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THE PHOTOCHEMICAL DECOMPOSITION OF α-DIAZOACETOPHENONE IN HYDROXYLIC SOLVENTS

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The photolysis of α-diazoacetophenone (I) in polar solvents is known to afford products derived from rearrangement of the carbon skeleton[1,2]. These products have been rationalized by assuming the intermediacy of a keto carbene which subsequently rearranges to a ketene[3]. Although the results strongly implicate the singlet keto carbene as the principal reactive intermediate in these rearrangements, alternate mechanisms may adequately explain the formation of the observed products. We now wish to present evidence which demonstrates conclusively that the singlet state is the reactive intermediate in the Wolff rearrangement.

Ultraviolet irradiation of a solution of α-diazoacetophenone in anhydrous methanol, utilizing a pyrex filter, gave methyl phenylacetate (63%) and trace amounts of acetophenone (<0.5%). When the photolysis was conducted in absolute ethanol, two components were detected by vapor phase chromatography and were shown to be ethyl phenylacetate (61%) and acetophenone (10%) by comparison with authentic material. The principal products from the direct photolysis of α-diazoacetophenone in iso-propanol were the i-propyl ester of phenyl acetic acid (57%) and acetophenone (23%).

$$PhCOCHN_2 \xrightarrow[ROH]{h\nu} PhCH_2CO_2R + PhCOCH_3$$

It was possible to generate the triplet keto carbene by selectively activating Michler's ketone in the presence of α-diazoacetophenone by using a uranium glass filter (cut-off 3300 A^{o}) so as to assure absorption of 99% of the light by the photosensitizer. Hammond has previously suggested that under these conditions the triplet keto carbene should be formed[4]. Energy transfer from Michler's ketone in the excited singlet

$$(p\text{-}Me_2NC_6H_4)_2CO \xrightarrow{h\nu} (p\text{-}Me_2NC_6H_4)_2CO^{*1} \rightsquigarrow (p\text{-}Me_2NC_6H_4)_2CO^{*3}$$

$$(p\text{-}Me_2NC_6H_4)_2CO^{*3} + PhCOCHN_2 \longrightarrow (p\text{-}Me_2NC_6H_4)_2CO + PhCOCHN_2^{*3}$$

$$PhCOCHN_2^{*3} \longrightarrow PhCOCH\uparrow\uparrow + N_2$$

state to ground state diazoacetophenone is endothermic and consequently does not compete with intersystem crossing of Michler's ketone from the singlet to the triplet state[4].

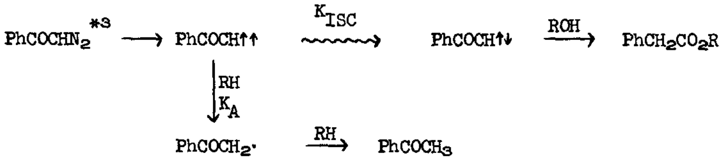
The sensitized photochemical decomposition of α-diazoacetophenone in i-propyl alcohol produced a species showing little tendency to undergo the Wolff rearrangement. The keto carbene generated by these conditions is relatively unreactive and exhibits radical properties as characterized by the large amounts of acetophenone. As is shown in Table I, the product distribution is markedly different from that found from the direct photolysis.

TABLE I

PRODUCTS OF REACTION OF KETO CARBENE FORMED
BY DIRECT AND SENSITIZED DECOMPOSITION OF I

	Direct			Photosensitized		
	MeOH	EtOH	i-PrOH	MeOH	EtOH	i-PrOH
$\frac{PhCH_2CO_2R}{PhCOCH_3}$	>300	5.9	2.5	7.3	1.1	<0.003

The fact that the over-all reaction of I in hydrogen donor solvents can be altered drastically by introducing a photosensitizer suggests that the singlet keto carbene is the precursor of the rearranged ketene. It is noteworthy, however, that the photosensitized decomposition of I in methanol and ethanol produced substantial amounts of the Wolff rearrangement. The process involving intersystem crossing of triplet keto carbene to the singlet state is endoenergetic and, as such, should not compete with hydrogen abstraction in a good hydrogen donor medium such as i-propyl alcohol (i.e. $K_{ISC} < K_A$). However, when methanol or ethanol is used as a hydrogen donor, abstraction of a hydrogen by the triplet becomes endothermic and, consequently, intersystem crossing of the triplet to the singlet may now compete with radical abstraction of hydrogen[5] ($K_{ISC} \sim K_A$).



$$\begin{tikzcd} \mathrm{PhCOCHN_2}^{*3} \arrow[r] & \mathrm{PhCOCH}\uparrow\uparrow \arrow[r, squiggly, "K_{ISC}"] \arrow[d, "\begin{array}{l}RH\\K_A\end{array}"] & \mathrm{PhCOCH}\uparrow\downarrow \arrow[r, "ROH"] & \mathrm{PhCH_2CO_2R} \\ & \mathrm{PhCOCH_2}\cdot \arrow[r, "RH"] & \mathrm{PhCOCH_3} & \end{tikzcd}$$

Alternatively, it might be reasoned that the excited triplet of I undergoes a competing intersystem crossing to a high vibrational level of ground state diazoacetophenone, which rearranges by way of a concerted mechanism. In view of the fact that collisional quenching of vibrationally ''hot'' molecules is the only process of appreciable probability in the condensed phase[6], we favor the scheme outlined above.

The results obtained from the direct photolysis of I can best be explained by assuming that the initially formed singlet diazoacetophenone is hydrogen bonded with the solvent. It could then decompose to a hydrogen-bonded singlet keto carbene which undergoes rearrangement. The amount of ester formed is related to the strength of the hydrogen bond which in turn can be correlated with the acidity of the hydrogen atom. As the strength of the hydrogen bond decreases, more intersystem crossing to the triplet occurs and larger amounts of acetophenone are formed.

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