The Photohydrolysis of Vinylic Esters

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RESULTS reported on the solution photochemistry of $\alpha\beta$-unsaturated ketones have indicated that addition reactions usually regarded as ionic may be facilitated by excitation of that chromophore.[1] We report here our results on the photohydrolysis of enol esters, specifically dimedone derivatives (I) in aqueous phosphate buffer solution, and preliminary studies of the mechanism of this process.

Certain dimedone derivatives were irradiated and the quantum yields of the disappearance of the starting material and appearance of enol† are listed in the Table. Isosbestic points were noted in the conversion, thus excluding the formation of absorbing intermediates other than transients.

These results indicate that irradiation of the dimedone derivative to its $S_1(n_1\pi^*)$ or $S_2(\pi_1\pi^*)$ state induced hydrolysis. The intervention of other intermediates was not excluded, and indeed on irradiation in the presence of 1·1M-acetone (94% of the light absorbed by the acetone) the methanesulphonate was hydrolysed with a quantum yield of 0·02. At these concentrations, energy transfer from singlet acetone seems improbable, and triplet–triplet energy transfer appears a more acceptable process.

TABLE

Quantum yields for ester hydrolyses

R	X	λ^a	pH[b]	$\Phi_{diss}{}^c$	Φ_{app}
H	OSO_2Me	235	5·32	0·04	0·03
H	OSO_2Me	235	5·91	0·03	0·02
H	OSO_2Me	313	7·00	0·03	0·03
Me	OAc	243	5·91	0·0045	0·003
H	Cl	245	5·91	0·0085	0·004

[a] The light source was a 200 w Osram high-pressure arc used in conjunction with a Bausch and Lomb 33-86-23 Monochromator.
[b] KH_2PO_4–Na_2HPO_4.
[c] Quantum yield of ester disappearance.
[d] Quantum yield of enol appearance. The reproducibility of the results was about ±10% except in the case of the acetate where it was near 50%.

Although this sensitised hydrolysis suggests that a triplet of dimedone is an intermediate,

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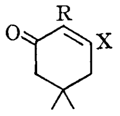
† The "dark" hydrolysis of dimedone enol acetate was too fast to allow determination of quantum yields but irradiation under similar conditions showed that hydrolysis could be accelerated by a factor of 2—3.

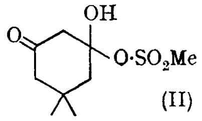
attempted quenching of the direct reaction with biacetyl [0·94 M; concentration of free biacetyl 0·22 M] was ineffective, which showed that such a triplet would be short-lived. The need for high quencher concentration in the quenching of the reaction of excited αβ-unsaturated ketones has been previously observed.[2] Further, the possibility of the intervention of other intermediates is not excluded.[3]

Irrespective of the nature of the excited state(s) involved, the most probable mechanism appeared to be overall addition of water to the ester to give the hemiketal (II) followed by ejection of the esterfying anion.

Such being the case, a comparable addition of water to cyclohexenone itself should be possible. This was found. On irradiation of cyclohexenone in phosphate buffer, a quantum yield of disappearance of 0·06 was observed, and on a preparative scale the structure of the ketol product was established by reduction to *trans*-cyclohexane-1,3-diol. It was also found that this addition could be sensitised with acetone (Φ = 0·06). These figures are close to those obtained for the methanesulphonate hydrolysis where collapse of the corresponding hemi-ketal would be expected to be the most efficient.



(I)



(II)

While the results cited appear to delineate the mechanism of hydrolysis, it is of permissive nature rather than compelling, and further evidence is being sought.

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[1] G. Bozzato, K. Schaffner, and O. Jeger, *Chimia (Switz.)*, 1966, **20**, 114; O. L. Chapman, J. B. Sieja, and W. J. Welstead, *J. Amer. Chem. Soc.*, 1966, **88**, 161; T. Matsuura and K. Ogura, *Bull. Chem. Soc. Japan*, 1967, **40**, 945; B. J. Ramsey and P. D. Gardner, *J. Amer. Chem. Soc.*, 1967, **89**, 3949.

[2] P. S. Eaton and W. S. Hurt, *J. Amer. Chem. Soc.*, 1966, **88**, 5038; unpublished results by M. Tchir and J.-P. Pete in these laboratories.

[3] See, for example, P. J. Kropp, *J. Amer. Chem. Soc.*, 1966, **88**, 4091.