The Photochemical Beckmann Rearrangement of Adamantanone Oxime

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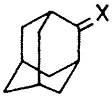
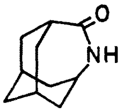
Summary The photolysis of adamantanone oxime (I) in acetic acid under a nitrogen stream at room temperature for 6 hr yields 4-azatricyclo[4,3,1,$1^{3,8}$]undecan-5-one (III) and adamantanone (II) in 89 and 8% yields, respectively, without any fragmentation product.

IRRADIATION of alicyclic ketoximes in methanol is known to produce lactams as the major products together with side-products (*e.g.*, alkanoic acid amides) as the fragmentation products, and cycloalkanones. However, in isopropyl alcohol, the fragmentations become the major reactions as exemplified by the photolysis of cyclohexanone oxime in methanol [yielding hexanolactam (46%), hexanoamide (5%), and cyclohexanone (3%)] and in isopropyl alcohol [yielding hexanoamide (52%), cyclohexanone (4%), and traces of hexanolactam].[1] Other examples involve the photolysis of norcamphor oxime in methanol (affording lactams as the major products, accompanied by primary amides[2]) and the photolysis of camphor oxime in methanol (yielding monocyclic nitriles as cleavage products without any Beckmann-type rearrangement product[3]). We now report the photochemical Beckmann rearrangement of adamantanone oxime (I), the result of which is quite different from those reported for other cycloalkanone oximes.[1-3]



(I) X = NOH
(II) X = O



(III)

(IV) R = CN
(V) R = CONH$_2$

(VI)

Irradiation† of a 0·1% solution of (I) [λ_{max} (n-C_6H_{14}) end-absorption, $\epsilon = 8$ at 250 nm) in acetic acid afforded 4-azatricyclo[4,3,1,$1^{3,8}$]undecan-5-one (III) and adamantanone (II) in 89 and 8% yields, respectively (Table). Irradiations in methanol and isopropyl alcohol yielded no trace of lactam (III) but only small amounts of bicyclo[3,3,1]non-6-ene-3-carbonitrile (IV) and ketone (II). The product analyses were based on g.l.c.‡ and t.l.c. in comparison with

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† All irradiations were carried out in a quartz cell with the light from a high-pressure mercury lamp (Eikosha PIH-100). Irradiations with a 60 w low-pressure mercury lamp for 12 hr. were ineffective in all solvents used (Table).

‡ Silicone SE-30 (5 wt. %) at 120°. At this temperature the oxime (I) was stable.

authentic samples of (VI),[4] bicyclo[3,3,1]non-6-ene-3-carboxamide (V),[4] and bicyclo[3,3,1]nonane-3-carboxamide (VI).§ These results are interesting in view of the exclusive formation of the Beckmann-type rearrangement product (III) in acetic acid under a nitrogen stream without the formation of fragmentation products such as (IV), (V), and (VI). The stability of (I) to photolysis in both methanol and isopropyl alcohol is in contrast to photolyses of other cycloalkanone oximes.[1–3]

Since it has recently been found that both the Beckmann[5] and the Schmidt[4,6] reactions of (I) and (II) have a strong tendency to afford a fragmentation product (IV), ascribable to the ideal geometrical constraint of the adamantanone ring,[4] the photo-induced Beckmann rearrangement of (I) provides an attractive synthetic route to the lactam (III) as a mechanistically interesting case in the photochemistry of oximes and oxazirans.[7] The fairly large quenching effect (Table) of oxygen[1] in the (I) → (III) rearrangement is indicative of the intervention of radical intermediates, though the detailed mechanism is uncertain at present.

Photolysis of adamantanone oxime[a]

	Yield (%)[c]			
Solvent[b]	Oxime (I)	Ketone (II)	Lactam (III)	Nitrile (IV)
AcOH/N_2	3	8	89	0
AcOH/O_2	85	11	4	0
MeOH/N_2	93·5	6	0	0·5
Pr^iOH/N_2[d]	97·5	1·5	0	0·5

[a] All irradiations were carried out at room temperature for 6 hr. [b] The solvents were dried and distilled before use; L. F. Fieser, "Experiments in Organic Chemistry," 3rd edn., D. C. Heath and Co., Boston, Mass., 1957, p. 289. [c] The yields were determined by quantitative g.l.c. In the absence of light the oxime (I) was stable and unchanged. [d] Unidentified minor product (<0·5%) was detected.

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§ (VI) m.p. 205·5—206·0°, was prepared from bicyclo[3,3,1]non-6-ene-3-carboxylic acid by hydrogenation, followed by amidation *via* the acid chloride.

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