Molecular Photochemistry. XVIII.[1] Type II Photoelimination and 3-Oxetanol Formation from α-Alkoxyacetophenones and Related Compounds

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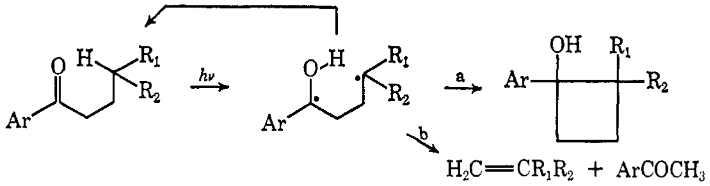
Abstract: The type II photoelimination and cyclization reactions of a series of α-alkoxyacetophenones have been studied. Quantum yields and rate constants for product formation were determined in several solvents. The results contrast with those for aryl alkyl ketones in several notable respects. A comparison of the reactivity of alkyl and alkoxy hydrogens toward intramolecular abstraction by a carbonyl excited state was examined by study of the photolysis of α-methoxybutyrophenones. Effects of aromatic substituents on the reactivity of α-alkoxyacetophenones and butyrophenone were also investigated. The results are discussed in terms of the generally accepted mechanisms of type II photoelimination and cyclization.

The intramolecular photoelimination and cyclization reactions of ketones bearing a γ-hydrogen have been the subject of intense recent investigation.[4-21] It is now generally accepted that for aryl alkyl ketones both reactions proceed by way of a triplet which leads to a 1,4-biradical intermediate which may either (a) cyclize, (b) undergo cleavage to form an olefin and an enol (which isomerizes to a methyl ketone), or (c) revert to the starting ketone by reabstraction of hydrogen (eq 1).



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The rate constant for formation of the biradical intermediate is increased by electron-releasing substituents on the γ-carbon[4,5] but the quantum yield for product formation does not correlate with the rate constant.[6-8] Thus in going from primary to tertiary γ-hydrogen abstraction the rate constant increases from 7.5 × 10^6 sec^{-1} to 4.5 × 10^8 sec^{-1} while Φ decreases from 0.35 to 0.25.[6,7] Much evidence has accumulated to show that n,π* triplet states are reactive toward intramolecular photoelimination and intermolecular photoreduction and that π,π* states are less reactive or unreactive.[7-9,12] Electron-releasing aromatic substituents increase the lifetime and cause general broadening of the phosphorescence emission[16,21] at 77°K. The same substituents decrease the rate constant and/or the quantum yield for type II photoelimination[9-11] or intermolecular photoreduction[12,13] at 25°. Aryl alkyl ketones with moderately electron releasing substituents such as methyl or methoxy have dual ^{3}(n,π*) and ^{3}(π,π*) emission and decreased reactivity, presumably due to mixing of the two states, whereas those with strongly electron-releasing or resonance interacting substituents such as hydroxyl, amino, or phenyl are unreactive and have lowest (π,π*)[9,14] or charge-transfer[14] triplet states.

Polar solvents can also increase the π,π* character of the triplet by stabilizing the π,π* state relative to the

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[1] (a) Part XVII: N. J. Turro and R. Engel, *Mol. Photochem.*, **1**, 359 (1969); (b) for a preliminary account, see N. J. Turro and F. D. Lewis, *Tetrahedron Letters*, 5845 (1968); (c) the authors thank the Air Force Office of Scientific Research (GrantAFOSR-68-1381) for their generous support of this work.

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[16] (a) R. N. Griffin, *Photochem. Photobiol.*, **7**, 159, 175 (1968); (b) N. C. Yang and S. Murov, *J. Chem. Soc.*, **45**, 4385 (1966).

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Table I. Quantum Yields[a] for the Formation of Acetophenone and 3-Oxetanol for α-Alkoxyacetophenones

Compd no	Ketone	Solvent	Φ_{II}[b]	Φ_{cy}[c]	Φ_{tot}[d]	Cy, %
1	$PhCOCH_2OCH_3$	C_6H_6	0.57	0.42	0.99	43
2	$PhCOCH_2OCH_2CH_3$	C_6H_6	0.38	0.59[e]	0.97	61
3	$PhCOCH_2OCH(CH_3)_2$	C_6H_6	0.59	0.40	0.99	40
4	*p*-MeO-**1**	C_6H_6	0.72	0.21	0.93	23
5	*p*-CF_3-**1**	C_6H_6	0.43	0.25	0.68	37
1		$(CH_3)_3COH$	0.29	0.10	0.39	26
2		$(CH_3)_3COH$	0.21	0.19[e]	0.40	48
3		$(CH_3)_3COH$	0.27	0.13	0.40	32
4		$(CH_3)_3COH$	0.69	0.12	0.81	15
5		$(CH_3)_3COH$	0.58	0.17	0.75	23
1		CH_3CN	0.40	0.10	0.50	21
2		CH_3CN	0.31	0.21[e]	0.52	40
3		CH_3CN	0.23	0.10	0.43	31
4		CH_3CN	0.77	0.11	0.88	13
5		CH_3CN	0.62	0.13	0.75	17

[a] Average of two or more determinations at 3130 Å. [b] Quantum yield for acetophenone formation. [c] Quantum yield for 3-oxetanol formation. [d] Product yields were essentially the same as α-alkoxyacetophenone loss. [e] *cis–trans* mixture.

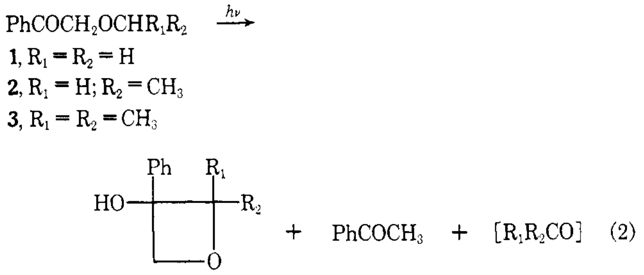
n,π* state. In highly polar media acetophenone[15a] and butyrophenone[15b] have lowest $^3(\pi,\pi^*)$ states. However, solvent effects are more complicated than substituent effects as the changeover from $^3(n,\pi^*)$ to $^3(\pi,\pi^*)$ is not well defined, dual emission of aryl alkyl ketones is often observed,[16] and detailed kinetic data are unfortunately lacking. The triplet state lifetime of valerophenone has been postulated to be solvent dependent.[17] Polar solvents also increase the quantum yield for product formation for aryl alkyl ketones.[8,17] The lower quantum yields in nonpolar solvents ($\Phi < 0.4$) are attributed to reversal of the hydrogen abstraction process which is retarded by hydrogen bonding of the biradical hydroxyl hydrogen in polar solvents.[17] Factors effecting the relative rates of reactions of the 1,4-biradical are not well understood and there are conflicting reports on the effect of structure upon the competition between elimination, cyclization, and hydrogen return.

We wish to report our relevant studies on the effect of structure and solvent upon the photochemistry of several α-alkoxyacetophenones, α-alkoxybutyrophenones, and related butyrophenones.

Results

Quantum Yields. α-Alkoxyacetophenones (**1–5**) were irradiated in degassed benzene, *t*-butyl alcohol, or acetonitrile solution (0.05–0.07 *M*) using a 450-W medium-pressure mercury lamp through Pyrex glass and a 1.0-cm filter solution of potassium chromate which served to isolate the 3130-Å line. Quantum yields were determined at 25° by simultaneous irradiation of actinometer solutions and glpc analysis for product formation after 5–15% conversion. The quantum yield for acetophenone and 3-oxetanol formation from **1** in benzene was independent of per cent reaction from 2 to 20%. Products were identified by preparative glpc and nmr analysis. Nmr data for the 3-oxetanols (see Experimental Section) were consistent with previous reports.[18,19] No products other than acetophenones and 3-oxetanols were observed. The results are given in Table I.

For **1–3** the total quantum yield is independent of structure but is solvent dependent dropping from ~1.0 in benzene to less than 0.5 in *t*-butyl alcohol and acetonitrile. Less pronounced solvent effects are observed for **4** and **5**. The percentage yields of 3-oxetanols are dependent upon both structure and solvent and are much higher than the yields of cyclobutanols formed from aryl alkyl ketones.[6,8] The largest amount of 3-oxetanol formation (61% in C_6H_6) is observed for the secondary γ-hydrogen case, **2**, analogous to the results of Barltrop[8] for aralkyl ketones, but in contrast with Wagner's report[6] that the yields of cyclobutanols decrease for the series primary > secondary > tertiary. The yield of 3-oxetanol also decreases with increased solvent polarity while no significant solvent effect on the cyclization/cleavage ratio was observed by Barltrop[8] for aralkyl ketones. For compound **2**, *cis*- and *trans*-3-oxetanols are formed. Partial resolution of the 3-oxetanol peak was achieved by glpc. In benzene the peaks had a 10:1 area ratio and in polar solvents a 4:1 ratio. Presumably the major component is the *trans* isomer by analogy to the 3-oxetanols from α-benzyloxyacetophenone.[19] Isolation of the 3-oxetanols by glpc and analysis by nmr showed only one methyl doublet.



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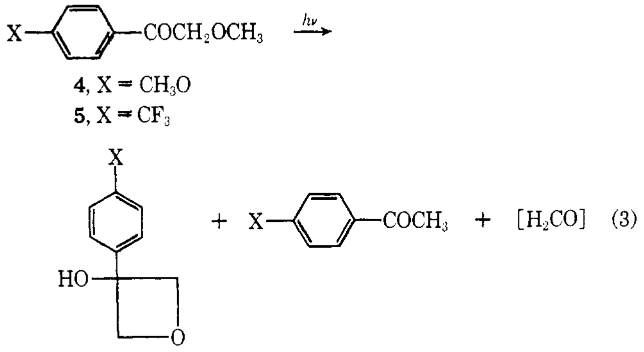

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Table II. Quantum Yields for Butyrophenone[a] and *p*-Methoxybutyrophenone

Compd no.	Ketone	Solvent	Φ_{II}[b]	Φ_{cy}[c]	Φ_{tot}
6	$PhCOCH_2CH_2CH_3$	C_6H_6	0.34		0.40[d]
7	*p*-MeO-**6**	C_6H_6	0.095	0.007	0.102[e]
6		$(CH_3)_3COH$	0.86		1.00[d]
7		$(CH_3)_3COH$	0.087	0.007	0.094[e]
6		CH_3CN	0.81		0.90[d]
7		CH_3CN	0.007	<0.001	0.007[e]

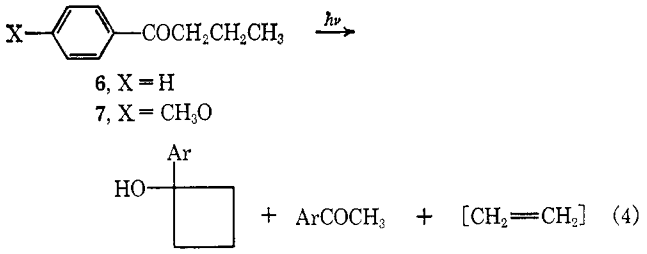
[a] Values from ref 20. [b] Quantum yield for acetophenone formation. [c] Quantum yield for cyclobutanol formation. [d] Loss of ketone. [e] Sum of product quantum yields.

Table III. Quantum Yields for α-Methoxybutyrophenones

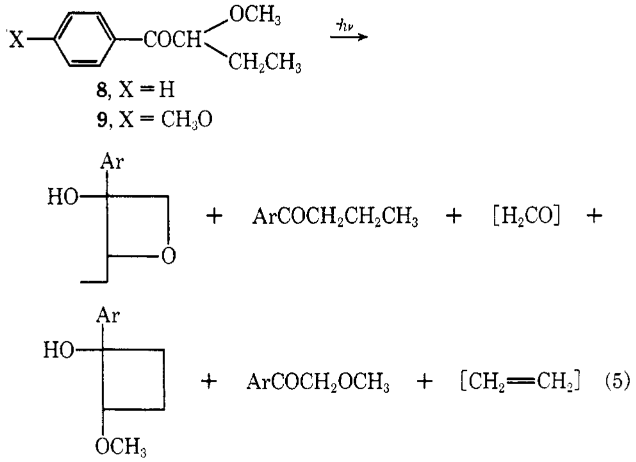
Compd no.	Ketone	Solvent	Φ_{BP}[a]	Φ_{cy}[b]	Φ_{MA}[c]	Φ_{tot}	Alkyl abs, %
8	$PhCOCH(OCH_3)CH_2CH_3$	C_6H_6	0.08	0.51	0.016	0.61	2.6
9	*p*-MeO-**8**	C_6H_6	0.16	0.60	0.012	0.83	1.5
8		$(CH_3)_3COH$	0.18	0.43	0.009	0.62	1.5
9		$(CH_3)_3COH$	0.37	0.48	0.014	0.88	1.6
8		MeCN	0.11	0.37	0.013	0.49	2.6
9		MeCN	0.12	0.61	0.001	0.73	0

[a] Quantum yield for butyrophenone formation. [b] Quantum yield for 3-oxetanol formation. [c] Quantum yield for α-methoxyacetophenone formation.

Quantum yields for elimination and cyclization product formation were also determined for *p*-methoxybutyrophenone (**7**) (eq 4) and are compared with literature results[20] for butyrophenone[22] (**6**) in Table II. Our results are in accord with the previous report[8] that **7** is photostable in acetonitrile, but reactive in nonpolar solvents. The quantum yield for acetophenone formation from butyrophenone[22] in benzene was found to be independent of per cent conversion from 0.6 to 10%.[22,23]



The reactivity of the n,π* carbonyl excited state toward intramolecular alkoxy *vs.* alkyl γ-hydrogen abstraction was determined for the α-methoxybutyrophenones **8** and **9**. The two possible elimination products and one cyclization product resulting from alkoxy hydrogen abstraction were the only products observed by glpc analysis for 5% conversion. Prolonged irradiation led to formation of acetophenone by a second type II from the primary photoproducts. Isolation of the 2-ethyl-3-phenyl-3-oxetanol by preparative glpc followed by nmr analysis showed the presence of only one, presumably the more stable *trans* isomer. The quantum yields are given in Table III. Alkyl abstraction accounts for 1.5–2.6% of the products except for **9** in acetonitrile where no alkyl abstraction is observed. Unusually large amounts of 3-oxetanol are observed under all conditions.



Rate Constants. Aralkyl ketones **1–9** were degassed and photolyzed in parallel in several solvents containing varying amounts of piperylene at 3130 Å to <15% maximum conversion. Relative quantum yields of elimination and/or cyclization products were determined by glpc analysis. Stern–Volmer treatment (plots of Φ_0/Φ *vs.* [quencher]) of the quenching data gave linear plots of slope $k_q\tau$, where k_q is the rate constant for quenching of the ketone triplet by piperylene and τ is the ketone triplet lifetime. Stern–Volmer slopes for **1** were the same for 6, 9, or 15% maximum conversion in benzene. Assumption of k_q values allows calculation of τ or $1/\tau$ values. Table IV gives the observed $k_q\tau$ values and calculated $1/\tau$ values. For **1–5**, **8**, and **9** identical Stern–Volmer slopes were obtained for quenching of both 3-oxetanol and acetophenone. A typical plot is shown in Figure 1. Stern–Volmer slopes varied by at most a factor of 2 for a given ketone in the different solvents; however, since k_q values are calculated from the Debye formula, larger differences in $1/\tau$ result when

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(22) The kinetics of type II photoelimination from 2-pentanone appears to be sensitive to per cent conversion: C. H. Bibart, M. G. Rockley, and F. S. Wettack, *J. Am. Chem. Soc.*, **91**, 2802 (1969).

(23) It was noted that the kinetics for type II elimination from 2-hexanone was not very sensitive to per cent conversion.[22]

Table IV. Quenching Constants in Different Solvents

Compd. no.	Ketone	C_6H_6 $k_q\tau$	C_6H_6 $1/\tau$,[a] sec^{-1}	$(CH_3)_3COH$ $k_q\tau$	$(CH_3)_3COH$ $1/\tau$,[a] sec^{-1}	CH_3CN $k_q\tau$	CH_3CN $1/\tau$,[a] sec^{-1}
1	$PhCOCH_2OCH_3$	1.6	3.2×10^9	2.3	1.0×10^9	1.2	9.2×10^9
2	$PhCOCH_2OCH_2CH_3$	0.60	8.4×10^9				
3	$PhCOCH_2OCH(CH_3)_2$	0.61	8.2×10^9				
4	*p*-MeO-**1**	42	1.2×10^8			39	2.8×10^8
5	*p*-CF_3-**1**	0.75	6.7×10^9			0.54	2.0×10^{10}
6	$PhCOCH_2CH_2CH_3$	670	7.5×10^6	770	3.0×10^6	780	1.4×10^7
7	*p*-MeO-**6**	1.0×10^4	5.0×10^5	2.1×10^4	1.1×10^5	0.75×10^4	1.5×10^6
8	$PhCOCH(OCH_3)CH_2CH_3$	6.5	7.7×10^8			8.4	1.3×10^9
9	*p*-MeO-**8**	120	4.2×10^7			180	6.1×10^7

[a] Values for the quenching rates were taken as[17] C_6H_6, 5×10^9 M^{-1} sec^{-1}; $(CH_3)_3COH$, 2.3×10^9 M^{-1} sec^{-1}; CH_3CN, 11.0×10^9 M^{-1} sec^{-1}.

these values are used. The presence of a β-oxygen has a strong rate-enhancing effect as is seen by comparison of $1/\tau$ for **1** and **6**. Electron-releasing *p*-methoxy groups decrease the rate constants by more than an order of magnitude while a *p*-trifluoromethyl group increases the rate constant. Stern–Volmer plots for **1**, **4**, and **5** are shown in Figure 2. Use of fumaronitrile in place of piperylene as a quencher for **1** gave a value of $k_q\tau = 2.0$ in benzene.

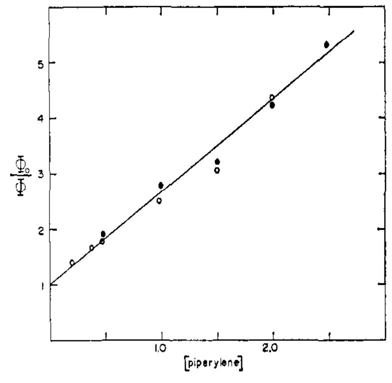


Figure 1. Stern–Volmer plots for quenching of acetophenone (○) and 3-oxetanol (●) formation from α-methoxyacetophenone in benzene.

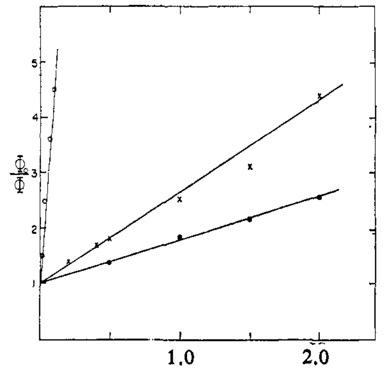


Figure 2. Stern–Volmer plots for quenching of acetophenone formation from α-*p*-dimethoxyacetophenone (○), α-methoxyacetophenone (×), and *p*-trifluoromethyl-α-methoxyacetophenone (●) in benzene.

Photoreduction. The rate of photoreduction of butyrophenone by benzhydrol (0.05–0.2 *M*) in several solvents was determined from a plot of $1/\phi$ for benzophenone formation *vs.* 1/[benzhydrol]. Linear plots were obtained with intercept/slope = $k_{ab}\tau$, where k_{ab} is the rate of hydrogen abstraction by triplet butyrophenone. A typical plot is shown in Figure 3. The results are given in Table V. Using the values of τ from Table IV, k_{ab} values can be obtained. In each solvent the slope and intercept values are nearly identical and thus differences in k_{ab} are due to assumed differences in τ. Photoreduction products from butyrophenone were not isolated.

Table V. Kinetic Data for Photoreduction of Butyrophenone by Benzhydrol

Solvent	Slope	Intercept	$k_{ab}\tau$	k_{ab}, l./mole sec
C_6H_6	1.28	2.5	2.0	1.5×10^7
$(CH_3)_3COH$	1.15	2.2	2.0	0.6×10^7
CH_3CN	1.30	2.6	1.9	2.8×10^7

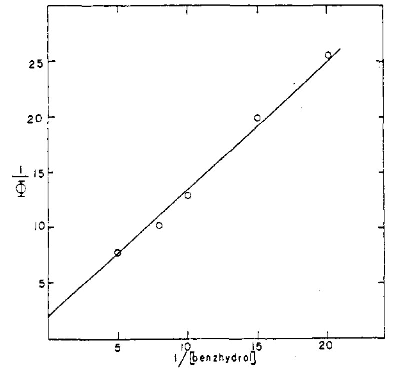


Figure 3. $1/\Phi$ plot for the photoreduction of butyrophenone in *t*-butyl alcohol.

Photoreduction of α-*t*-butoxyacetophenone (**10**) in isopropyl alcohol was studied to provide a model for the triplets of the α-alkoxyacetophenones. **10** is photostable at 3130 Å in benzene solution. In either neat isopropyl alcohol or isopropyl alcohol–benzene, **10** is reduced to give acetone (Φ = 0.40 in neat isopropyl alcohol) and approximately equal amounts of acetophenone and *t*-butyl alcohol (eq 6). Quenching of acetone formation by added piperylene and Stern–Volmer analyses give the rate constant for intermolecular

$$\underset{\mathbf{10}}{PhCOCH_2OC(CH_3)_3} \xrightarrow[(CH_3)_2CHOH]{h\nu} (CH_3)_2CO + PhCOCH_3 + (CH_3)_3COH \quad (6)$$

photoreduction, $k_{ab} = 4 \pm 1 \times 10^5$ l./mole sec, and the rate constant for deactivation of triplet, $k_d = 8 \pm 1 \times 10^6$ sec^{-1}. The quantum yield for intersystem crossing of **10** in benzene was found to be 1.0 ± 0.1.

The photoreduction of *p*-methoxypropiophenone by 1.0 *M* isopropyl alcohol–benzene was studied to provide a model for *p*-methoxybutyrophenone triplets. The values obtained were $k_{ab} = 2.6 \times 10^3$ l./mole sec and $k_d = 6.0 \times 10^5$ sec^{-1}. The photoreduction products were not isolated.

Absorption and Emission Spectra. The α-alkoxyacetophenones **1** and **4** have noticeably more diffuse emission in a nonpolar, ether–pentane (EP) glass at 77°K than do acetophenone or butyrophenone; however, some structure is observed and the spectra seem to possess $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ emission characteristics. In more polar solvents (EP + ethanol) emission from **1** and **4** becomes more diffuse than that from butyrophenone. Furthermore, the long lifetime emission from **4** has a shorter lifetime in EP (88 msec) than in EP + ethanol (204 msec). By contrast, acetophenone has a lifetime of 25 msec in EP. It can be concluded that the α-alkoxyacetophenones have somewhat more $^3(\pi,\pi^*)$ character than butyrophenone in rigid glasses. Barltrop[8] has found that *p*-methoxybutyrophenone (**7**) has a lowest $^3(n,\pi^*)$ state in a nonpolar glass, but has a lowest $^3(\pi,\pi^*)$ state in a polar glass. Ketones thought to have a lowest $^3(n,\pi^*)$ state have a low intensity ($\epsilon < 100$) long wavelength absorption maxima whereas those thought to have a lowest $^3(\pi,\pi^*)$ do not, for the limited number of aryl alkyl ketones studied.[8] The unsubstituted α-alkoxyacetophenones **1**, **2**, **3**, **8**, and **10** show normal n,π* absorption in nonpolar solvent (λ_{max} 323–340 nm (ϵ 56–80)) whereas the *p*-methoxy compounds **4** and **9** have higher molar absorptivities (ϵ_4 113, ϵ_9 190). In acetonitrile the α-alkoxyacetophenone n,π* absorption appears as a shoulder on the intense π,π* absorption. Thus, the absorption data support the conclusion that the α-alkoxyacetophenones have predominantly $^3(n,\pi^*)$ states with increasing $^3(\pi,\pi^*)$ character in polar solvents.

Discussion

Analysis of our results is best achieved in terms of the following generally accepted mechanism for aralkyl ketone photolysis where A is the ketone, Q a quencher, SH a hydrogen donor, B_3 is a triplet biradical formed

$$A_0 \xrightarrow{h\nu} A_1 \xrightarrow{k_{ST}} A_3$$

$$A_3 \xrightarrow{k_d} A_0$$

$$A_3 + Q_0 \xrightarrow{k_q} A_0 + Q_3$$

$$A_3 + SH \xrightarrow{k_{ab}} HA\cdot + S\cdot$$

$$A_3 \xrightarrow{k_r} Bi_3$$

$$Bi_3 \xrightarrow{k_{ST'}} Bi$$

$$Bi \xrightarrow{k_{-r}} A_0$$

$$Bi \xrightarrow{k_{II}} \text{acetophenone}$$

$$Bi \xrightarrow{k_{cy}} \text{cyclization}$$

directly from A_3, and Bi is the singlet biradical which decomposes to products. The singlet biradical is probably formed with unit efficiency ($\Phi_{ST'} = 1$) since return of the biradical to the ketone triplet should be a highly endothermic process (Figure 4). The quantum yield for the formation of Bi becomes, in the absence of quencher or hydrogen donor

$$\Phi_{Bi} = \left(\frac{k_r}{k_r + k_d}\right)\Phi_{ST}$$

where Φ_{ST} is the quantum yield for triplet formation. The quantum yield for type II (cyclization and fragmentation) products is

$$\Phi_{tot} = \Phi_{Bi}\left(\frac{k_{II} + k_{cy}}{k_{II} + k_{cy} + k_{-r}}\right)$$

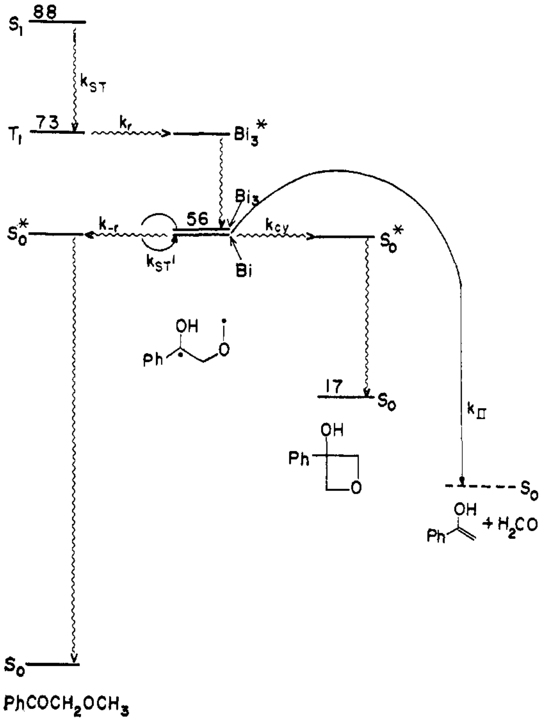
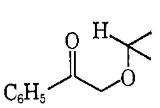


Figure 4. Energy level diagram for α-methoxyacetophenone, the biradical intermediate, and photoproducts. See the Appendix for the method of calculation and the assumptions involved. Energies in kcal/mole.

It is assumed that only the triplet state is involved in the intramolecular reactions of aromatic ketones due to their rapid rate of intersystem crossing ($k_{ST} \sim 10^{10}$ for acetophenone[21]) and because Stern–Volmer plots of quenching of aromatic ketones do not level off at high concentration of quencher.[5] However, for **2**, **3**, and **5**, $1/\tau$ has a value comparable to k_{ST}. Although Φ_{ST} was found to be 1.0 ± 0.1 for **10** by the triplet counting method, this does not rule out intramolecular singlet reaction since piperylene should not efficiently quench the short-lived singlets of **1**–**5**.[22] The fact that Stern–Volmer plots for both quenching of elimination and cyclization by piperylene are linear and superimposable to both (a) high piperylene concentration (3 *M*) and (b) extent of quenching (>70%) is the best evidence that both reactions proceed through a common triplet state.

In view of previous results on photoelimination reactions the results on α-alkoxyacetophenones **1**–**3** are unusual in several respects: (a) remarkably rapid reaction rates, (b) high quantum yields in benzene, (c) high yield of cyclization product, (d) inverse solvent effect on quantum yield relative to butyrophenone. The intramolecular rate constant for **1** (3.2×10^9 sec^{-1}) is much faster than for butyrophenone (7.5×10^6 sec^{-1}). An ether oxygen lowers the bond dissociation energy for C–H homolysis relative to methylene. For example for $\mathrm{H_3CCH_2CH_2}\!\wr\!\mathrm{H}$, $\Delta H = 98$ kcal/mole[24] and for $\mathrm{H_3COCH_2}\!\wr\!\mathrm{H}$, $\Delta H = 91$ kcal/mole.[25] However, if stabilization of the biradical alone accounted for the rate increase, **3** and **11** should have essentially the same rate constant. Wagner[6] has determined $1/\tau$ for **11** to be 7.0×10^8 sec^{-1}, more than an order of magnitude slower than **3**. The possibility that the ether oxygen has an activating effect on the carbonyl group is unlikely in view of the emission of **1** and **4** at 77°K which has more π,π^* character than that of butyrophenone. A more plausible explanation is that the ether oxygen lowers the entropy requirements for the formation of the six-membered transition state necessary for hydrogen abstraction. This is reasonable in view of the small activation energy for butyrophenone photoelimination.[8,9] It should be pointed out that the enhanced rate for α-alkoxyacetophenones relative to aryl alkyl ketones is also consistent with a concerted reaction in which product formation from the excited ketone triplet yields an excited triplet carbonyl compound (see Figure 4, however).



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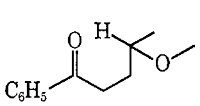

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The relative rate constants for **1**–**5** in benzene solution are easily rationalized on the basis of structural considerations. Abstraction of a secondary or tertiary hydrogen occurs more readily than for a primary hydrogen. An electron-withdrawing *p*-trifluoromethyl increases the rate of abstraction by a factor of 2, probably increasing the n,π^* character of the triplet state. A *p*-trifluoromethyl group was found to increase the rate of acetophenone photoreduction by a factor of 7.[13] An electron-donating *p*-methoxy group decreases the rate constant by a factor of 25, presumably due to increased π,π^* character of the triplet state. A similar decrease (15-fold) is observed for substitution of a *p*-methoxy group on butyrophenone (Table IV). It is interesting to note that the *p*-methoxy group does not lower the quantum yield for α-methoxyacetophenone (Table I) as it does for butyrophenone (Table II) or for valerophenone.[17] This is reasonable, for as long as $k_r \gg k_d$, no decrease in the quantum yield should accompany the decrease in k_r. The fact that $1/\tau$ for **2** and **3** are virtually identical while $1/\tau$ for secondary and tertiary aryl alkyl ketones differ by a factor of 6 indicates that we may be near the upper limit for the rate of γ-hydrogen abstraction. The small difference in selectivity for primary *vs.* secondary *vs.* tertiary abstraction (1:8:12)[26] relative to aryl alkyl ketones (1:28:180)[6,7] parallels the selectivities of *t*-butoxy radicals toward intermolecular abstraction of alkoxy (1:3.7:4.3) *vs.* alkyl (1:13:68)[27] hydrogens and is indicative of the greater ease of abstraction of alkoxy hydrogens relative to alkyl hydrogens.

The quantum yields of **1**–**3** in benzene are nearly unity (Table I) as opposed to values of less than 0.5 for butyrophenones. Quantum yields of unity are consistent with totally efficient biradical formation ($k_r \gg k_d$) in accord with $k_d = 8 \pm 1 \times 10^6$ sec^{-1} measured for α-*t*-butoxyacetophenone. Also, biradical reaction must be faster than reversal to starting ketone ($k_{II} + k_{cy} \gg k_{-r}$). Wagner has postulated that the inefficiency for butyrophenones is due to competition of biradical reversal with reaction.[17]

Clearly the factors which govern the reactions of the 1,4-biradicals generated by type II hydrogen abstraction are not well understood. Whereas elimination is the predominant (>80%) reaction for dialkyl and aryl alkyl ketones, 3-oxetanol formation accounts for as much as 61% of the biradical products from α-alkoxyacetophenones. Wagner[6] claims that cyclization from aralkyl ketones decreases going from primary > secondary > tertiary, thus paralleling the increase in free-radical disproportionation:coupling ratios.[28] However, more accurate determination of cyclobutanol yields by Barltrop[8] together with the results in Table I clearly belies such a generalization. The decrease in cyclization relative to disproportionation for the tertiary radicals could be due to steric considerations. The unfavorable *cis*-1,2-phenylmethyl interaction necessary in the 3-oxetanol from **3** can be avoided in **2**. Both **2** and valerophenone[17] preferentially form the *trans*-cyclization products which indicates steric requirements are significant for cyclization. A small solvent effect resulting in less cyclization in polar solvents analogous to that observed by Wagner[17] for valerophenone is observed. Also, the *trans*:*cis* ratio for the 3-oxetanols decreases from 10:1 to about 4:1 in polar solvents. Both results are consistent with the interpretation that increased solvation or hydrogen bonding to the biradical makes cyclization more difficult because of steric factors.

The most puzzling aspect of the results in Table I is the twofold decrease in total quantum yield in polar solvents. This is the reverse of the effect observed for dialkyl and aralkyl ketones. A much smaller inverse solvent effect on quantum yield is observed for *p*-methoxy-α-methoxyacetophenone (**4**) and none at all on *p*-trifluoromethyl-α-methoxyacetophenone (**5**). The solvent effect could be due to either decreased efficiency of biradical formation (k_d *vs.* k_r) or decreased efficiency of product formation by the biradical (k_{-r} *vs.* $k_{II} + k_{cy}$). The former explanation could be the result of increased $^3(\pi,\pi^*)$ character in polar solvents. Emission studies on **1** and **10** showed an increase in the lifetime of the long-lived component of the emission in polar solvents; however, the general structure of the emission was not substantially changed and was still predominantly (n,π^*) in character. Increased $^3(\pi,\pi^*)$ character in polar solvents in the case of **4** results in a large decrease in rate constant with no decrease in quantum yield, the exact opposite of the solvent effect on **1**–**3**. Increased $^3(\pi,\pi^*)$ character would also be expected to *decrease* k_d rather than increase it. For example, photoreduction studies yield a value $k_d = 1.6 \times$

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[24] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[25] L. F. Loucks and K. J. Laidler, *Can. J. Chem.*, **45**, 2785 (1967).

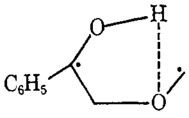
[26] Normalized to allow for the number of abstractable γ-hydrogens.

[27] C. Walling and M. J. Mintz, *J. Am. Chem. Soc.*, **89**, 1515 (1967).

[28] S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Soc.*, **16**, 412 (1965).

10^6 for acetophenone and 1.6×10^5 for *p*-methylacetophenone which is believed to possess more $^3(\pi,\pi^*)$ character in its triplet state than acetophenone.[13] Thus, solvent shifting of $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states cannot account for the solvent effect. Finally, any explanation that requires k_d values over 10^9 is untenable in view of present knowledge of decay rates for aryl alkyl ketones (*e.g.*, k_d values for acetophenone, **10**, and 4-methoxypropiophenone are all *less* than 10^7 sec^{-1}).

We are left then with the alternative explanation that the solvent effect on quantum yield is due to increased efficiency of return of the biradical intermediate to starting ketone in polar solvents. Wagner[17] has suggested that hydrogen bonding of the biradical hydroxyl proton in polar solvents should impede back-transfer to the γ-carbon and thus decrease k_{-r} relative to k_{II} and k_{cy}. Hydrogen bonding is more complicated for the α-alkoxyacetophenones due to the presence of the internal ether oxygen. It is possible that in nonpolar solvents the hydroxyl proton is internally hydrogen bonded to the ether oxygen, thus preventing back transfer to the γ-carbon. Intramolecular hydrogen bonding in vicinal hydroxy ethers is moderately strong as long as geometrical restrictions do not prevent coplanarity.[29] Such an intermediate (**12**) could also account for the high yield of 3-oxetanol. In polar solvents, intermolecular hydrogen bonding would compete with the intramolecular bonding to the ether oxygen as well as tie up hydroxyl protons and could thus occur with unpredictable results. Clearly the situation is more complex than for aryl alkyl ketone derived biradicals so that a different biradical solvent effect is not surprising.



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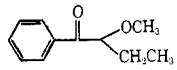
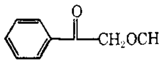
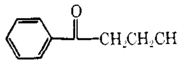
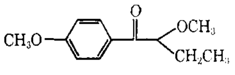
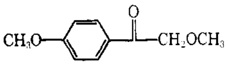
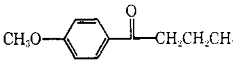
Another example of an inverse solvent effect has been reported by Barltrop[8] for *p*-methoxybutyrophenone (**7**); however, quantum yields and rate constants were not reported. Our results for **7** are compared with those for **6** in Table II and confirm the dramatic (>tenfold) decrease in quantum yield upon going from benzene or *t*-butyl alcohol to acetonitrile. Purification of acetonitrile did not alter the result. Furthermore, no increase in $k_q\tau$ (Table IV) is observed in acetonitrile relative to the other solvents. Thus, if a crossover from $^3(n,\pi^*)$ to $^3(\pi,\pi^*)$ lowest state occurs in acetonitrile, no increase in τ accompanies the decrease in quantum yield—the same result as observed for the α-alkoxyacetophenones.

In order to disentangle some of these solvent and structural effects, compounds **8** and **9**, which possess some of the essential features of both α-alkoxyacetophenones and butyrophenones, were investigated. From the quantum yields in Table III it is obvious that alkoxy hydrogen abstraction is much more rapid than alkyl abstraction, in accord with the results for the isolated molecules **1** and **6**. From the per cent alkyl abstraction and the assumption that biradical formation leads to products ~40% of the time in benzene and ~80% of the time in acetonitrile[20] for alkyl abstraction, rate constants for alkyl abstraction from **8** and **9** can be estimated and are given in Table VI. The rate constants estimated for alkyl abstraction by **8** and **9** are abstraction rates (k_r) and not reciprocal lifetimes ($1/\tau$) as no k_d term is contained in the rate constant. The consideration of k_d is only important when $k_d \gtrsim k_r$ as is apparently the case for **9** in acetonitrile in view of the 20-fold difference between k_r for alkyl abstraction from **9** and $1/\tau$ for **7**. Otherwise, for both **8** and **9** alkoxy abstraction is slightly slower and alkyl abstraction slightly faster than in the isolated molecules. Thus, it can safely be concluded that the rate enhancement effect of the β-oxygen is not due to strong perturbation of the carbonyl. The quantum yields for **8** and **9** (Table III) are interesting on two accounts. First, 2-ethyl-3-aryl-3-oxetanol is the major product in all cases. As the biradical will be formed with aryl and ethyl groups *trans*, the steric effect appears to enhance ring formation rather than retard it. Second, the quantum yield for alkyl abstraction from **9** drops markedly in going from benzene and *t*-butyl alcohol to acetonitrile and the total quantum yield for both **8** and **9** shows a similar solvent effect.

Table VI. Rate Constants for Alkoxy *vs.* Alkyl Abstraction

Compd no.	Ketone	C_6H_6, $1/\tau$ sec^{-1}	CH_3CN, $1/\tau$ sec^{-1}
8		7.7×10^8 5.0×10^7	1.3×10^9 4.2×10^7
1		3.2×10^9	9.2×10^9
6		7.5×10^6	1.4×10^7
9		4.2×10^7 1.6×10^6	6.1×10^7 7.5×10^4
4		1.2×10^8	2.8×10^8
7		5.0×10^5	1.5×10^6

There are two possible explanations for the effect of solvent upon quantum yield for **7** and for alkyl abstraction from **9**. Either (a) the carbonyl triplet state is equally reactive in polar and nonpolar solvents but biradical deactivation competes with reaction in acetonitrile or (b) the carbonyl triplet state is less reactive in acetonitrile so that triplet decay competes with biradical formation. In case a, all inefficiency is in the biradical decomposition step and therefore $1/\tau = k_r^a$. In the second limit (case b) radiationless decay of the triplet competes with biradical formation ($1/\tau = k_r^b + k_d^b$). In this case $k_r^b = \Phi_{BR}(1/\tau)$. If the quantum yield for biradical formation (Φ_{BR}) is approximated by Φ_{II}/Φ_p, where $\Phi_p = \Phi_{II}$ for the unsubstituted ketone, then values for k_r and k_d may be estimated. This method and the assumptions have been discussed by Wagner.[6] The results are given in Table VII. For case a, we are forced to accept increased reactivity from the more π,π^* triplet in the polar solvent ($k_r^a = 1/\tau$), contrary to expectation. For case b, the decrease in Φ_{II} and Φ_{BR} in polar solvent is accompanied by the expected decrease in k_r. The value for k_r^b in acetonitrile is of the same

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[29] M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965).

order of magnitude as k_r for alkyl abstraction from **9** (Table VI). Also the k_d values derived in case b are in good accord with the value measured for the model compound *p*-methoxypropiophenone in 1 *M* isopropyl alcohol–benzene ($k_d = 6.0 \times 10^5$). In view of these results it is not surprising that no solvent effect on the quantum yield of **4** is observed. Since $1/\tau > 10^8$, k_d would not be expected to compete with biradical formation. Also it seems unlikely that the inverse solvent effect observed for **1**–**3** could be an example of case b as k_d values comparable to $1/\tau$ for **1**–**3** are without precedent.

Table VII. Kinetic Data for *p*-Methoxybutyrophenone Photoelimination (See Text)

Solvent	Φ_{II}	Φ_{BR}	k_r[a]	k_r[b]	k_d[b]
C_6H_6	0.10	0.27	5.0×10^5	5.0×10^4	4.5×10^5
CH_3CN	0.01	0.011	1.5×10^6	2.0×10^4	1.5×10^6

An interesting feature of the data in Table IV is the fact that although $k_q\tau$ values vary over four orders of magnitude for the ketones studied, the $k_q\tau$ values for a given ketone do not differ by more than a factor of 2 in the solvents studied. That is, *Stern–Volmer slopes are essentially solvent independent for the solvents studied.* The same result is observed by Wagner[17] for valerophenone quenching in benzene, *t*-butyl alcohol, and acetonitrile. The values of $1/\tau$ in Table IV are calculated by the usual method of assuming that k_q is the diffusion-controlled rate constant (k_{diff}) calculated from the Debye equation. The weakness of this assumption is illustrated by the fact that for benzene, the only solvent in which k_q for triplet energy transfer is well documented, the experimental value (5×10^9 l./mole sec) is below the calculated k_{diff} (1×10^{10} l./mole sec). Also, benzene and acetonitrile, which have almost identical viscosities, are assigned different k_q values. Furthermore, Wagner has shown that triplet quenching by piperylene is not diffusion controlled in solvents of low viscosity.[30]

Thus, by imposing questionable k_q values on similar $k_q\tau$ values the conclusion that τ is inversely dependent on solvent viscosity is reached. The alternative hypothesis, that τ is constant and that some factor other than diffusion-controlled quenching (in solvents of such similar viscosity) is rate determining, seems no less reasonable. Direct measurement of τ in various solvents, perhaps by flash photolysis, could resolve this question. In lieu of such results the solvent dependence for photoreduction of butyrophenone by benzhydrol was investigated. Butyrophenone was chosen since $k_q\tau$ values had been determined and the lifetime was long enough to allow competitive photoreduction. Benzophenone formation by hydrogen abstraction from benzhydrol occurs with the following quantum yield

$$\Phi = \Phi_{ST}\left(\frac{k_{ab}[A^3][RH]}{k_{ab}[A^3][RH] + (k_r + k_d)[A^3]}\right)(\beta)$$

where Φ_{ST} for butyrophenone is unity and β is the efficiency with which benzophenone is formed after hydrogen abstraction from benzhydrol. A $1/\Phi$ plot has

$$\frac{1}{\Phi} = \frac{1}{\beta}\left(1 + \frac{k_r + k_d}{k_{ab}[RH]}\right)$$

an intercept of $1/\beta$ and a slope of $1/\beta[(k_r + k_d)/k_{ab}]$. The resulting values for $k_{ab}\tau$ as well as for the slopes and intercepts (Table V) were the same within the experimental error for all three solvents. Thus $k_{ab}\tau$ as well as $k_q\tau$ is independent of solvent. Since energy transfer and photoreduction differ in rate by over two orders of magnitude it seems unlikely that both should show the same solvent dependence. More likely, τ is independent of solvent, and quenching and abstraction rates do not change in these solvents. Thus $1/\tau$ values such as those in Table IV should have less emphasis attached to them than the experimentally measured $k_q\tau$ values until better values for k_q are obtained.

In conclusion, solvent and substituent effects on the photochemistry of α-alkoxyacetophenones and related aryl alkyl ketones have been investigated. Whereas substituent effects which cause changes in $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states are reasonably well understood, solvent effects on triplet state lifetimes and reactivity are more difficult to interpret. Also, the extent of mixing or interaction between n,π^* and π,π^* states of similar energy is poorly understood. The assumption that triplet quenching is strictly diffusion controlled should be viewed with reservations. Finally, the factors which govern 1,4-biradical reactions remain largely undetermined.

Experimental Section

Preparation of Ketones. Butyrophenone (Eastman), *p*-methoxybutyrophenone (K & K), and *p*-methoxypropiophenone (Aldrich) were purified by preparative glpc or distillation prior to use. α-Methoxy-, α-ethoxy-, α-isopropoxy-, and α-*t*-butoxyacetophenone were prepared by the method of Newman and Beal[31] from α-diazoacetophenone[32] and the corresponding alcohol. α-Methoxy-*p*-trifluoromethylacetophenone (mp 50–51°) and α-*p*-dimethoxyacetophenone (mp 39–40°) were also prepared from the appropriate α-diazoacetophenone and methanol. α-Methoxybutyrophenone and α-methoxy-*p*-methoxybutyrophenone were prepared by the reaction of α-cyanopropyl methyl ether with phenylmagnesium bromide and *p*-anisylmagnesium bromide, respectively.[33] All ketones were purified by preparative glpc (5 ft × 0.25 in. 20% FFAP on Chromosorb W), and their structures confirmed by nmr and mass spectra. Analytical glpc showed all to be >98% pure.

Solvents and Materials. Benzene was spectrograde further purified by refluxing over phosphorus pentoxide and distillation. Acetonitrile was chromatoquality distilled from calcium hydride. *t*-Butyl alcohol was reagent grade distilled from LAH. Isopropyl alcohol (Fisher CP) was used as received. Benzhydrol (Matheson Coleman and Bell) was recrystallized twice from petroleum ether. Piperylene (Chemical Samples) was distilled prior to use.

Identification of Photoproducts. Benzene solutions (10 ml) containing 0.2–0.4 g of ketone were photolyzed for several hours with a 450-W Hanovia medium-pressure mercury vapor lamp through Pyrex. Preparative glpc on either a 5 ft × 3/8 in. column of 20% SE 30 on Chromosorb P or a 5 ft × 0.25 in. column of 20% FFAP on Chromosorb W at 150–180° was used to collect the acetophenones and 3-oxetanols. Acetophenones had nmr spectra identical with those of commercial samples. Nmr data for the 3-oxetanols are summarized in Table VIII.

Quantum Yields. Solutions 0.05–0.08 *M* in ketone and about 0.005 *M* in hexadecane in purified solvents were degassed and sealed in 10-mm O.D. Pyrex tubes. The tubes were then photolyzed on a merry-go-round apparatus at 23 ± 2° using a Hanovia 450-W medium-pressure mercury lamp and a potassium chromate filter solution to isolate 3130-A irradiation. Photolyses were carried to 10% or less conversion. The solutions were analyzed on an Aero-

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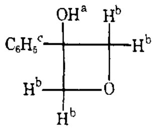
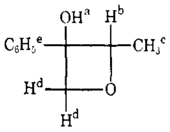
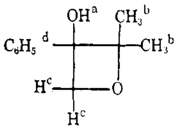
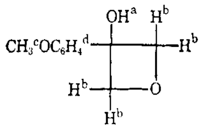
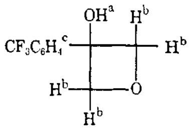
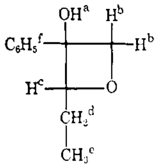
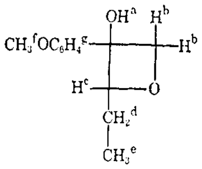
[30] P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).

[31] M. S. Newman and P. F. Beal, *ibid.*, **72**, 5161 (1950).

[32] M. S. Newman and P. F. Beal, *ibid.*, **71**, 1506 (1949).

[33] H. R. Henze, G. W. Benz, and G. S. Sutherland, *ibid.*, **71**, 2122 (1949).

Table VIII. Summary of Nmr Data for 3-Oxetanols

3-Oxetanol	τ, ppm
	a 6.25 (s), b 5.22 (s), c 2.6 (m)
	a 6.81 (s), b 5.11 (q, J = 7 Hz), c 9.56 (d, J = 7 Hz), d 5.36 (AB, J = 8 Hz), e 2.6 (m)
	a 7.20 (s), b 8.50 (s), c 6.05 (s), d 2.8 (m)
	a 6.28 (s), b 5.22 (s), c 6.22 (s), d 2.81 (A_2B_2, $\Delta\nu_{AB}$ = 40 Hz, $J_{AB} = J_{A'B'}$ = 9 Hz)
	a 6.40 (s), b 5.26 (s), c 1.90 (A_2B_2, $\Delta\nu_{AB}$ = 24 Hz, $J_{AB} = J_{A'B'}$ = 8 Hz)
	a 6.75 (s), b 5.39 (AB, J = 7 Hz), c 5.32 (t, J = 7 Hz), d 8.23 (q, J = 7 Hz), e 9.11 (t, J = 7 Hz), f 2.7 (m)
	a 6.75 (s), b 5.42 (AB, J = 7 Hz), c 5.37 (t, J = 7 Hz), d 8.24 (q, J = 7 Hz), e 9.12 (t, J = 7 Hz), f 6.22 (s), g 2.83 (A_2B_2, $\Delta\nu_{AB}$ = 35 Hz, $J_{AB} = J_{A'B'}$ = 9 Hz)

graph Hi-Fi 1200 gas chromatograph with a calibrated 5 ft × $^1/_8$ in. column of 4% QF-1 and 1% Carbowax 20M on Chromosorb G with temperature programming between 100 and 190°. Actinometers were photolyzed simultaneously. Either a butyrophenone secondary actinometer (Φ_{II} = 0.34)[6] or benzophenone–benzhydrol[34] or uranyl oxalate[35] actinometers were used. Each quantum yield was the average of three or more analyses of two or more solutions. Reproducibility for simultaneously irradiated samples was ±5% and the over-all accuracy of the reported values was ±10%.

Quenching Studies. Samples were prepared, degassed, and analyzed in the same way as for quantum yield determination except that varying amounts of piperylene were added to the solution. Four or more concentrations of piperylene, in addition to blanks containing no piperylene, were used for each Stern–Volmer plot. Linear least squares fits had standard deviations of <10% and repeated determinations agreed to within ±10%.

Photoreduction of α-*t*-Butoxyacetophenone. The rate constants for photoreduction and triplet deactivation of α-*t*-butoxyacetophenone were determined by piperylene quenching of photoreduction for 0.07 *M* solutions of ketone and 0.01 *M* dioxane internal standard in either 3.28 *M* isopropyl alcohol–benzene solution or neat (13.1 *M*) isopropyl alcohol. Degassed solutions containing varying amounts of piperylene were photolyzed at 3130 Å and analyzed for acetone formation by glpc on a 10 ft × $^1/_8$ in. column of 20% Carbowax 20M on Chromosorb P. Quantum yields were determined using uranyl oxalate actinometry. Preparative glpc on a 3 ft × 0.25 in. column of Carbowax 20M on Chromosorb P at 150° gave acetophenone and *t*-butyl alcohol (identified by their nmr spectra) as the only major products of photoreduction.

Photoreduction of *p*-Methoxypropiophenone. The photoreduction of 0.07 *M* ketone with 1.0 *M* isopropyl alcohol in benzene was quenched with piperylene (1 × 10^{-3} to 1 × 10^{-4} *M*). Benzophenone–benzhydrol actinometers were photolyzed simultaneously. Analysis for acetone by glpc using toluene as an internal standard was the same as for α-*t*-butoxyacetophenone reduction.

Photoreduction of Butyrophenone. Benzene, *t*-butyl alcohol, and acetonitrile solutions of 0.09 *M* butyrophenone and 0.002 *M* hexadecane internal standard containing 0.05–0.20 *M* benzhydrol were degassed and photolyzed at 3130 Å for 2 hr. Analysis for benzophenone formation employed the same glpc conditions as used for quantum yield determination. Blanks containing no benzhydrol served as actinometers.

Intersystem Crossing Ratio of α-*t*-Butoxyacetophenone. The method of Lamola and Hammond[36] was used. Degassed benzene solutions of 0.08 *M* α-*t*-butoxyacetophenone and 0.06 *M* benzophenone each 0.2 *M* in *trans*-piperylene were irradiated for 3 hr at 3130 Å. Analysis for piperylene isomerization was on a 12 ft × $^1/_8$ in. column of 20% silver nitrate on Chromosorb W (75%) and 25% ββ-oxy on Chromosorb W (25%). The value obtained was Φ_{ST} = 1.0 ± 0.1.

Spectra. Phosphorescence spectra were taken at 77°K using an Aminco-Bowman spectrofluorimeter with a phosphorescence attachment. Phosphorescence lifetimes were determined using a mercury Pen Ray lamp and a mechanical shutter. The decay of the emission was monitored by using an Amperex XP 1010 phototube and a Tektronix oscilloscope. Uv spectra were recorded on a Cary 14 and mass spectra on a Hitachi–Perkin-Elmer RMU-6D.

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Appendix

Heats of formation for α-methoxyacetophenone and its photoproducts were estimated by the method of Benson.[37] The heat of formation of the biradical was estimated from the heat of formation for the hydrol of α-methoxyacetophenone, the bond dissociation energies of the benzyl and methoxy C–H bonds, and the heats of formation of two hydrogen radicals. The dissociation energy of the benzyl bond was taken as 80 kcal/mole and the methoxy bond as 91 kcal/mole.[25] The heats of formation of the elimination products, acetophenone enol (~35 kcal/mole) and formaldehyde (31 kcal/mole), are not included in Figure 4 since heats (enthalpies) of formation are not an appropriate measure of the free energy change for a complex fission reaction which will have a very large positive entropy term. The position of the energy level for elimination products in Figure 4 is meant to indicate only that the elimination reaction is more exothermic than the cyclization reaction. The heats of formation of α-methoxyacetophenone, the biradical, and the 3-oxetanol are probably a valid measure of their relative free energies as entropy differences among these molecules are expected to be small. When the heats of formation of the photoproducts are taken into consideration, all of the singlet and triplet states of the products are above 90 kcal/mole relative to the ground state of α-methoxyacetophenone.

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(34) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).

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(36) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

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Therefore, the formation of electronically excited photoproducts is highly improbable, based on energetic considerations.

Similar calculations on butyrophenone and its photoproducts gave analogous results except that the biradical is 67 kcal/mole above the butyrophenone ground state. Formation of the biradical from butyrophenone triplet is thus calculated to be *exothermic* by several kilocalories per mole. This is not in accord with the experimental results of Pitts[9] and Barltrop;[8] however, it should be noted that these calculations do not take conformational factors into account.

The Photocycloaddition of Acetone to 1-Methoxy-1-butene. A Comparison of Singlet and Triplet Mechanisms and Singlet and Triplet Biradical Intermediates[1]

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Abstract: The photocycloaddition of acetone to *trans*-1-methoxy-1-butene (**2**) and *cis*-1-methoxy-1-butene (**3**) has been studied in detail. Four isomeric oxetanes (**4, 5, 6,** and **7**) are formed in good yield. Sensitized *cis–trans* isomerization of the butene also occurs. Kinetic analysis and quantum yield studies reveal that both acetone singlets and acetone triplets are involved in oxetane formation. The stereochemistry of the initial butene is partially retained in the isomeric oxetanes when acetone singlets attack **2** or **3**, but is almost completely scrambled when acetone triplets attack **2** or **3**. The rate constants for attack of acetone singlets or triplets on a given butene are nearly equal. In addition, the selectivity of attack is the same for attack by acetone singlets or triplets on C_1 and C_2 of a given butene. These results are interpreted in terms of reaction of acetone excited states on methoxybutene to yield singlet or triplet biradical intermediates, depending on the spin state of the attacking acetone molecule. Our results are considered in light of other work on oxetane formation and 1,4 biradicals, and the mechanism of sensitized *cis–trans* isomerization of **2** and **3** is briefly discussed.

The photocycloaddition of ketones to olefins (the Paterno–Buchi reaction)[4] to form oxetanes was discovered at the turn of this century.[5] Although development was slow, recent study has shown the reaction to be synthetically useful.[4] The reaction[4] is known to occur also with olefins and aldehydes, quinones, α-diketones, α,β-unsaturated ketones, α-keto esters, and acyl cyanides.

In general, triplet ketones are the chemically active species[4,6] in the Paterno–Buchi reaction, although cases are now known for which ketone singlets[7] initiate attack on the ethylene. For the case of electron-rich olefins (alkenes and alkoxylethylenes) the reaction is believed to involve electrophilic attack by the n,π^* triplet ketone state to generate preferentially the most stable of the possible biradical intermediates formed by addition of carbonyl oxygen to the carbon–carbon double bond.[8] These conclusions are derived from the following evidence: (a) the stereochemistry of the major oxetane adduct is predicted from Markovnikov addition (which generally also results in formation of the most stable biradical intermediate);[9] (b) the cycloaddition is retarded by triplet quenchers;[10] (c) ketones which undergo efficient photochemical reduction through the n,π^* triplet also add efficiently to olefins;[6a,11] (d) the stereochemistry of the oxetanes formed is scrambled and essentially the same mixture of isomeric oxetanes is formed starting with either *cis* or *trans* olefin.[7b]

During the last few years considerable effort has been directed toward the elucidation of the mechanism of photocycloaddition of aryl carbonyl compounds to olefins,[6] but relatively little quantitative work on the addition of alkyl ketones to olefins has been reported.

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(11) The use of photochemical efficiency (quantum yield) as a guide to excited state reactivity is particularly hazardous and often misleading as has been often pointed out: N. J. Turro, *J. Chem. Educ.*, **44**, 536 (1967).