Tetrahedron Letters No. 36, pp 3139 - 3142, 1974. Pergamon Press. Printed in Great Britain.

PHOTOCHEMISTRY OF 2,3-DIAZA-6-OXABICYCLO[3.1.0]HEX-2-ENE

Louis E. Friedrich,* Nedie L. de Vera, Wayne P. Hoss and James T. Warren
Department of Chemistry, University of Rochester, Rochester, New York 14627

(Received in USA 3 June 1974; received in UK for publication 19 July 1974)

There have been several recent reports[1] of the thermal and photoreactions of substituted 2,3-diazabicyclo[3.1.0]hex-2-enes 1. In all cases the isolated products resulted from fragmentation of one or both C—N bonds. This behavior was expected and is overall quite analogous to the chemistry of pyrazolinenes[2a]

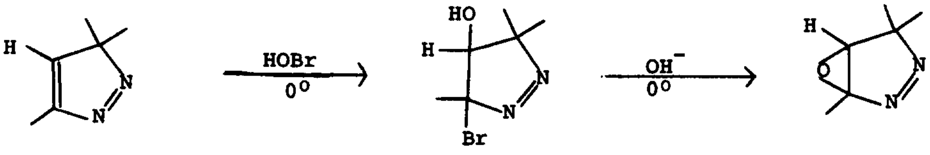
olefin, bicyclobutane,

and diazo products

1

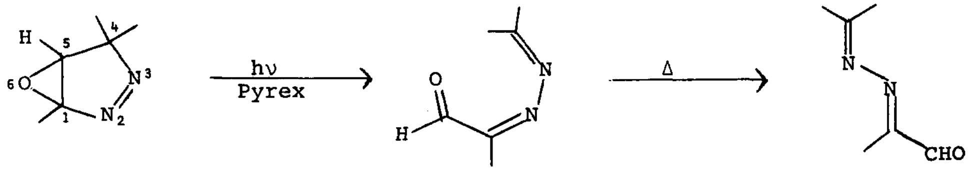
and pyrazolines.[2b] We have found that when C-6 of compound 1 is replaced by oxygen, photochemical initiation results in a rearrangement that does not extrude N_2 or involve breaking the C—N bonds.

Our starting material 4, was made by treatment of pyrazolenine 2[3] with *N*-bromoacetamide and perchloric acid in 90% aqueous acetone to give 15-40% crude yields of the bromohydrin 3 (stereochemistry undetermined).[4] Elimination of HBr with aqueous NaOH generated the epoxide 4 in *ca.* 50% yield which was purified by vpc on Carbowax 20M at 120°.[5]



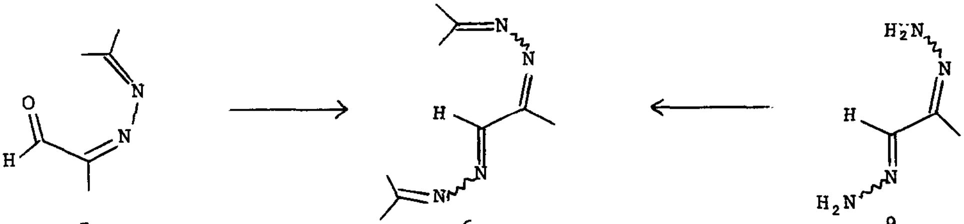
2 3 4

Photolysis of epoxide 4 in benzene through Pyrex, either with or without benzophenone, gave no identifiable products resulting from loss of nitrogen. Rather a >95% yield of azine 5a was observed by nmr. The initial azine (stereochemistry undetermined, but presumed (*Z*)) rearranged to an isomeric azine 5b (presumed (E)) when purified by vpc (Carbowax 20M at 120°) although room temperature removal of the benzene under reduced pressure caused no isomerization.[6]



4 5a 5b

The structure of the initial azine 5a was established by treatment of the azine with acetone hydrazone in benzene solution. The resulting diazine 6[7] (stereochemistry undetermined) which was purified by vpc (10% SE-30 at 140°), was synthesized by treatment of pyruvaldehyde dihydrazone 9[8] with acetone. All spectra of the two samples of diazine 6, purified by vpc (10% SE-30 at 140°), were identical.[9]



5a 6 9

Photolysis of 2,3-diazabicyclo[3.1.0]hexenes 1 by n,π* excitation of the azo group[10] causes cleavage of the weak C—N bonds. In the rearrangement of epoxide 4 to azine 5, these bonds are actually strengthened, and the reaction seems to be dominated by a vinylagous epoxide-carbonyl rearrangement, the same as found when cyclopentadiene monoepoxide thermally rearranges to pentadienal.[11] Strikingly, the uv maximum at 357 nm for epoxide 4 is similar to that for 3,5,5-trimethylpyrazolenine in EtOH, 355 nm (ε 260). Contrastingly, azo compounds 1 in hexane or ethanol have a maximum at 328-334 nm (ε 149-335),[1a,b] similar to that for 3,3,5-trimethylpyrazoline at 325 nm (ε 371) in MeOH.[12] We therefore believe that in epoxide 4, there is substantial resonance between the epoxide group and the pi system of the azo moiety. As such, n,π* excitation weakens the epoxide bonds and initiates the well-known epoxide-carbonyl rearrangement.

Thermolysis of epoxide 4 leads to a > 90% yield of mesityl oxide.[13] No azine **5a-b** was formed; a control experiment showed that at 175^{0}, azine **5a** rearranged to **5b** and was sufficiently stable to be detected if formed. In the ground state manifold, the fragmentation of the weak C—N bonds dominates the reaction course. Such is found in the thermal *and* photochemistry of compounds **1** where the cyclopropane and azo groups weakly interact.

Acknowledgement - We thank the National Science Foundation and Merck Company Foundation for financial aid.

REFERENCES

1. (a) P. G. Gassman and W. J. Greenlee, *J. Amer. Chem. Soc.*, **95**, 980 (1973); (b) D. F. Eaton, R. G. Bergman and G. S. Hammond, *ibid.*, **94**, 1351 (1972); (c) D. H. Aue and G. S. Helwig, *Tetrahedron Lett.*, 721 (1974); (d) M. Franck-Neumann and C. Buchecker, *ibid.*, 2659 (1969); (e) M. I. Komendantov and R. R. Bekmukhametov, *J. Org. Chem. USSR*, 427 (1971).
2. (a) G. L. Bloss, W. A. Böll, H. Heyn and V. Dev, *J. Amer. Chem. Soc.*, **91**, 173 (1968); (b) D. E. Greer and J. W. McKinley, *Cand. J. Chem.*, **49**, 105 (1971).
3. G. L. Closs, L. E. Closs and W. Böll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963).
4. Bromohydrin **3**: mp 94-95^{0}; uv (isopropanol) 338 nm (ε 79); ir (CCl_4) 3400 cm^{-1}; nmr ($CDCl_3$) δ 4.23 (br. d, *J* = 4 Hz, 1), 2.93 (br. d, *J* = 4 Hz, 1), 2.07 (s,3), 1.48 (s,3), 1.43 (s,3). Addition of D_2O caused the δ 2.93 to disappear and the δ 4.23 became a singlet; *Anal.* Calculated for $C_6H_{11}N_2BrO$: 34.80; H, 5.36; N, 13.53; Br, 38.59. Found: C, 34.68; H, 5.41, N, 13.78; Br, 38.63.
5. Epoxide **4**: bp ~50^{0} (4 mm); uv (pentane) 361 nm (ε 296); uv (isopropanol) 357 nm (ε 286); ir (CCl_4) 1381, 1361, 1088, 865 cm^{-1}; nmr (CCl_4) δ 3.15 (s,1), 1.99 (s,3), 1.35 (s,3), 1.22 (s,3); ms (70 eV) 126 (3), 97 (1), 83 (100), 56 (71), 55 (90), 43 (68); *Anal.* Calculated for $C_6H_{10}N_2O$: C, 57.12; H, 7.99; N, 22.21. Found: C, 56.84; H, 8.15; N, 22.06.
6. Azine **5a**: uv (pentane) 416 (ε 79), 386 (79), 368 (130), 246 nm (9,400); ir (neat) 1686, 1639, 1429, 1364, 1253, 1028 cm^{-1}; nmr (CCl_4) δ 1.98 (s,3), 2.06 (s,3), 2.08 (s,3), 10.40 (s,1); ms (70 eV) *m/e* 126 (parent,1) 83 (11),

57 (63), 56 (100), 42 (85).

Azine **5b**: uv (pentane) 252 (ε 20,000), 228 nm (26,100); ir (neat) 2798, 1698, 1641, 1591, 1429, 1364, 1258, 1023 cm^{-1}; nmr (CCl$_4$) δ 1.84 (s,3), 1.86 (s,3), 2.12 (s,3), 9.54 (s,1); ms (70 eV) *m/e* 126 (parent,1) 83 (9), 57 (71), 56 (100), 42 (71).

7. Diazine **6**: uv (MeOH) 264 (ε 44,000), 228 nm (30,000); ir (neat) 1650, 1439, 1368, 1259 cm^{-1}; nmr (CCl$_4$) δ 7.83 (s,1), 2.05 (s,9), 2.02 (s,3), 1.88 (s,3); ms (70 eV) 180 (parent,1), 124 (55), 112 (28), 97 (27), 84 (9), 70 (8), 56 (100). Since vpc collection of azine **5a** produced (*Z*)-(*E*) isomerization, we presume that diazine **6** is similarly equilibrated.
8. T. K. Liao, F. Baiocchi and C. C. Cheng, *J. Org. Chem.*, **30**, 560 (1965).
9. Acetone hydrazone-d_6, prepared by condensation of acetone-d_6 and hydrazine, was reacted with azine **5a** to produce diazine **6**. The diazine was purified by vpc (3% SE-30 at 100°): nmr (CCl$_4$) δ 7.83 (s,1), 2.05 (s,6), 1.88 (s,3). The formation of only diazine-d_6 (no diazine-d_{12}) precludes the exchange of acetone hydrazone and the azine moiety of product **5a**.
10. For a recent review on the spectroscopic characteristics of azo groups, see H. Rau, *Angew. Chem. Int. Ed.*, **12**, 224 (1973).
11. P. Schiess and H. L. Chia, *Helv. Chim. Acta*, **53**, 485 (1970).
12. R. J. Crawford, A. Mishra and R. J. Dummel, *J. Amer. Chem. Soc.*, **88**, 3959 (1966).
13. 2,3-Dimethylcrotonaldehyde, a possible oxabicyclobutane fragmentation product, was not observed in > 3% yield. Contrastingly, oxidation of 1,3,3-trimethylcyclopropene with peracid gives a 79:21 mole ratio of 2,3-dimethylcrotonaldehyde and mesityl oxide, respectively. See L. E. Friedrich and R. A. Fiato, *J. Amer. Chem. Soc.*, accepted for publication.