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PHOTOLYSIS OF PODOCARPONITRILE OXIDE AND MESITONITRILE OXIDE*

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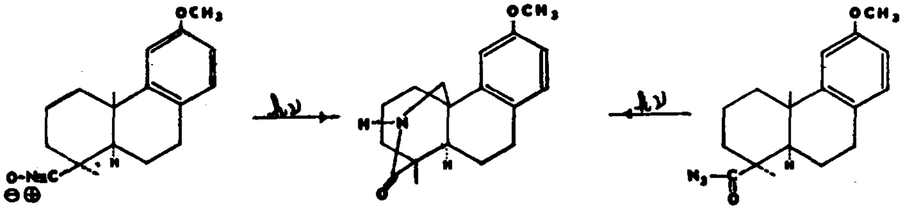
Recently, the stable O-methyl podocarponitrile oxide(I) became readily available by oxidation of podocarpinal syn-oxime with lead tetraacetate(1). It was of interest to us to determine whether irradiation of nitrile oxide I would lead to bridging reactions similar to those reported by ApSimon and Edwards(2), who obtained lactam II upon irradiation of the acid azide III.



I II III

Irradiation*** of a 0.4% hexane solution of I gave in approximately 25% yield a product identified as II by comparison of spectra with that of an authentic sample****, and by mixed melting point determination. Irradiation of a 0.4% methanol solution gave similar results. Because of the strong absorption of the anisole ring of I, the absorption maximum of the nitrile oxide could not be determined.

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*** Rayonet Photochemical Reactor; peak intensity of light: 2537 Å

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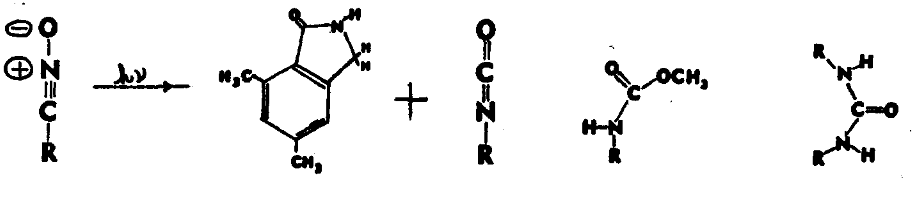
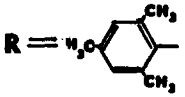
We also investigated the photochemistry of mesitonitrile oxide (IV) (6), prepared by lead tetraacetate oxidation of syn-mesitaldoxime (1). Irradiation of a 0.4% pentane solution of IV gave V (m.p. 166.5 - 168°) and VIII (sublimes without decomposition at 345°), each in approximately 20% yield



IV V VI VII VIII



The infrared spectrum of the photolysis solution still showed a strong peak at 2290 cm^{-1}, corresponding to appreciable amounts of starting material, and a shoulder at 2270 cm^{-1}, indicative of a small amount of isocyanate VI. The latter product was present in too small yield to be adequately characterized.

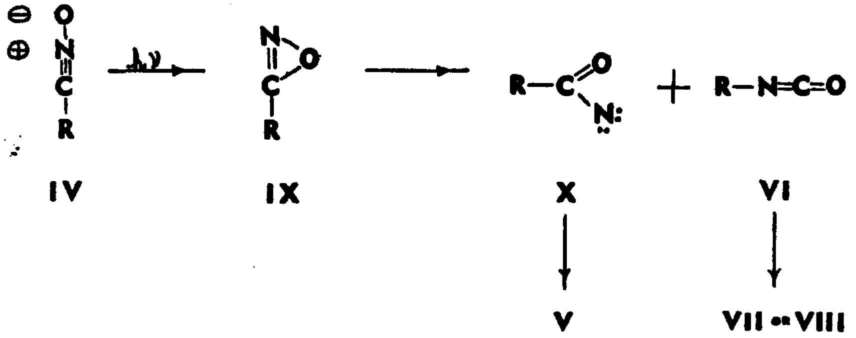
When the photolysis of IV was carried out in methanol, lactam V and urethane VII (m.p. 99 - 101°) were formed almost exclusively in approximately equimolar proportions.

Urethane VII was most likely produced by a dark reaction of isocyanate VI with solvent. Its structure was proven by comparison with a sample synthesized from isocyanate VI(3) and methanol.

The structure of urea VIII was proven by comparison with a sample synthesized from isocyanate VI (3) and 2,4,6-trimethylaniline. It was probably produced in the photolysis by a dark reaction of isocyanate VI with traces of water.

The NMR spectrum of V showed two singlets at δ 2.38 and 2.70 (3H), an unresolved aromatic signal centered at 7.13 (2H), a two proton singlet at 4.39, and a broad signal centered at 8.38 (1H) p.p.m. One of the methyl groups of the starting nitrile oxide had disappeared, and was replaced by a methylene group, the chemical shift of which was appropriat for the environment suggested, and different from the analogous grouping in oxindole (3.47δ). The i.r. of V showed absorption at 3180 cm^{-1} (N-H) and lactam absorption at 1680 cm^{-1} (in KBr). The u.v. spectrum in ethanol or 80% sulfuric acid was similar to that of benzamide, and different from acetanilide.

No mechanistic study has been done as yet. However, the similarity of product formed from the nitrile oxide and acid azide (2) lead us to suggest the following pathway:



Acyl nitrene X which is analogous to that suggested by ApSimon and Edwards(2), would abstract hydrogen from a neighbouring alkyl group, thus leading to lactam V. Similar results have been reported by other workers(4). Isocyanate VI itself was found to be stable when photolyzed under these conditions in pentane. Therefore, it is not an intermediate in the formation of lactam V. Nitrene insertion into C-H bonds of solvent, which has been observed by other workers(5), has not yet been detected in our case.

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