Tetrahedron Letters No. 48, pp 4205 - 4206, 1974. Pergamon Press. Printed in Great Britain.

MECHANISTIC ASPECTS OF THE PHOTOCHEMICAL FORMATION OF α,β-UNSATURATED KETONES FROM THEIR OXIMES

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(Received in UK 7 October 1974; accepted for publication 17 October 1974)

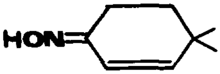
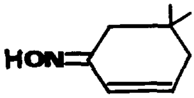
Ketone formation has been observed in the photolysis of the corresponding oximes$^{1)}$. In the case of α,β -unsaturated ketoximes it has - apart from E,Z isomerization - been shown to be the major or even exclusive reaction$^{2-5)}$. Two key points attract attention in this conversion: the formation of the carbon-oxygen bond and the fate of the nitrogen. The second point seems$^{2,6)}$ to be well established and is confirmed by our own results, as hydrazine - most probably via the intermediate diimide - is formed in the reaction. As for the first point, oxaziridines have been proposed as intermediates, although they have been merely invoked on the basis of subsequent reactions which are characteristic for these 3-membered heterocycles. The oxaziridine was suggested to give the ketone either directly$^{2)}$ or by dimerization followed by decomposition of an intermediate azo-compound$^{6)}$.

We investigated the photolysis (λ = 254nm) of the diastereoisomeric mixtures of 4,4- and 5,5-dimethyl-2-cyclohexenoneoxime in isooctane. In both cases the corresponding ketones an hydrazine were the only new products formed. The latter was identified by its reaction with p-dimethylaminobenzaldehyde$^{7)}$. The quantum yields for the disappearance of starting material increased with concentration (Table). This finding eliminates the possibilities of both a monomolecular conversion and the dimerization of the oxaziridine to give the enone, and rather suggests a bimolecular reaction step of either the excited oxime or the primary photoproduct (e.g., the oxaziridines, provided that these do not convert to any other products within our limits of detection) with the ground state oxime. In sensitized runs using 254nm light and acetone and benzene solutions, E,Z isomerization of the oximes (detected by nmr spectroscopy) was observed while ketone formation did not occur. Furthermore, the quantum yields were not affected by the presence of oxygen. This suggests that the ketone formation is likely to proceed from the excited singlet state of the oxime.

Table

UV-Data of Oximes and Quantum Yields for Disappearance (and Enone Formation)

(Isooctane, λ = 254nm, T = 25^{o})

Compound	UV		ϕ_{254}	
	λ_{max}	ε_{max}	c 8.10^{-3}mol/l	c 4.10^{-2}mol/l
	225	16600	2,4.10^{-2}	3,9.10^{-2}
	226	14700	2,9.10^{-2}	4,2.10^{-2}

Experimental: The oximes were prepared by the procedure of Montgomery$^{8)}$. The configurational isomers were not separated. The quantum yields were measured with an electronically integrating actinometer$^{9)}$ combined with vpc (5% SE 30 on chromosorb G-AW-DMCS at 140^{o}, internal standard: tetradecane).

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Financial support of the Fonds National Suisse de la Recherche Scientifique (grant no. 2.8220.73) is gratefully acknowledged.