_\gamma}{k_\gamma + k_d} \right) \left(\frac{k_{elim} + k_{ey}}{k_{elim} + k_{ey} + k_{cis}} \right) \quad (1)$$

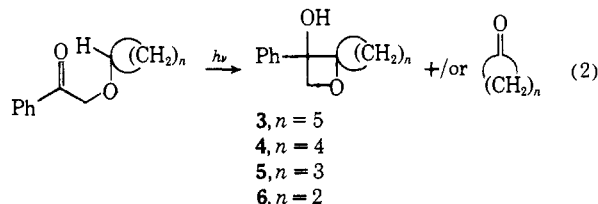
(1) (a) Columbia University; (b) Northwestern University; (c) Research Corporation Graduate Fellow, 1971-1973.

(2) F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970).

(3) (a) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971); (b) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7480 (1972).

(4) The standard mechanism does not apply when the alkyl chain bears (*inter alia*) an amino, olefinic, or β -phenyl group: (a) D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 1153 (1971); (b) P. J. Wagner, A. E. Kempainen, and T. Jellinek, *ibid.*, **94**, 7512 (1972); (c) P. J. Wagner, P. A. Kelso, A. E. Kempainen, A. Haug, and D. R. Graber, *Mol. Photochem.*, **2**, 81 (1970).

made toward understanding the behavior of the 1,4-biradical intermediate.³⁻⁵ In the process of exploring the synthetic prospects for the type II reaction,^{5b,6} we have investigated the photochemistry of several α -cycloalkoxyacetophenones (3-9).⁷ It was hoped that suitably substituted α -cyclopropoxyacetophenones would provide a useful route to substituted cyclopropanones and/or that biradical cyclization would provide the novel family of 1-oxaspiro[3.*n*]alkanes (eq 2). In the course of our investigations it became ap-



parent that while the standard mechanism (Scheme I) was an adequate basis for understanding the behavior of ketones 3-5, it was inadequate in the case of α -cyclopropoxyacetophenone (6) and its methyl-substituted derivatives.

Results

The α -cycloalkoxyacetophenones were synthesized by reaction of the appropriate alcohol with diazoacetophenone in the presence of boron trifluoride.⁸ Stereochemical assignments of the dimethylated derivatives ($n = 2$) are based on established synthetic methods for the preparation of dimethylcyclopropanols and confirmed by nmr analysis. The diazo coupling reaction does not alter alcohol stereochemistry (see Experimental Section). Ketones 1-9 all display characteristic n, π^* ultraviolet absorption (λ_{max} 325 nm ($\epsilon \sim 75$)) and ir spectra ($\nu^{CO} \sim 5.86$ and 5.91μ).

(5) (a) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852 (1972); (b) F. D. Lewis, R. W. Johnson, and R. A. Ruden, *ibid.*, **94**, 4292 (1972); (c) P. J. Wagner, *et al.*, *ibid.*, **94**, 7506 (1972).

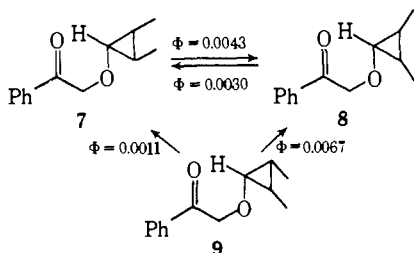
(6) N. J. Turro, R. B. Gagosian, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 4752 (1970).

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(8) M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.*, **72**, 5161 (1950).

Irradiation of ketones **3–6** in dilute benzene solution resulted in rapid and essentially quantitative conversion to acetophenone, cycloalkanones, and oxaspiranes (eq 2). No other products were detected by analytical gas chromatography. The formation of cyclopropanone from ketone **6** was established by nmr and ir analysis of methylene chloride or deuteriochloroform solutions irradiated to moderate conversions at -60° . Prolonged irradiation of the dimethylcyclopropoxyacetophenones **7–9** under similar conditions led to formation of isomeric oxaspiranes and trace amounts of acetophenone with no detectable dimethylcyclopropanones. At lower conversions the major products were oxaspiranes and starting ketone with isomerized cyclopropane rings. Both oxaspirane formation and methyl isomerization appear to be well-behaved, first-order photochemical reactions. Figure 1 illustrates the results for ketone **9** (cis-endo) which isomerizes to **7** (cis-exo) and **8** (trans) upon irradiation in methylene chloride at -15° . Such plots were linear to 15% conversion. Ketone **7** is isomerized to **8** and *vice versa*; however, no detectable **9** is formed from **7** or **8**. These relationships are summarized in Scheme II.

Scheme II



Quantum yields for acetophenone and oxaspirane formation from ketones **3–6** were determined using standard procedures (Table I). Values for α -isopropoxy-

Table I. Quantum Yield and Kinetic Data for α -Cycloalkoxyacetophenones

Ketone	Φ_{elim}	Φ_{cy}	$k_q\tau$	$1/\tau, \text{sec}^{-1} \times 10^9$
2 ^a	0.59	0.40	0.61	8.2
3	0.38	0.20	0.56	8.9
4	0.33	0.28	0.72	6.9
5	0.40	0.42	1.5	3.3
6	0.018	0.059	21	0.24

^a Values from ref 2.

acetophenone (**2**) are included in Table I for purposes of comparison. Quantum yields for loss of ketone and isomerization of **7–9** are given in Table II. The difference between these values was taken to be the maximum quantum yield for type II processes (mainly oxaspirane formation). This assumption is justified by the good mass balance for high conversion runs. Addition of *tert*-butyl alcohol to the benzene solutions had little or no effect on the quantum yields. Triplet lifetimes for ketones **3–9** were determined by standard Stern–Volmer quenching experiments. The slopes of linear Stern–Volmer plots equal $k_q\tau$, where k_q is the rate constant for quenching of the ketone triplet by piperylene and τ is the triplet lifetime. Assumption of the value 5×10^9

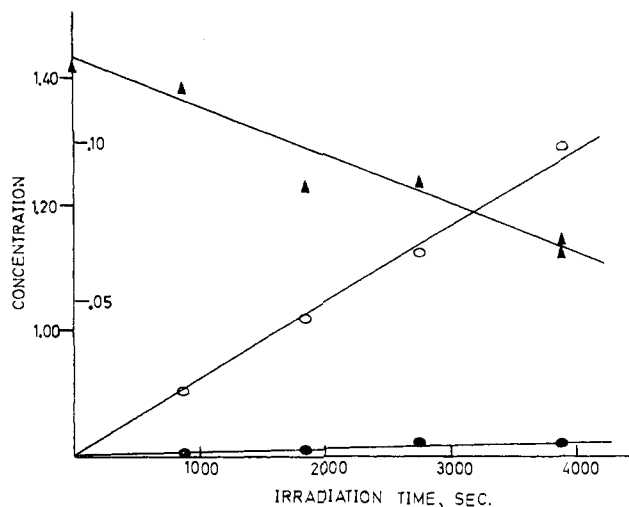


Figure 1. Disappearance of **9** (cis-endo, Δ) and appearance of **8** (trans, \circ) and **7** (cis-exo, \bullet). Concentrations in arbitrary units with the larger scale for disappearance of **9**.

Table II. Quantum Yields and Kinetic Data for α -Cyclopropoxyacetophenones

Ketone	Φ_{-K} ^a	Φ_{isom} ^b	Φ_{II}	$k_q\tau$	$1/\tau, \text{sec}^{-1} \times 10^9$
6 (unsubs)	0.077		0.077	21	0.24
7 (cis-exo)	0.015	0.0043 (8)	0.011	4.4	1.1
8 (trans)	0.0060	0.0030 (7)	0.003	2.3	2.2
9 (cis-endo)	0.023	0.0011 (7) 0.0067 (8)	0.015	0.65	7.7

^a Total quantum yield for loss of starting ketone. ^b Parentheses refer to product of isomerization.

$M^{-1} \text{sec}^{-1}$ for k_q in benzene solution allows calculation of τ or $1/\tau$ (Tables I and II).

The effect of deuteration at the γ position upon quantum yields and kinetics was investigated for ketone **7**. Fully deuterated and protiated α -methoxyacetophenones (**1**) were also investigated to provide a basis for comparison. The results are given in Table III.

Table III. Deuterium Isotope Effects

Ketone	Φ_{-K}	Φ_{isom}	Φ_{II}	$k_q\tau$	$1/\tau, \text{sec}^{-1} \times 10^9$
7h	0.015	0.0043	0.011	4.4	1.1
7d	0.025	0.0078	0.017	10.7	0.47
1h ^a	0.99		0.99	1.6	3.1
1d				8.9	0.56

^a Values from ref 2.

The isotope effects on the rate of triplet decay ($1/\tau$) for **7** and **1** are 2.4 and 5.5, respectively. Deuteration of ketone **7** also results in increased quantum yields for loss of ketone and isomerization.

Finally, the ability of cyclopropyl ethers to deactivate n, π^* carbonyl triplet states was investigated. Highly degassed solutions of benzophenone in purified Freon solvent at 25° phosphoresce. Static phosphorescence quenching and direct lifetime measurements were used to determine triplet quenching rate constants. 1,1-Diethoxycyclopropane quenches benzophenone phosphorescence at a rate ($1.6 \times 10^6 M^{-1} \text{sec}^{-1}$)

comparable to those for simple aliphatic ethers ($3-9 \times 10^6 M^{-1} \text{sec}^{-1}$).

Discussion

The results for the α -cycloalkoxyacetophenones 3-5 (Table I) can readily be understood in terms of the standard mechanism for type II photochemical reactions (Scheme I). The high total quantum yields for cyclization and elimination require efficient formation of the 1,4-biradical intermediate. Thus the triplet lifetime is primarily determined by the rate constant for γ -hydrogen abstraction ($1/\tau = k_\gamma$) as is normally observed.²⁻⁵ Rate constants for γ -hydrogen abstraction are known to reflect the strength of the γ CH bond.^{2,3} The similar reactivities of ketones 3 and 4 and α -isopropoxyacetophenone (2) are as expected since tertiary CH homolysis occurs in each case. The decrease in $1/\tau$ for ketone 5 probably reflects the increase in activation energy for a cyclobutane *vs.* cyclopentane CH bond.^{9,10} *It is important to note that there is no concomitant decrease in the quantum yields for cyclization and elimination from ketone 5.*

α -Cyclopropoxyacetophenone (6) shows both a large decrease in $1/\tau$ (40-fold) and quantum yield (\sim tenfold) when compared to ketones 2-4. The decrease in $1/\tau$ may in part reflect the increased strength of the γ CH bond.⁹ The low quantum yields for product formation can be explained in terms of the standard mechanism (Scheme I) if (a) biradical disproportionation is much more rapid than cyclization and elimination or (b) a new triplet deactivation process competes with γ -hydrogen abstraction ($k_d > k_\gamma$). In cases where biradical cyclization and elimination are sterically hindered, low product quantum yields have been attributed to predominant disproportionation of the biradical.^{5a,b} That this is probably not the case for ketone 6 is indicated by the high quantum yield for ketone 5, which should have similar steric requirements for biradical cyclization and elimination. In addition, the methyl substituent and isotope effects (*vide infra*) mitigate against efficient biradical formation. We are left then with the necessity of postulating a pathway for triplet deactivation which can effectively compete with γ -hydrogen abstraction. This pathway must be much more rapid than normal radiationless decay of acetophenone and related alkyl phenyl ketones ($k_d < 10^6 \text{sec}^{-1}$).¹¹ For ketone 6 a decay rate constant $> 10^8 \text{sec}^{-1}$ would be necessary to explain the low quantum yields for product formation.

Methyl substitution of the cyclopropyl ring of ketone 6 has a pronounced effect on both the triplet lifetime and the photochemical reactions (Table II). The occurrence of cyclopropane isomerization is without precedent in type II reactions. Ring cleavage of conjugated cyclopropyl ketones¹² and enones¹³ is a well-

known photochemical process. However, in these cases excitation alters the electron densities in the cyclopropane ring, whereas for ketones 6-9, absorption and emission spectra show no evidence of interaction between the n, π^* excited state and cyclopropane ring. Cyclopropyl isomerization could in principle occur *via* opening and reclosure of a biradical intermediate followed by disproportionation to ground-state ketone. Whereas cyclopropyl ring opening within the lifetime of the biradical appears energetically feasible, reclosure of the allylic biradical does not.¹⁴ The allylic biradical would be expected to form olefinic products more rapidly than isomerized cyclopropyl ketone. Thus it is significant that no olefinic products are formed even upon prolonged irradiation of ketones 6-8. Abstraction of a δ hydrogen by carbonyl n, π^* excited states has been reported in several cases.¹⁵ Formation of a 1,5-biradical intermediate might account for epimerization at a single carbon, but cannot account for first-order isomerization of ketone 9 to both 7 and 8. An additional failure of both the 1,4- and 1,5-biradical mechanisms is their inability to account for the variation in triplet lifetime for ketones 6-9.

The observation of cyclopropyl isomerization is consistent with the formation of either an electronically or vibrationally excited cyclopropane ring. Both triplet sensitization¹⁶ and thermolysis¹⁷ of dialkylcyclopropanes results in cyclopropane *cis-trans* isomerization and isomerization to propylenes. In either case, *cis-trans* isomerization is much more rapid than isomerization to propylenes. Interconverting 1,3-biradical intermediates¹⁷ nicely explains the observed isomerization quantum yields (Table II). Steric interactions in the dimethyl cyclopropyl ethers should follow the order $9 \gg 7 > 8$. Thus it is not surprising that (a) the total isomerization quantum yields follow the same order, (b) no 9 is formed from 7 or 8, and (c) more 8 than 7 is formed from 9.

Intramolecular triplet sensitization of the cyclopropane ring by the aromatic carbonyl seems unlikely for several reasons. First, the triplet energy of dimethylcyclopropane is estimated to be 87 kcal/mol,¹⁶ or 14 kcal/mol greater than the n, π^* triplet energy of α -cycloalkoxyacetophenones.² Second, cyclopropyl ethers are not particularly efficient intermolecular quenchers of carbonyl n, π^* triplet states. A model cyclopropyl ether, 1,1-diethoxycyclopropane, quenches benzophenone room temperature phosphorescence at a rate no greater than that for simple aliphatic ethers. Finally, a triplet energy transfer mechanism for carbonyl deactivation poses difficulties in accounting for the effects of methyl substitution and deuteration upon the triplet lifetime.

Whereas the formation of an electronically excited cyclopropane ring is unlikely, interaction between the carbonyl and cyclopropane chromophores cannot be ruled out. Several years ago Hoffmann¹⁸ predicted the existence of low lying $\Delta \rightarrow \pi^*$ states with charge-transfer character in molecules which possess carbonyl

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(16) J. A. Bell, *J. Amer. Chem. Soc.*, **87**, 4966 (1965).

(17) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

(18) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965).

and cyclopropyl units. Such a $\Delta \rightarrow \pi^*$ transition has recently been observed at 180 nm for conjugated cyclopropyl ketones.¹⁹ The long wavelength (300 nm) absorption band is also assigned partial $\Delta \rightarrow \pi^*$ character. The weakened cyclopropane bonding postulated by Hoffmann for $\Delta \rightarrow \pi^*$ states is in accord with the numerous examples of ring cleavage of conjugated cyclopropyl ketones.^{12,13} Evidence for similar interactions in β - and γ -cyclopropyl ketones is less compelling. The n, π^* absorption bands of acyclic ketones²⁰ and cyclooctanones²¹ are slightly red shifted by β - and γ -cyclopropyl substituents. The photochemical behavior of these ketones is also influenced by the presence of the cyclopropyl group; however, cyclopropane ring opening is not observed.^{20,22}

As previously discussed, cyclopropane isomerization (Scheme II) is consistent with the formation of a vibrationally excited cyclopropane. Methyl substitution of the cyclopropane ring of ketone **6** also leads to a decrease in the triplet lifetime and the quantum yield for type II product formation (Table II). The observations of decreased triplet lifetimes and cyclopropane isomerization are possibly related and can be attributed to efficient electronic-vibrational energy transfer from the carbonyl n, π^* triplet to the cyclopropane ring.

There have been a number of recent attempts to apply the concepts of intramolecular radiationless transitions to photochemical reactions.²³⁻²⁵ The rate of radiationless decay and photochemical reactions which result from excitation of specific molecular vibrations both depend on the vibrational overlap (Franck-Condon) integral for the vibration(s) involved in the transition. The largest Franck-Condon factors are found for anharmonic high-frequency vibrations such as CH stretching. Isotopic substitution can modify vibrational overlap Franck-Condon factors and thereby alter the rate of radiationless decay. Lin and Bersohn²⁶ and Rice, *et al.*,²³ have pointed out the importance of distinguishing between promoting modes which are responsible for the electronic transition and accepting modes which provide a sink for the electronic energy. For example, deuterium substitution studies of naphthalene showed that the CH symmetric stretching modes are accepting rather than promoting.²⁶

In order to obtain further information about the nonradiative decay and cyclopropane isomerization processes, the effect of γ deuteration on the behavior of ketone **7** was investigated (Table III). The small quantum yields for loss of ketone for both **7h** and **7d** indicate that radiationless decay is the predominate photoprocess. Thus the observed isotope effect of 2.4 on $1/\tau$ reflects a decrease in the rate of radiationless decay and implicates the γ CH bond in the decay process.³⁷ It is important to note that the magnitude of the

isotope effect is considerably smaller than those for α -methoxyacetophenone ($k_H/k_D = 5.5$) or phenyl *n*-octyl ketone ($k_H/k_D = 4.8$)⁴ for which γ -hydrogen abstraction is the predominant photoprocess. The smaller kinetic effect for ketone **7** provides further evidence that γ -hydrogen abstraction followed by biradical disproportionation is not the major pathway for radiationless decay.

In addition to increasing the triplet lifetime, γ deuteration of ketone **7** results in increased quantum yields for type II and isomerization product formation. Negative deuterium isotope effects on type II quantum yields have previously been observed and attributed to retarded biradical disproportionation.³⁰ The observation of an increased quantum yield for cyclopropane isomerization as well as an increased triplet lifetime for **7d** again suggests that the radiationless decay and isomerization pathways are related. In short, there are two competing pathways for the excitation energy in α -cyclopropoxyacetophenones. The type II process (eq 2) undoubtedly proceeds *via* γ -hydrogen abstraction, for which the rate constant should be insensitive to methyl substitution in the cyclopropane ring. The competing radiationless decay process must involve the cyclopropane ring in order to explain the observed dependence of triplet lifetime on methyl substitution. The isomerization reaction must be related to radiationless decay barring an inordinately large secondary isotope effect on the γ -hydrogen abstraction mechanism (eq 2).

In view of the appreciable kinetic isotope effect on the triplet lifetime, it is attractive to propose that the electronic energy flows preferentially into the γ CH stretching vibration and that the cyclopropane C_2-C_3 bond serves as an accepting mode or energy sink. Such a model is analogous to that proposed by Heller²⁵ for hydrogen abstraction reactions. There are two obvious problems with such a model. First, if the γ CH stretching mode is selectively excited, the pronounced effect of methyl substituents on the rate of radiationless decay is difficult to explain. Secondly, as pointed out by Yip and Siebrand,³¹ vibrational redistribution in solution would be so rapid as to preclude cleavage of the C_2-C_3 bond. It seems more likely that the flow of energy is into the entire cyclopropane system. A large geometry change in the cyclopropane ring could provide better vibrational overlap than γ CH stretching and thus explain both the effect of methyl substituents on the rate of radiationless decay and the isomerization quantum yields. A small amount of $\Delta \rightarrow \pi^*$ charge-transfer character in the lowest triplet state would account for the necessary change in cyclopropane geometry. Direct energy flow into the cyclopropane system would be expected to show a kinetic

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(27) Surprisingly large secondary deuterium isotope effects ($k_H/k_D \sim 1.7$) have recently been reported for base-catalyzed cleavage of dibromocyclopropanone²⁸ and silver-catalyzed cleavage of a bicyclobutane.²⁹ Since the isotope effect for ketone **7** is on radiationless decay and not ring opening, it seems unlikely that these observations are related.

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isotope effect as the sum of all Franck-Condon factors determines the rate of radiationless decay. Since the ability of a CH stretch to act as an accepting mode is diminished by deuteration, it is not surprising that the quantum yield for cyclopropane isomerization of ketone **6** increases upon γ deuteration.

In summary, we find that the photochemical behavior of ketones **1-5** can readily be understood in terms of the normal type II mechanism. For α -cyclopropoxyacetophenone (**6**) chemically nonproductive radiationless decay competes with the type II reaction. Methyl substitution of the cyclopropane ring markedly increases the rate of radiationless decay and also results in an unexpected isomerization of the cyclopropane ring. Both the radiationless decay and cyclopropane isomerization are believed to result from electronic-vibrational energy transfer from the carbonyl n, π^* triplet to the cyclopropane ring. In view of the methyl substituent effects, the C_2-C_3 stretching mode is probably directly involved in promoting the radiationless decay. The low quantum yield for cyclopropane isomerization indicates that C_2-C_3 bond scission competes inefficiently with vibrational relaxation of the molecule. The effect of deuterium substitution on the triplet lifetime and isomerization quantum yield are in accord with this explanation.

Finally, it should be pointed out that while the proposed mechanism for nonradiative decay and photoisomerization has not been previously encountered in investigations of type II photoreactions, it probably is not an isolated phenomenon. Carroll and Hammond³² have recently concluded that both chemical reactions and radiationless decay are accelerated in 3-methyl-1-phenoxybut-2-ene, relative to anisole. They suggest that radiationless decay may be accelerated by easily breakable bonds even when actual scission of the bond does not occur. Clearly, radiationless decay and photochemical reactions which involve specific molecular vibrations are similar processes. Further experimental work in this area should allow for meaningful comparisons with the rapidly developing theory of intramolecular radiationless transitions.

Experimental Section

α -Cycloalkoxyacetophenones **3-5** were prepared by the reaction of diazoacetophenone with cyclic alcohols in the presence of boron trifluoride³³ and purified by distillation. Cyclobutanol was prepared by the method of Caserio.³⁴ Pmr spectral data are given in Table IV. Uv spectra (hexane): **3**, λ_{\max} 326 nm (ϵ_{\max} 61); **4**, λ_{\max} 325 nm (ϵ_{\max} 61); **5**, λ_{\max} 327 nm (ϵ_{\max} 57).

Table IV. Pmr Data for α -Cycloalkoxyacetophenones^a

Ketone	Aromatic	-CH ₂ O	γ -H	Cycloalkyl
3	7.9, 7.4	4.5	3.4	1.3-2.0
4	7.9, 7.4	4.5	3.9	1.5-1.7
5	7.9, 7.4	4.4	4.0	1.5-2.2
6^b	7.9, 7.4	4.7	3.5	0.4-0.7

^a Chemical shifts (δ , ppm) in CCl₄. ^b Chemical shifts in CDCl₃.

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(33) M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.*, **72**, 5161 (1950).

(34) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

α -Cyclopropoxyacetophenone (**6**). Cyclopropanol was prepared according to the method of Depuy.³⁵ Purification of the crude cyclopropanol was accomplished through preparative scale vapor phase chromatography, vpc, on a 6-ft aluminum column packed with 20% FFAP coated Chromosorb W. Column temperature was maintained at 90° to avoid excessive losses of cyclopropanol. Cyclopropanol was obtained in better than 95% purity and was stored no longer than several days at -20° before subsequent use: pmr (CDCl₃) δ 0.5 (sh mult, 4), 3.4 (br mult, 1), 4.3 (br s, -OH, 1).

To 10 ml of methylene chloride was added 500 mg (3.40 mmol) of α -diazoacetophenone followed by 200 mg (3.46 mmol) of cyclopropanol. The solution was cooled with stirring to -18° in an ice-salt bath and was maintained under a slight positive pressure of dry nitrogen. By means of a syringe, 10 μ l of freshly distilled boron trifluoride etherate was injected rapidly into the solution. Stirring and cooling were maintained for 0.5 hr during the steady evolution of nitrogen. An additional 10 μ l of boron trifluoride etherate was added and the solution was stirred for an additional 0.5 hr. It was then diluted with 30 ml of ether and decanted onto 50 ml of a saturated sodium bicarbonate solution. The ether layer was separated, and the aqueous layer was extracted with several 30-ml portions of ether. The combined extracts were dried over magnesium sulfate, and the solvent was rotary evaporated. The crude brown oily residue was bulb-to-bulb distilled at high vacuum, then purified by preparative scale vpc on a 20% SE-30 Chromosorb W packed aluminum column at 160°: pmr data given in Table IV; ir ν_{\max} (CCl₄) 3.48, 5.08, 5.25, 5.49 (overtone), 5.92 (doublet C=O), 6.23, 6.30 μ (aromatic); uv (hexane) λ_{\max} 325 nm (ϵ_{\max} 70).

α -(*cis*-*exo*-2,3-Dimethylcyclopropoxy)acetophenone (**7h**) and α -(*cis*-*endo*-2,3-Dimethylcyclopropoxy)acetophenone (**9**). A mixture of *cis*-2,3-dimethylcyclopropanols³⁶ and α -diazoacetophenone in methylene chloride containing boron trifluoride etherate was stirred at room temperature until evolution of nitrogen was complete. Separation of the isomeric products was readily achieved by preparative vpc at 170°. The major *cis*-*exo* isomer, retention time 44 min, was collected as a clear oil in high isomeric purity: pmr (CCl₄) δ 1.0 (br s, 8), 2.9 (t, coupling, $J = 2$ Hz, 1), 4.7 (s, 2), aromatic multiplets centering at 7.9 (2) and 7.5 (3); ir ν_{\max} (CCl₄) 3.98, 5.05, 5.24, 5.48 (overtone), 5.86, 5.91 (doublet C=O), 5.23, 5.28 μ (aromatic); uv (hexane) λ_{\max} 325 nm (ϵ_{\max} 72).

Anal. Calcd for C₁₃H₁₆O: C, 76.43; H, 7.91. Found: C, 76.59; H, 8.00.

The minor *cis*-*endo* isomer **9** had a vpc retention time of 53 min: pmr (CDCl₃) δ 1.1-0.6 (br mult, 2), 1.0 (sh mult, 6), 3.4 (t, coupling, $J = 6$ Hz, 1), 4.7 (s, 2), aromatic multiplet absorptions at 7.9 (2) and 7.5 (3); ir (CCl₄) ν_{\max} 3.98, 5.05, 5.25, 5.48 (overtone), 5.86, 5.91 (C=O doublet), 5.23, 5.28 μ (aromatic); uv (hexane) λ_{\max} 325 nm (ϵ_{\max} 77).

Anal. Calcd for C₁₃H₁₆O: C, 76.43; H, 7.91. Found: C, 76.17; H, 7.82.

α -(*Deuterio*-*cis*-*exo*-2,3-dimethylcyclopropoxy)acetophenone (**7d**). The mixture of 1-deuterio-*cis*-2,3-dimethylcyclopropanols³⁶ was reacted with α -diazoacetophenone utilizing exactly the same procedure as for the preparation of **7h**: pmr (CCl₄) δ 1.0 (br based s, 8), 2.9 (t, coupling, $J = 2$ Hz, 0.08), 4.7 (s, 2), aromatic protons as multiplets centered at 7.9 (2) and 7.5 (3); uv (hexane) λ_{\max} 325 nm (ϵ_{\max} 70). The isotopic purity was 92% monodeuteration.

α -(*trans*-2,3-Dimethylcyclopropoxy)acetophenone (**8**). Starting with *trans*-2,3-dimethylcyclopropanol,³⁶ the procedure was analogous to that for *cis*-*exo*. Vpc retention time was 38 min: pmr (CDCl₃) δ 0.6 (br mult, 1), 0.95, 1.15 (crude doublets, 6), 3.15 (4-line multiplet, 1), 4.7 (s, 2), aromatic protons as multiplets centered at 7.9 (2) and 7.5 (3); ir (CCl₄) ν_{\max} 3.5, 5.07, 5.27, 5.48 (overtone), 5.9 (C=O doublet), 6.23, 6.28 μ (aromatic); uv (hexane) λ_{\max} 325 nm (ϵ_{\max} 72).

Anal. Calcd for C₁₃H₁₆O₂: C, 76.43; H, 7.91. Found: C, 76.35; H, 7.86.

Preparative Scale Irradiations. Dilute benzene solutions of ketones **3-6** were irradiated under argon using a 450-W, medium-pressure mercury lamp in a Pyrex immersion well. The oxaspiranes, cycloalkanones, and acetophenone were isolated by chromatography on silica gel with benzene-ethyl acetate solvent. Spectral data for the oxaspiranes have been reported.^{7b} Irradiation of **6** at -40 to -60° in CH₂Cl₂ and CDCl₃ solvent was moni-

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tored by pmr. Appearance of singlets at δ 2.59 and 1.73 is indicative of the formation of acetophenone and cyclopropane, respectively.³⁷

Quantum Yields and Quenching Studies. Degassed benzene solutions of 0.05–0.4 M ketone were irradiated in sealed Pyrex tubes. The tubes were irradiated on a merry-go-round apparatus using a 450-W lamp and a potassium chromate filter solution to isolate the 313-nm irradiation. Variable-temperature runs used a small merry-go-round in an unsilvered quartz dewar containing 95% ethanol using an external light source. Temperature regulation was achieved with a Haake thermoregulator by circulating methanol through a coiled heat exchanger contained within the quartz dewar. Light intensities were calculated using the type II reaction of valerophenone ($\Phi_{\text{cleavage}} = 0.33$) as a secondary actinometer.³⁸ Irradiated solutions were analyzed by flame ioniza-

tion vpc using a 6 ft \times 1/8 in. column of 4% QF-1 and 1% Carbowax 20M on Chromosorb G for ketones 3–6 and a 15 ft \times 1/8 in. column of SE-30 on Chromosorb P at 150° for ketones 6–9. Deuterium isotope effects were determined by simultaneous irradiation of protio and deuterio samples. Stern–Volmer quenching studies were conducted using procedures identical with those used in the quantum yield studies. Solutions of desired 1,3-pentadiene concentrations were prepared by mixing appropriate quantities of a standard benzene stock solution of quencher with benzene solutions of substrate.

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Single Photon Counting and Magic Multipliers in Direct Measurement of Singlet Excited State Di- π -methane Rearrangement Rates in the Picosecond Range. Mechanistic Organic Photochemistry. LXXXIII^{1a,b}

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Abstract: A single photon counting technique utilizing an on-line PDP-8/I computer was devised and employed to obtain exceedingly rapid rates of singlet excited state decay and rearrangement. In this approach the computer was used both as a multichannel analyzer and also for on-line systematic reiterative convolution, fitting the results to theory. This permitted measurement of rates of decay which were faster than the lamp flash. Additionally, a powerful technique was developed for determination of those rates which were too rapid to measure at room temperature; this utilized a magic multiplier which gives the ratio of room-temperature to low-temperature rates. The rates obtained by this direct procedure were compared with those obtained earlier by an indirect procedure. Singlet excited state decay rates were measured for naphthalene and tetraphenylethylene for evaluation of the method. Both decay and the di- π -methane rearrangement rates were obtained for the excited singlets of 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene, 1,1-diphenyl-3,3,5-trimethyl-1,4-hexadiene, 1,1,3,3-tetraphenyl-5-methyl-1,4-hexadiene, and 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. The rates of rearrangement increased in the preceding sequence with the triphenylpentadiene rearranging at $k_r = 5.8 \times 10^8 \text{ sec}^{-1}$ and the tetraphenylpentadiene at $k_r = 1.4 \times 10^{11} \text{ sec}^{-1}$. Also, there was a nearly perfect ratio between rate of singlet decay and rate of di- π -methane rearrangement. The decay rates increased in the above order with the same two compounds being at the extremes with rates of $k_{\text{dt}} = 7.2 \times 10^{10} \text{ sec}^{-1}$ and $k_{\text{dt}} = 1.8 \times 10^{13} \text{ sec}^{-1}$, respectively. This order of reactivity correlates nicely with expectation based on a rate-limiting bridging step of the π - π^* excited singlet. In the case of decay, evidence was obtained for electronic relaxation at the stage of the bridged biradicaloid species.

In connection with our previous investigations² we were particularly intrigued by the possibility of correlating the reaction rates for rearrangement of the excited singlets of a series of acyclic di- π -methane reactants to structural variations. While there is a tendency in photochemistry, at its present stage of development, to utilize quantum yields as a measure of reactivity, quantum yields really afford only the tendency

of the excited state to form product relative to all other competing processes. Ideally, one should have the absolute rate for unimolecular rearrangement of the excited state of interest.

In our last study on this subject,² we described an indirect method for obtaining such excited state rate constants. Indeed, the method has proven useful for deriving relative rate constants. Nevertheless, it was clear that an absolute method was needed. Additionally with a large number of singlet di- π -methane rearrangements now known,^{2,3} it was of considerable interest to

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