PHOTOCHEMISTRY OF OXIMINOKETONES

PHOTOCHEMICAL TRANSFORMATIONS OF L-OXIMINOCYCLODODECANONE

A. Stojiljković and R. Tasovac Department of Chemistry, Faculty of Sciences, and Institute for Chemistry, Technology and Metallurgy, Beograd, Yugoslavia

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Numerous papers are dealing with the photoexcited states and modes of photoreactions of carbonyl group in different systems(1), but the photochemistry of ketones having an \measuredangle -oximino group has not been studied so far. On the other hand the photoreactions of only some oximino-compounds have been reported, ketoximes being found to undergo <u>syn-anti</u>-isomerization(2), the Beckmann type rearrangement and cleavage to carbonamides(3) with intermediate formation of oxaziridine(4), or to different cleavage reactions as in the case of camphoroxime(5). Therefore, it seemed of interest to study the photoreactions of oximinoketones, and in this paper we report, in preliminary form, on the photolysis of \measuredangle -oximinocyclododecanone.

 α -Oximinocyclododecanone(I), m.p. 74-75°C, was prepared in 80-90% yield by the oximation of cyclododecanone with methyl nitrite, and was characterized by its analysis (Found: C, 67.96; H, 10.05; N, 6.73. Calc. for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63%), i.r.(3260 cm⁻¹, 1660 cm⁻¹?, u.v., n.m.r. and mass spectra. The configuration of the oximino group of I was found to be <u>anti</u> to the carbonyl from the observed bathochromic shift from 233 to 284 mµ in alkaline media(6).

The irradiations were performed using a high pressure mercury Hanau lamp NK 6/20, under nitrogen, at a temperature of <u>oe</u> 18° C, in quartz immersion cell fitted with a cold water jacket. The solutions were 0.4% (g/ml) in I, about 250 ml being contained by the apparatus. The changes during photolysis

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were traced by TLC, and the irradiations were carried out until no further significant increase in photoproducts was noted.

Irradiation of a mechanically stirred solution of I (1 g) for 2 hrs afforded two photoproducts, while after 35 hrs of exposure the r.m. contained four products in addition to the starting material. The irradiations were interrupted after 45 hrs since no further variations in product composition were observed. Repeated experiments yielded photoproducts in more or less the same product ratio. Evaporation of the solvent in vacuo afforded a semisolid residue which was separated by column chromatography on silica gel using mixtures of ethyl acetate and cyclohexane as eluents. After removal of the unchanged starting material (I, 0.6 g), the first photoproduct (II) was collected (0.07 g) as white material, m.p. 50-52°C. Its analysis (Found: C, 68.35; H, 10.26; N, 6.70. Calc. for C12H21NO2: C, 68.21; H, 10.02; N,6.63%), i.r., u.v. and n.m.r. spectral characteristics permit the assignment of an isomerization product of I, namely that of the syn-isomer of I. This assignment is supported by the fact that II isomerizes easily on standing into I. The second photoproduct isolated (III, 0.12 g) was found to be a keto-nitrile of a molecular formula C₁₂H₁₉NO (Found: C, 74.47; H, 9.98; N, 7.2⁰. Calc. for C12H16NO: C, 74.57; H, 9.91; N, 7.21%)& Mol. wt. from mass spectrum:193. Further structure proof was provided by the hydrolysis of III into the corresponding keto acid (IIIa), by boiling with 10% potassium hydroxide (Found: C, 67.43; H, 9.87. Calc. for C₁₂H₂₀O₃: C, 67.89; H, 9.50%). Mol. wt.: 212. The assignment of the structures III and IIIa is consistent with the spectral characteristics of these compounds. The third photoproduct (IV) was shown to be ω -cyanoundecanoic acid, m.p. 55°C (lit. 57°C)(7). (Found: C, 68.35; H, 9.86; N, 6.43. Calc. for C12H21NO2: C, 68.21; H, 10.02; N, 6.63%). Mol. wt.: 211. This product was identical with the acid obtained by second-order Beckmann rearrangement of I. The same acid was isolated in the preparation of diazocyclododecanone, by the action of chloramine on I (8). The fourth photoproduct (V) was isolated in the form of a white crystalline substance (0&05 g), m.p. 120-122°C and was found to isomeric with I(Found: C, 67.99;

H, 10.05; N, 6.48. Calc. for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63%). Mol. wt.: 211. On the basis of these and other spectral characteristics it was assigned the structure of 1-hydroxy-ll-oximino-bicyclo(8.2.0)decane. The conversion of I into II, III, IV and V was found to occur in 40%, based on I consumed.

It is of interest to note that the photolysis of I takes a different course from that of oximes published so far (3,4), and that in a way reminds us of the pyrolysis and photolysis of camphoroxime (5). The intermediacy of the oxaziridine ring (4) postulated in the photolysis of ketoximes is excluded since no photoproduct originating from oxaziridine derivative could be isolated.

The formation of the cyano group in products III and IV may be envisaged by proceeding via the photochemical fission of the N-O bond giving and intermediate radical -CO-C- whose formation is followed by simultaneous N. fission of the bond adjacent to carbonyl, producing a new radical with cyano group and excited carbonyl; the latter leads to III by losing hydrogen alpha to the cyano group, and to IV by recombination with HO. radicals originating from the initial cleavage of the N-O bond.



In the formation of IV the intermediacy of a ketene is excluded since the methyl ester of IV instead of the free acid would be obtained.

In view of the results outlined the photolysis of α -oximinocyclododecanone(I) can be represented by the following scheme:

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The possibility of activation of hydrogen in the \measuredangle -position to the cyano group leading to III, and that in the \$-position to carbonyl leading to cyclobutynol formation (V) is not unexpected. Unfortunately, it is not feasible with the evidence available to make a choice between several configurations possible for V.

From the results cited above it follows that the photolysis of \ll oximinocyclododecanone gives rise to geometrical isomerization, ring contraction, second-order Beckmann rearrangement and photocyclization.

Other cyclic oximinoketones are under investigation.

References

- 1. A.Schönberg "Preparative Organic Photochemistry", Springer Verlag, Berlin, Heidelberg, New York, 1968, pp. 23-47.
- 2. G.Ciamician and P.Silber, Ber., 36, 4268 (1903).
- 3. R.T.Taylor, M.Douek and G.Just, Tetrahedron Letters, 1966, 4143.
- 4. T.Oine and T.Mukai, Tetrahedron Letters, 1969. 157.
- 5. T.Sato and H.Obase, Tetrahedron Letters, 1967, 1633.
- 6. D.H.R.Barton and J.M.Beaton, <u>J.Am.Chem. Soc.</u>, <u>83</u>, 4083 (1961). M.P.Cava,
 E. J.Glamskowski and Q.A.Asmed, <u>J.Org.Chem.</u>, <u>32</u>, 2644 (1967).
- 7. J.A.Perkins and A.O.Cruz, <u>J.Am.Chem.Soc.</u>, <u>49</u>, 1073 (1927).
- 8. A.Stojiljković and R.Tasovac, unpublished paper.