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STERIC EFFECTS IN THE PHOTOREDUCTION OF ARYL ALKYL KETONES[1]

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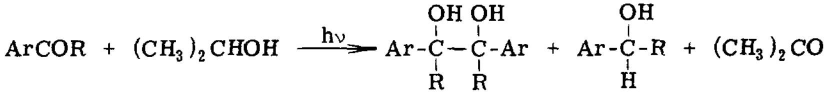
Although the photoreduction reactions of benzophenone,[2] acetophenone[3] and their aryl-substituted derivatives have been extensively studied, the analogous reactions of α-substituted acetophenones remain largely uninvestigated. Pronounced steric effects have been observed for ground state reductions of aryl alkyl ketones.[4,5] The rate of aryl alkyl ketone reduction by sodium borohydride is known to decrease with increasing α-substitution[4] whereas the opposite trend is observed for hydrogenation on palladium.[5] In view of the present lack of knowledge about steric effects on photoreductions and on photochemical reactions in general, it appeared interesting to investigate the photoreduction of a series of aryl alkyl ketones.

Photolysis of 1 - 3 in 2-propanol-benzene solvent resulted in the formation of acetone, a mixture of *dl* and *meso* pinacols, and the corresponding hydrol as the only detectable photoproducts (eq 1). Quantum yields for product formation depend on the initial 2-propanol concentration, but in all cases $\Phi_{(CH_3)_2CO} = \Phi_{pinacol} + \Phi_{hydrol}$ and the ratio of pinacol to hydrol remains constant.



$$\mathrm{ArCOR} + (CH_3)_2CHOH \xrightarrow{h\nu} \mathrm{Ar}-\overset{OH}{\underset{R}{C}}-\overset{OH}{\underset{R}{C}}-\mathrm{Ar} + \mathrm{Ar}-\overset{OH}{\underset{H}{C}}-R + (CH_3)_2CO \qquad (1)$$

1, $R = CH_3$ 2, $R = CH_2CH_3$ 3, $R = CH(CH_3)_2$ 4, $R = C(CH_3)_3$

Quantum yields determined in 2.0 M 2-propanol-benzene are given in Table I. In contrast to the behavior of 1 - 3, 4 gave no photoreduction products. The major product from 4 at low conversions is benzaldehyde ($\Phi = 0.13$), presumably formed by α-cleavage

TABLE 1. Quantum yields and kinetic data for aryl alkyl ketone photoreductions in 2-propanol-benzene.

Ketone	$\Phi_{(CH_3)_2CO}{}^a$	$\Phi_{pinacol}$	Φ_{hydrol}	k_r M^{-1} sec^{-1} ^{b}
1	0.35	0.34	0.007	7.5×10^5
2	0.23	0.19	0.033	4.4×10^5
3	0.12	0.071	0.049	1.3×10^5

[a] Quantum yielf for acetone formation at 3130 Å from degassed solutions of 0.1 M ketone in 2.0 M 2-propanol-benzene using benzophenone-benzhydrol actinometry. Average of two or more determinations, at conversions of less than 10%.

[b] Rate constant for hydrogen abstraction obtained from linear Stern-Volmer plots using 1,3-pentadiene as quencher of acetone formation. k_q was taken as 5×10^9 M^{-1} sec^{-1}. Limits of error ± 10%.

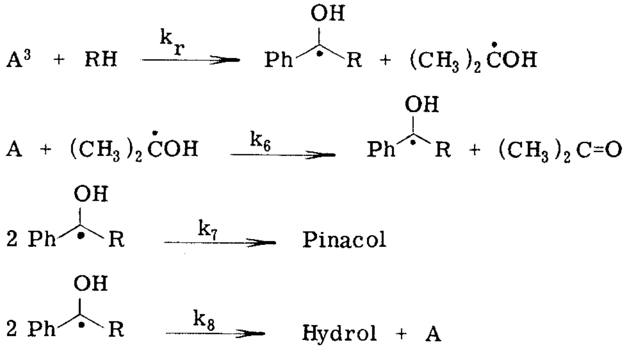
followed by hydrogen abstraction. Prolonged photolysis of 4 is reported to give hydrobenzoin *via* photoreduction of the initially formed benzaldehyde.[6]

The mechanism for photoreduction of 1 - 3 (A) by 2-propanol (RH) in the presence of added quencher (Q) can be described by the following equations.

$$A \xrightarrow{h\nu} A^1 \xrightarrow{k_{ST}} A^3 \qquad (2)$$

$$A^3 \xrightarrow{k_d} A \qquad (3)$$

$$A^3 + Q \xrightarrow{k_q} A + Q^3 \qquad (4)$$



$$A^3 + RH \xrightarrow{k_r} Ph\dot{C}(OH)R + (CH_3)_2\dot{C}OH \qquad (5)$$

$$A + (CH_3)_2\dot{C}OH \xrightarrow{k_6} Ph\dot{C}(OH)R + (CH_3)_2C{=}O \qquad (6)$$

$$2\ Ph\dot{C}(OH)R \xrightarrow{k_7} \text{Pinacol} \qquad (7)$$

$$2\ Ph\dot{C}(OH)R \xrightarrow{k_8} \text{Hydrol} + A \qquad (8)$$

$$\frac{1}{\Phi} = \frac{k_r[RH] + k_d}{k_r[RH]} + \frac{k_q[Q]}{k_r[RH]} \qquad (9)$$

Standard Stern-Volmer analysis (eq 9) for the variation in $1/\Phi$ with quencher concentration allows the calculation of k_r. Values for k_d obtained from the intercept of Stern-Volmer plots in 2 M 2-propanol-benzene are anomalously large due to the presence of a quenching impurity

TABLE 2. Quantum yields and kinetic data for aryl alkyl ketone photoreduction in 2 M 2,4-dimethyl-3-heptanol-benzene.

Ketone	Φ	k_r M^{-1} sec^{-1}
1	0.185	2.8×10^5
2	0.130	2.5×10^5
3	0.055	0.6×10^5

in commercial 2-propanol.[7] However, k_d values for 1 - 3 obtained from quenching plots in 0.1 M 2-propanol-benzene or from $1/\Phi$ vs $1/[RH]$ plots are the same within the experimental error ($k_d = 3 \pm 1 \times 10^5$ sec^{-1}) and are in agreement with the value for acetophenone obtained by phosphorescence decay measurements.[8] It is seen that the quantum yield for acetone formation and rate constant for hydrogen abstraction (k_r) decrease with increasing α-substitution, whereas there is no corresponding increase in the rate constant for triplet decay (k_d). That is, the decrease in reactivity does not result from a shortened triplet lifetime. Furthermore, ketones 1 - 4 all exhibit essentially identical characteristic n,π^* emission spectra[9] at 77° K in EPA glasses with all 0'-0 bands at 73.4 ± 1.0 kcal/mole. Thus the decrease in the rate constant for hydrogen abstraction in going from 1 to 3 is probably due to neither a change in triplet energy nor an increase in the π,π^* character of the excited state.

The simplest and most attractive explanation for the observed structural effect is that increased steric hindrance makes abstraction of a hydrogen from 2-propanol increasingly more difficult. Further evidence for a steric requirement for hydrogen abstraction by aryl alkyl ketones was obtained by employing 2,4-dimethyl-3-heptanol as the hydrogen donor. The resulting quantum yields for 2,4-dimethyl-3-heptanone formation and rate constants for hydrogen abstraction given in Table 2 reflect a substantial decrease in reactivity when compared to the 2-propanol results. The marked decrease in reactivity is most likely due to the increased steric requirements of the alcohol.[10]

The formation of both pinacol and hydrol products from 1 - 3 deserves comment. If we assume that the hydrol is formed by disproportionation of the ketyl radical (eq 8) rather than by disproportionation of the originally formed radical pair (eq 5),[11] then the hydrol to pinacol ratio reflects the relative rate constants for ketyl radical disproportionation (k_8) and combination (k_7). The increase in k_8/k_7 in going from 1 - 3 therefore is indicative of the increasing steric requirements for pinacol formation from the initially formed ketyl radical.

The rate constant for α-cleavage of 4 was determined by Stern-Volmer analysis of the quenching of benzaldehyde formation by added piperylene. The value obtained, $k_\alpha = 2.3 \times 10^7$ sec^{-1}, is two orders of magnitude greater than the rate constant for photoreduction of 3. Thus it is not surprising that photoreduction of 4 does not noticably compete with α-cleavage. The predominance of α-cleavage from 4 is analogous to the results observed for t-butyl alkyl ketones.[12]

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