Selectivity in the Photoisomerization of 3*H*-Azepines

By ROBERT A. ODUM* and BERNARD SCHMALL

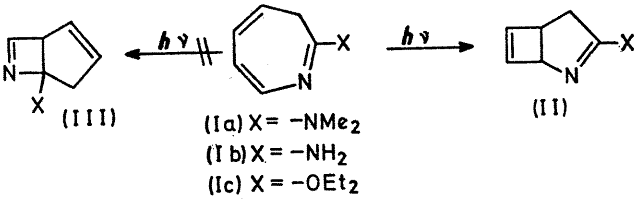
(*Department of Chemistry, Brooklyn College, The City University of New York, Brooklyn, New York* 11210)

Summary Some 2-substituted-3*H*-azepines are reported to photoisomerize to 2-azabicyclo[3,2,0]hepta-2,6-dienes.

PHOTOCHEMICAL intramolecular cycloadditions of 3*H*-azepines (I) should be disrotatory processes because of the constraints imposed by the seven membered ring. Simple considerations of the initial interactions developing in the highest occupied orbital of the first excited state on proceeding along the reaction co-ordinates† leads to the conclusion that 2-azabicyclo[3,2,0]hepta-2,6-dienes (II) and 6-azabicyclo[3,2,0]hepta-2,6-dienes (III) are allowed products.

Irradiation of dilute pentane solutions of (Ia) (medium pressure Hanovia lamp, Corex filter) yielded (IIa) (70%). Similar reactions of (Ib) and (Ic) using low-pressure mercury lamps gave (IIb) (45%) and (IIc) (60%). No products of the type (III) were identified in any irradiations.‡ A brown polymer accounted for the remainder of the reactant.

The structures assigned to (IIa), (IIb), and (IIc) are consistent with elemental analyses and u.v., i.r., and n.m.r.§ spectral data. The ring-proton portions of the n.m.r. spectra, which are strikingly similar, is particularly decisive in distinguishing between the isomeric 2-aza-bicyclo-[3,2,0]hepta-2,6-dienes (II) and 6-aza-bicyclo[3,2,0]hepta-2,6-dienes (III). Each compound has a 1H doublet in the range of τ 3·60—3·64 and a 1H triplet in the range of τ 3·8—3·89 with no additional absorptions below τ 5·00. Since the



(III)

(Ia) X = $-NMe_2$

(Ib) X = $-NH_2$

(Ic) X = $-OEt_2$

(II)

---

† Arguments for the validity of such an approach when dealing with molecules in which there is little symmetry were presented in a review article (ref. 1), "Conservation of Orbital Symmetry").

‡ No volatile products other than those reported were detected except on photolysis of 2-ethoxy-3*H*-azepine, when an uncharacterised impurity in the product was present (<3%). Its structure cannot alter the basic observation of selectivity in the photoisomerization.

§ N.m.r. spectra were measured at 60 MHz with Me_4Si as the internal standard. Spectra of (IIa) and (IIc) in CCl_4 and of (IIb) in [$^2H_5$]pyridine.

cyclopentene olefinic protons is bicyclo[3,2,0]hepta-2,6-diene[2] appear at τ 4·36 and in 1-methoxybicyclo[3,2,0]-hepta-3,6-diene at 4·13 [3] and since cyclobutene protons in similar compounds[3,4] appear in the range of τ 3·40—3·92, only structure (II) is consistent with this feature on the basis of chemical shift and number of protons $< \tau$ 5·00. Spin-coupling constants of these protons in each compound are 2·5—2·8 Hz, further supporting the structure assignment since those for olefinic protons in cyclobutenes are reported to be 2·5—3·7 Hz and in cyclopentenes, 5·4—7·0 Hz.[5] The bridgehead hydrogens appear as two 1H multiplets at τ 5·05—5·29 and 6·72—6·77, and the methylene hydrogens, as a 2H multiplet at τ 7·57—7·62.

The reasons for the observed selectivity are obscure. Chapman and his co-workers[3] reported the photoisomerization of 1-ethoxycyclohepta-1,3,5-triene to 1-ethoxybicyclo-[3,2,0]hepta-3,6-diene in direct contrast to the mode of reaction of 2-ethoxy-3*H*-azepine (Ic), its heterocyclic analogue. A unique structural feature of compounds (III), which were not formed in these reactions, is the 1-azetine system. A number of 1-azetine compounds are reported as products in light-induced intramolecular electrocyclizations.[6] However, in these reactions an alternative intramolecular cycloaddition reaction path did not exist and the formation of 1-azetine did not require the concomitant loss of amidine or imidate ester resonance energy, a possible deciding factor on the course of the reaction.

(*Received, August 28th* 1969; *Com.* 1321.)

---

[1] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.

[2] W. G. Dauben and R. L. Cargill, *Tetrahedron*, 1961, **12**, 186.

[3] G. W Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *J. Amer. Chem. Soc.*, 1967, **89**, 2979.

[4] E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Annalen*, 1965, **682**, 1; O. L. Chapman and E. D. Hoganson, *J. Amer. Chem. Soc.*, 1964 **86**, 498; L. A. Paquette, *ibid.*, p. 500; L. A. Paquette and W. C. Farley, *J. Org. Chem.*, 1967, **32**, 2725; L. A. Paquette, *J. Amer. Chem. Soc.* 1964, **86**, 4092.

[5] O. L. Chapman, *J. Amer. Chem. Soc.*, 1963, **85**, 2014; G. V. Smith and H. Kriloff, *ibid.*, p. 2016; P. Laszlo and P. von R. Schleyer, *ibid.*, p. 2017.

[6] C. Lohse, *Tetrahedron Letters*, 1968, 5625.