Photoreaction of 2-Dimethylamino-4,5-dihydro-3*H*-azepine

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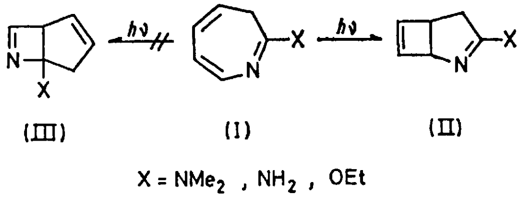
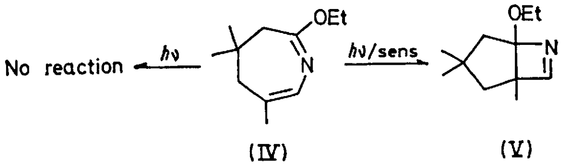
Summary Irradiation of 2-dimethylamino-4,5-dihydro-3*H*-azepine (VI) is reported to yield 1-dimethylaminocyclopentene (VII) and 4,5-trimethylenepyrimidine (VIII); 1-dimethylamino-7-azabicyclo[3,2,0]hept-6-ene (IX) is postulated to be an intermediate in this reaction.

Photoisomerizations of 3*H*-azepines (I) to 2-azabicyclo-[3,2,0]hepta-2,6-dienes (II) were reported earlier.[1] Since none of the alternate products (III) with the 7-azabicyclo-[3,2,0]hepta-3,6-diene skeleton was found, the possibility of forcing closure in this manner by suitable structural changes was explored. In the interim, Koch and Brown reported that 2-ethoxy-4,4,6-trimethyl-4,5-dihydro-3*H*-azepine (IV) was photostable but was converted into 1-ethoxy-3,5,5-trimethyl-7-azabicyclo[3,2,0]hept-6-ene (V) with triplet sensitizers.[2] We report an unusual reaction of 2-dimethylamino-4,5-dihydro-3*H*-azepine (VI) without triplet sensitization.

Selective hydrogenation of 2-dimethylamino-3*H*-azepine[3] over 5% Pd on charcoal produced (VI) (70%) and 2-dimethylamino-4,5,6,7-tetrahydro-3*H*-azepine (30%). Compound (VI) was characterized by elemental analysis and i.r., n.m.r., and mass spectra. The u.v. spectrum taken in hexane had a single maximum at 266 nm (ϵ 3660) with an absorptivity at 310 nm which is approximately one-tenth that of the maximum.

Irradiation of 10^{-3}M solutions of (VI) in pentane under nitrogen with 310 nm lamps and Pyrex filter† gave (VII) (50%)† and (VIII) (30%).‡ The products were isolated by preparative g.l.c., and the structures of the eneamine (VII)[4] and pyrimidine (VIII)[5] were established by comparison of their i.r., n.m.r., and mass spectra with samples prepared by syntheses described elsewhere. Triplet sensitization with xanthone resulted in conversion of (VI) into polymeric material which was not characterized.





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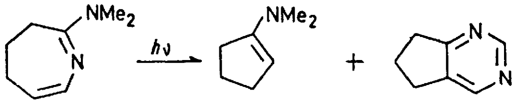
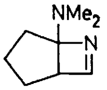
† Compound (VIII) isomerized when 253·7 and 310 nm lamps were used without filters. This isomerization was minimized with the longer wavelength lamps and completely suppressed by the addition of a Pyrex filter. The reaction was too slow with 350 nm lamps.

‡ Yields are based on the stoicheiometry, $2C_8H_{14}N_2 \rightarrow C_7H_{13}N + C_7H_8N_2 + C_2H_7N$.

Although the transformation of (VI) to (VII) and (VIII) is a novel reaction, the five-membered ring in both products argues for a reaction path in which (IX) is formed by initial electrocyclization of (VI). There are several plausible paths for proceeding from (IX) to (VII) and (VIII), but the data do not permit a distinction at present.



(VI) (VII) (VIII)



(IX)

The contrast in photoreactivity of the dihydroazepines, (IV) and (VI), is surprising since (IV) is photostable to the output of a medium-pressure mercury lamp with a Vycor filter and (VI) readily reacts when irradiated anywhere in a wide range of wavelengths, and since (IV) isomerizes with triplet sensitization but (VI) yields polymeric material under these conditions.

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