The Photolysis of Norcamphor Oxime: Effect of Base

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Summary The photochemical Beckmann rearrangement of norcamphor oxime is retarded by the addition of small amounts of base.

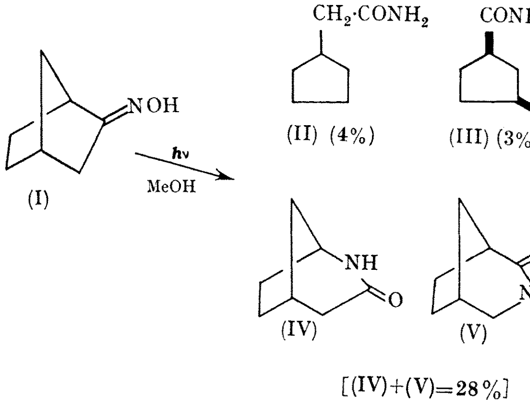
THE photolysis of camphor oxime yields, in addition to parent ketone, various nitriles as the only reported products.[1] This result, which has also been noted by Just and his co-workers,[2] is at variance with the "normal" photochemical reaction of oximes to yield amides.[2–4]

In order to determine whether or not the photochemical "second-order" Beckmann rearrangement would prove to be a general process for the bicyclo[2,2,1]heptanone oximes, we examined the photolysis of norcamphor oxime (I). The photochemistry of (I) closely resembles that of aldoximes and acyclic and monocyclic ketoximes, no evidence of nitrile formation being found. Moreover, we report supporting evidence for the intermediacy of oxaziridines in the photochemical rearrangement of oximes to amides.

Irradiation[†] of de-gassed 1—2% solutions of norcamphor oxime (I) in anhydrous methanol[5] proceeded slowly. At these concentrations the u.v. spectrum of (I) showed end-absorption which tailed into the 2537 Å region, and the low extinction coefficient (ϵ 5 at 2500 Å in hexane solution) undoubtedly accounts in part for the slow reaction. After 24 hr. approximately 50% of (I) was unreacted. The four principal products[‡] were isolated after this time by preparative g.l.c.[§] Yields [based on the amount of (I) photolysed] were determined by quantitative g.l.c. Control experiments demonstrated that methanolic solutions of (I) were stable in the dark, and that photolysis of a mixture of (IV) and (V) in methanol failed to produce (II) or (III).

The structure of (II) was established by comparison with an authentic sample of cyclopentaneacetamide. The bicyclic lactams(IV) and (V) were obtained as an oily mixture which failed to separate on several g.l.c. columns. Identification was made by comparison with a mixture of (IV) and (V) prepared by an alternative method.[6] Lithium aluminium hydride reduction of the lactams yielded the corresponding amines which were separable by g.l.c. and had the same retention times as an authentic mixture of 2- and 3-azabicyclo[3,2,1]octane.[6] The structure of (III) (m.p. 155—157°) was deduced from its high-resolution mass spectrum (molecular ion *m/e* 127·0995; $C_7H_{13}NO$ requires *m/e* 127·0997) and other spectral data. The *cis*-stereochemistry was assigned on the basis of the mode of formation of (III).

Recent work implicates oxaziridine intermediates in the photochemistry of oximes.[3,4,7] Oine and Mukai observed oxaziridine formation to be faster in protic solvents than in aprotic solvents, and suggested ". . . a protonation may be involved in some step of the rearrangement or the oxaziridine-formation may proceed *via* a polarized excited state."[7] We found that irradiation of methanolic solutions containing molar ratios of (I) : sodium methoxide of approximately 6 : 1 resulted in a reduction in the rate of oxime consumption and lactam formation by comparison with reaction in "neutral" media. Moreover, determination of oxaziridine concentration by the usual iodometric method[4,8] revealed oxaziridine concentrations to be significantly lower in basic media than in neutral solution. While admittedly not conclusive evidence, these observations suggest the intermediacy of an oxaziridine in the photochemical rearrangement of (I), and also suggest that protonation facilitates oxaziridine formation.



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[†] Rayonet photochemical reactor, peak energy of source at 2537 Å; quartz reaction vessels.
[‡] Norcamphor was also isolated and identified as the 2,4-dinitrophenylhydrazone.
[§] 20 ft. × ¾ in. column, 30% Se 52 on 45/60 Chromosorb W at 180°.

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