

TYPE II PHOTOELIMINATION AND 3-OXETANOL FORMATION
 FROM α -ALKOXYACETOPHENONES^{*1}

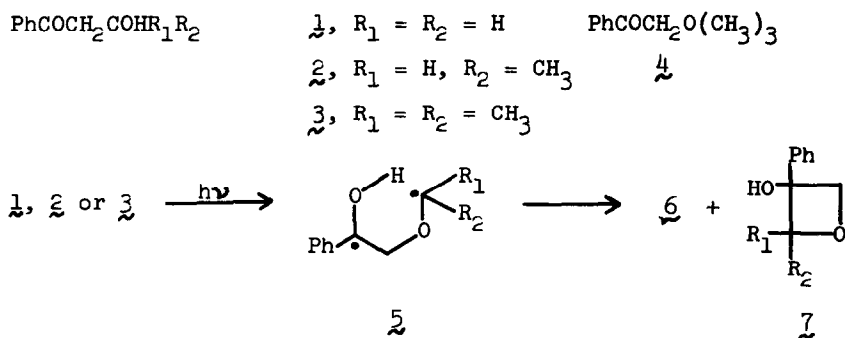
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(Received in USA 24 August 1968; received in UK for publication 16 October 1968)

The intramolecular abstraction of a γ -hydrogen by photoexcited aryl alkyl ketones has excited recent synthetic³ and mechanistic⁴ studies. Although γ -hydrogen abstraction is believed to be a primary photochemical process, the isolated products^{5,6,7} result from cleavage (Type II elimination) and cyclization of an intermediate biradical (e.g., **5**). We report here our relevant studies of the γ -hydrogen abstraction reactions of the α -alkoxyacetophenones **1**, **2** and **3** to yield acetophenone (**6**) and the alcohols **7**.



The following results (Table 1) are of interest and require explanation: (a) the quantum yields for **6** and **7** decrease from ~ 1.0 in C_6H_6 to ~ 0.45 in CH_3CN and $(\text{CH}_3)_3\text{COH}$; (b) the rate constants for formation of **6** and **7** are remarkably large when compared to those for acetophenones with alkyl side

* The authors thank the Air Force Office of Scientific Research AFOSR-68-1381 for their generous support of this work.

chains;⁶ (c) the quantum yields and rate constants for formation of 6 and 7 are essentially insensitive to starting ketone structure in a given solvent but the product ratio 6/7 depends significantly on both the solvent and starting ketone.

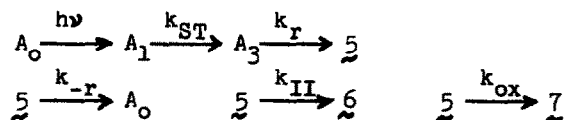
Table 1. Quantum yields^a for the formation of acetophenone and oxetanol from 1, 2 and 3.

Ketone	Solvent	Φ_{II}^b	Φ_{ox}^c	Φ_{tot}^e	$k_r \times 10^{-9} \text{sec}^{-1f}$
<u>1</u>	C ₆ H ₆	0.57	0.42	0.99	3.2
<u>2</u>	C ₆ H ₆	0.38	0.59 ^d	0.97	8.4
<u>3</u>	C ₆ H ₆	0.59	0.40	0.99	8.2
<u>1</u>	(CH ₃) ₃ COH	0.29	0.10	0.39	1.0
<u>2</u>	(CH ₃) ₃ COH	0.21	0.19 ^d	0.40	---
<u>3</u>	(CH ₃) ₃ COH	0.27	0.13	0.40	---
<u>1</u>	CH ₃ CN	0.40	0.10	0.50	9.2
<u>2</u>	CH ₃ CN	0.31	0.21 ^d	0.52	---
<u>3</u>	CH ₃ CN	0.23	0.10	0.43	---

(a) Average of two or more determinations at 3130 Å. Conversions 15% or less. Uranyl oxalate actinometry precision + 5%; (b) Quantum yield for acetophenone formation; (c) Quantum yield for oxetanol formation; (d) cis-trans-mixture; (e) Product yields were essentially identical to α -alkoxyketone loss; (f) Rate constant for intramolecular hydrogen abstraction obtained from linear Stern-Volmer plots using 1,3-pentadiene as quencher of acetophenone and oxetanol formation. Values for triplet quenching rates (K_q) were taken as:⁶ benzene, $5 \times 10^9 \text{sec}^{-1}$, (CH₃)₃COH, $2.3 \times 10^9 \text{sec}^{-1}$, CH₃CN, $11.0 \times 10^9 \text{sec}^{-1}$.

The photoreduction of 4 in isopropanol was studied in order to provide a model for the triplets of α -alkoxyacetophenones.⁸ The rate constant for intermolecular photoreduction⁹ is $4 \pm 1 \times 10^5$ l/mole-sec and the rate constant for deactivation of triplet 4 is $8 \pm 1 \times 10^6 \text{sec}^{-1}$. The quantum yield for photoreduction of 4 in neat isopropanol is 0.40 and Φ_{ST} was found to be 1.0 ± 0.1 . The phosphorescence emission spectra of both 1 and 4 at 77°K displays a longer lived and more diffuse structure than that of either 6 or butyrophenone.

The mechanism proposed for the Type II reaction of valerophenone⁶ may serve as a starting point for our analysis (A = 1, 2 or 3).



The extremely fast rate constants for intramolecular hydrogen abstraction may be due to stabilization of the transition state leading to $\underline{5}$ by the ether oxygen or lowering of the entropy requirements for the formation of the six-membered transition state necessary for hydrogen abstraction. Since $\Phi_{ST} \sim 1$ for $\underline{4}$ we shall assume the same situation obtains for $\underline{1}$, $\underline{2}$ and $\underline{3}$. Furthermore, using the triplet deactivation of $\underline{4}$ as a model for $\underline{1}$, $\underline{2}$ and $\underline{3}$ indicates that $k_d \ll k_r$. Thus the quantum yields for formation of $\underline{6}$ and $\underline{7}$ are

$$\Phi_{II} = \frac{\Phi k_{II}}{k_{II} + k_{ox} + k_{-r}} \qquad \Phi_{ox} = \frac{\Phi k_{ox}}{k_{II} + k_{ox} + k_{-r}}$$

Wagner⁶ proposed that biradical formation is totally efficient and that k_{-r} competes with k_{II} and k_{ox} in nonpolar solvents ($\Phi < 1$) but not in polar solvents ($\Phi \sim 1$) for valerophenone. Unless the ether oxygen of $\underline{1} - \underline{3}$ (relative to CH_2) plays a special role in binding the solvent, thereby lowering k_{II} and k_{ox} relative to k_{-r} , an alternative rationale for our results must be sought.

The emission spectra of $\underline{1}$ and $\underline{4}$ at 77°K suggest a substantial degree of interaction between the π, π^* and n, π^* states which indicates that these two states should be comparable in energy in polar solvents.¹⁰ Since π, π^* states are generally unreactive toward type II photoelimination, increased population of the π, π^* state should decrease the quantum yield for formation of $\underline{5}$ by decreasing the concentration of A_3 which may also explain the observation that the rate constant for hydrogen abstraction does not show an appreciable solvent effect, whereas the quantum yield does decrease markedly. It also explains the insensitivity of quantum efficiency to starting ketone structure in a given solvent since the concentration of n, π^* states should be nearly the same for $\underline{1}$, $\underline{2}$ and $\underline{3}$ and k_r is very fast in all three cases. However, a more dramatic change than observed in the slopes of our Stern-Volmer plots is ex-

pected on the basis of this mechanism. The sensitivity of the $\frac{6}{7}$ ratio to solvent and starting ketone structure may reflect changes in the transition states leading to the products. The decrease in cyclic products in polar solvents is attributed to increased steric interference⁶ for oxetanol formation due to hydrogen bonding of 5.

Leermakers¹¹ has shown that the quantum yield for disappearance of butyrophenone is maximized in moderately polar solvents, but decreases in highly polar solvents. Since the $n, \pi^* - \pi, \pi^*$ triplet splitting is less for α -alkoxyacetophenones than for aryl alkyl ketones, diminished reactivity is noticeable in moderately polar solvents. Finally, these results illustrate the hazards of relating reactivity with quantum yield when information about return processes (e.g. k_{-r}) is unavailable.

Acknowledgement. We are pleased to thank Mr. J.C. Dalton for helpful discussion of this work and for his help in obtaining emission spectra of 1 and 4.

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