Intramolecular Abstraction of Aldehydic Hydrogen by Ketone Triplets: Formation of 2-Hydroxy-2-phenylcycloalkanones

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Irradiation of 4-oxo-4-phenylbutanal (1) leads, *via* intramolecular abstraction of the aldehydic γ -hydrogen atom, to mixtures of acetophenone and 2-hydroxy-2-phenylcyclobutanone (2), and an abstraction rate constant of 8 ± 1 × 10⁸ s⁻¹, equal to the highest rate constant so far measured for a γ -substituted butyrophenone derivative has been obtained in steady state triplet quenching studies; the high reactivity of aldehydic hydrogen atoms toward abstraction is indicated further by an approximately 2 : 1 δ (aldehydic) : γ (methylene) abstraction preference in the case of the homologous compound 5-oxo-5-phenylpentanal (3), which affords 2-hydroxy-2-phenylcyclopentanone (4) as the major photoproduct.

The low dissociation energy of aldehydic carbon-hydrogen bonds [ca. 87 vs. ca. 92 kcal mol⁻¹ (1 kcal = 4.184 kJ) for tertiary carbon-hydrogen bonds]¹ indicates that aldehydes should be excellent internal hydrogen atom donors toward the $n \rightarrow \pi^*$ excited states of carbonyl compounds. However, since 1906, when Thiele and Bunther first described the photochemistry of *o*-phthalaldehyde,² only scattered reports have appeared which bear on this problem.³ As part of a systematic study of photochemical reactions involving the intramolecular abstraction of aldehydic hydrogen atoms, we report here on the photochemistry and kinetic behaviour of a prototypical example, 4-oxo-4-phenylbutanal (1) (Scheme 1).

4-Oxo-4-phenylbutanal (1) was prepared by the method of Larcheveque, Valette, and Cuvigny.⁴ Irradiation in benzene or moist acetonitrile at $\lambda > 290$ nm (Pyrex) afforded mixtures of acetophenone and 2-hydroxy-2-phenylcyclobutanone (2) in proportions which varied with the length of irradiation. At low conversions, cyclobutanone (2) was virtually the sole product, while prolonged irradiation led to acetophenone in essentially quantitative yield. Ketene, which presumably accompanies acetophenone formation, was not detected. Owing to its rather unstable nature, cyclobutanone (2) was characterized as its acetate, a known material.⁵ Independent photolysis of (2) in Pyrex afforded acetophenone as the sole detectable product. This explains the time dependence of the photoproduct ratio. Irradiation of keto-aldehyde (1) under conditions where the absorption of photoproduct (2) is very low (uranium glass filter, $\lambda > 340$ nm), leads to chemical yields of (2) of ca. 70% at complete conversion.

The quantum yield for the formation of 2-hydroxy-2phenylcyclobutanone (2) at 313 nm and <6% conversion is 0.30 in benzene and 0.40 in acetonitrile containing 2% water. Such increases in quantum yield with increasing Lewis basicity of the solvent are typical of the Norrish type II process of phenyl alkyl ketones, and have been attributed to retardation of reverse hydrogen atom transfer as the result of hydrogen bonding of the 1,4-biradical intermediate to the solvent.⁶ A further similarity between (1) and phenyl alkyl ketones was its behaviour in the presence of the triplet energy quencher 2,4-dimethylhexa-2,4-diene. Linear Stern–Volmer plots were obtained in benzene from which a $k_{a}\tau$ value of 5.63 dm³ mol⁻¹



Scheme 1



was calculated. Using a value of 5×10^9 dm³ mol⁻¹ s⁻¹ for the quenching rate constant, k_q , in benzene,⁷ and assuming that $\tau = 1/k_H$, a value for k_H , the γ -hydrogen atom abstraction rate constant, of $8 \pm 1 \times 10^8$ s⁻¹ is obtained. The larger than usual error in this number is due to imprecision in the gas chromatographic quantification of photoproduct (2).

Keto-aldehyde (1) thus undergoes γ -hydrogen atom abstraction with a rate constant equal to that of the most reactive substituted butyrophenone derivative, y-N, Ndimethylaminobutyrophenone $(8.0 \times 10^8 \text{ s}^{-1})$.⁸ This led us to predict that in 5-oxo-5-phenylpentanal (3), seven-membered transition state (δ) aldehydic hydrogen atom abstraction will be preferred to abstraction of the six-membered transition state methylenic (γ) hydrogen atom which should be *deacti*vated by the adjacent electron-withdrawing aldehyde group.9 This was shown to occur experimentally (Scheme 2). 5-Oxo-5phenylpentanal (3) was prepared by the method of Larcheveque, Valette, and Cuvigny,⁴ and photolysed through a uranium glass filter in benzene to afford an approximately 2:1 mixture of 2-hydroxy-2-phenylcyclopentanone (4) and acetophenone. It is interesting to speculate on what the upper limit to 'remote' aldehydic hydrogen atom abstraction might be. The answer to this question and the characterization of other aspects of this variant of the Norrish type II process are under active investigation.

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