Tetrahedron Letters No.34, pp. 4143-4148, 1966. Pergamon Press Ltd.
Printed in Great Britain.

PHOTOLYSIS OF OXIMES

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(Received 27 December 1965; in revised form 9 June 1966)

Recently, we reported on the photolysis of α,β-unsaturated aldoximes, which gave the corresponding nitriles (1). We now wish to report on the photolysis of ketoximes.

Irradiation of a 1% solution of cyclohexanone oxime in methanol in a nitrogen atmosphere gave caproamide, caprolactam and cyclohexanone(*1). The reaction was also carried out in iso-propanol (IPA). Product yields are summarized in Table I, as well as the effect of oxygen on the product distribution.

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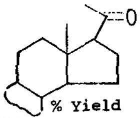
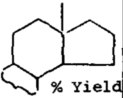
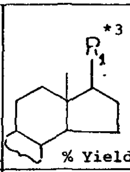
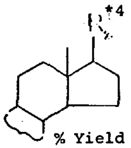
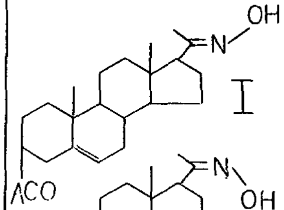
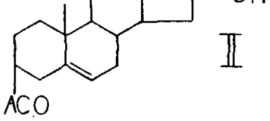
*1 The photoproducts were isolated by preparative g.l.c. and identified by comparison with an authentic sample. All irradiations were carried out in a quartz cell using lamps with peak energy at 2537A° (Rayonet Photochemical Reactor Model 1061) for two hours.

TABLE I Photolysis of Cyclohexanone Oxime

Conditions	Cyclohexanone % Yield	Cyclohexanone Oxime % Yield	Caproamide % Yield	Caprolactam % Yield
MeOH/N_2	3	28	5	46
MeOH/O_2	23	<1	<1	22
IPA/N_2	4	36	52	<1
IPA/O_2	4	9	6	5

Similar photochemical behaviour was also observed for a number of other saturated ketoximes, such as 3,3,5,5-tetramethylcyclohexanone oxime, coprastanone oxime, 17β-acetoxy-4,4-dimethylandrost-5-en-3-one oxime and pregnenolone oxime (I), which gave Beckmann type rearrangement products, cleavage products (amides), and ketones corresponding to starting material. Results for the anti- and syn-isomer of the latter are summarized in Table II. The photolysis in methanol, under a nitrogen atmosphere, of five-membered ring ketoximes such as camphor oxime and 3β-acetoxyandrost-5-en-17-one oxime proceeded extremely slowly and seemed to take a different course.

TABLE II*2

	 % Yield	 % Yield	 % Yield	 % Yield	Oxime Isomer % Yield
 I	16	40	24	13	4
 II	13	39	22	20	-

*2 Both irradiations were performed in methanol in a helium atmosphere. Yields are based on converted starting material, and were determined by g.l.c. for all compounds except the oximes. The oximes could not be detected by g.l.c. and the yield of II in the photolysis of I is therefore based on isolation from t.l.c.

*3 R_1 = $NHCOCH_3$

*4 R_2 = $CONHCH_3$

Irradiation of pregnenolone oxime (I) in ethanol and ethylene glycol gave results similar to those obtained in methanol. In anhydrous ether, dioxane-water, t-butanol and iso-propyl ether, the photolysis was very slow, and none of the above products were detected.

Irradiation of the oxime acetate of I did not give any cleavage or rearrangement product. All oximes were stable in the dark to the solvents used.

The photolysis in methanol of two α,β unsaturated ketoximes, testosterone oxime and pregna-5, 16-diene-3β-ol-20 one acetate oxime, was also investigated. In those instances, rapid syn-anti isomerization was observed, followed by slow and extensive decomposition.

The formation of Beckmann type rearrangement products by photolysis of oximes has but one precedent known to us. Amin and de Mayo (2) have reported that irradiation of benzaldoxime gives benzamide as one of the photoproducts. The photoreaction in methanol was in that case slow and the yield of benzamide was low.

Saturated oximes have an absorption maximum below 210 mμ (3) (probably π-π^*). No other maximum can be observed at longer wavelength. The primary photo-excitation step is therefore due either to a π-π^* or a highly forbidden n-π^* transition. If a n-π^* transition is responsible for the photoreaction, the absorption band must be below 300 mμ since irradiation with a long-wavelength lamp (300-400 mμ, peak energy at 350 mμ) gave no reaction.

Examination of the data summarized in Table I shows that the cleavage reaction leading to amide formation is suppressed by using oxygen, and strongly enhanced by using iso-propanol instead of methanol as a solvent. This indicates that the intermediate displays selectivity in abstracting hydrogen from solvent and is in all probability a biradical. Additional evidence for this can be adduced from the results in the pregnenolone oxime (I,II) photolysis, in which the cleavage reaction occurs preferentially to form the more stable alkyl radical.

The suppression of the cleavage reaction by oxygen can best be rationalized by postulating a triplet as an excited intermediate (4), although a singlet cannot be rigorously ruled out at this stage, in particular, since all attempts at photosensitizing the reaction have failed in our hands.

Further work to establish the scope of the reaction and its mechanism is in progress.

Acknowledgment

We wish to acknowledge financial support by the National Research Council of Canada, in form of grants-in-aid and Scholarships (M.D.).

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