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AZIRINE PHOTOCHEMISTRY: CYCLIZATION OF 2-STYRYL-2H-AZIRINES TO BENZAZEPINES[1]

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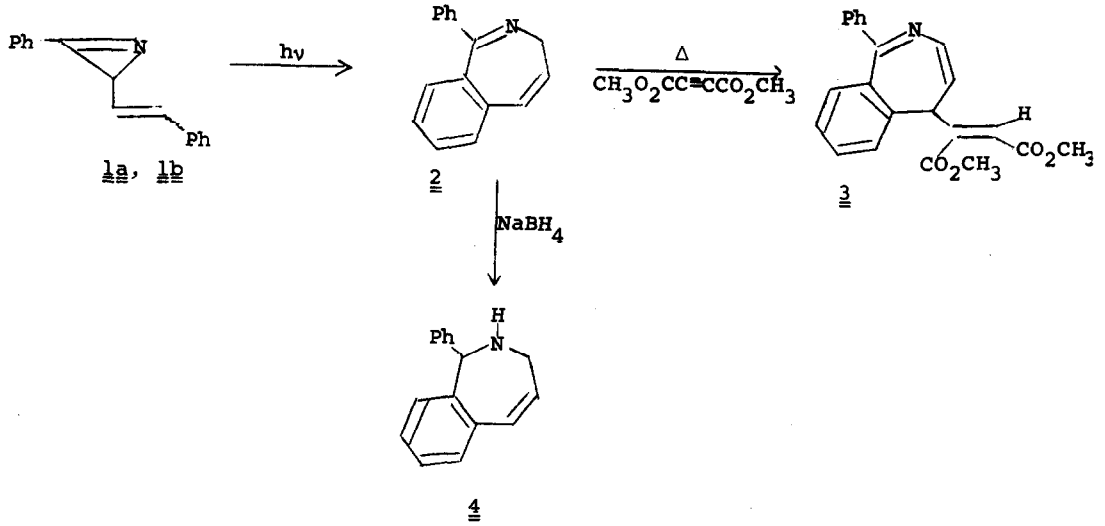
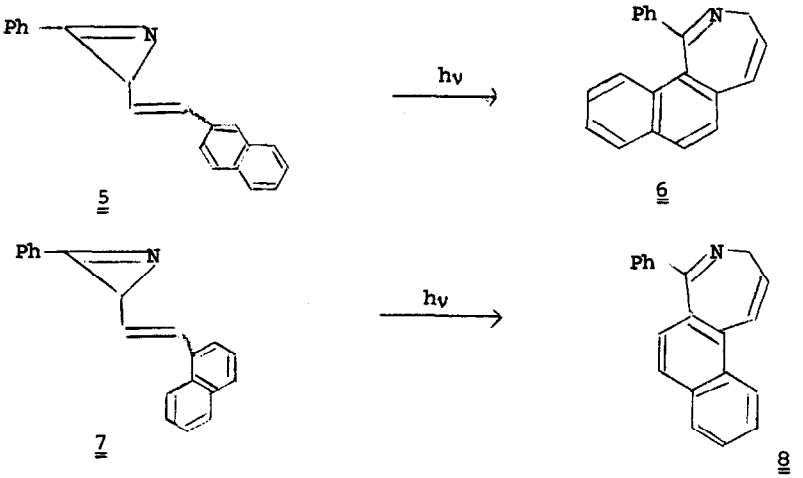
In the preceding communication we reported several examples of the intramolecular cyclization of 2-vinyl substituted 2H-azirines to 5-membered heterocyclic rings.[1] The results clearly showed that the photochemical reactions proceeded through nitrile ylide intermediates while the thermal reactions involved vinyl nitrenes. These results have stimulated us to begin a general investigation of the scope and mechanistic details of the intramolecular cyclization of unsaturated arylazirines. In this communication we describe the photocyclization of several styryl-substituted 2H-azirines to substituted benzazepines.

An unusual aspect of the intramolecular photocyclization of unsaturated azirines is exemplified in our study of the photochemistry of (E)- and (Z)-3-phenyl-2-styryl-2H-azirines (1a, 1b). Irradiation of (E)-and/or (Z)-azirine (1a or 1b) in benzene with Corex filtered light gave rise to one major product(80%) which was identified as 1-phenyl-3-H-2-benzazepine (2) on the basis of its spectral properties[2] and chemical behavior: λ_{max}^{KBr} 6.20μ; λ_{max} (95% ethanol) 228 nm (ε 17,500); nmr (100 MHz) τ 6.20 (2H, d, J = 7.0Hz), 3.60 (1H, dt, J = 10.0 and 7.0 Hz), 3.10 (1H, d, J = 10.0 Hz), and 2.40-2.80 (m, 9H). The coupling constants observed with this compound are essentially identical to those reported for closely related systems.[3] Chemical support for the structure of 2 was obtained by heating equimolar quantities of 2 with dimethylacetylene dicarboxylate. The major product isolated was a crystalline solid, mp 171-172°, whose structure was identified as dimethyl (1-phenyl-5H-benzazepin-5-yl)maleate (3) on the basis of its spectral properties.[4] Further support for the structure of benzazepine 2 was provided by its reduction with sodium borohydride to 2,3-dihydro-1-phenyl-1H-2-benzazepine (4).[5]



We found that the photoconversion of unsaturated 2H-azirines to the 7-membered azepine ring is a general phenomenon when the substituent attached to the double bond is an aryl group. Thus, irradiation of either (E)-and/or (Z)-2-[2-(β-naphthyl)vinyl]-3-phenyl-2H-azirine (5a, 5b) gave a single crystalline (85%) product whose structure was identified as 1-phenyl-3-H-naphth(1,2-c)-azepine (6) on the basis of its spectral properties.[6] Similarly, irradiation of (E)-and/or (Z)-2-[2-(α-naphthyl)vinyl]-3-phenyl-2H-azirine (7a, 7b) gave 1-phenyl-3H-naphth(2,3-c)azepine (8) in high yield (80%).[7]



It is worthwhile to briefly discuss some of the salient features of the nmr spectra of these azepines, since they appear to be markedly different. At room temperature, the two methylenic protons present in structure 8 appear as a very broad singlet. Variable temperature nmr studies indicate that the coalescence temperature for these hydrogens occurs at 25°. Cooling a sample of 8 to -30° caused the methylenic protons to appear as two distinct signals at τ 7.20 and 5.76 with the same shift and multiplicity as was noted for azepine 6 at room temperature.[6] When a sample of 8 was heated at 115°, the methylenic protons appeared as a doublet at τ 6.20 (2H, J = 7.0Hz). Examination of Dreiding models show that a minor steric interaction between the ortho hydrogens of the phenyl and naphthyl rings exist in the transition state for ring flipping with azepine 8. The non equivalence of the pseudoaxial and equatorial hydrogens of azepine 6 implies a quite rigid structure, one in which the barrier to inversion is significantly high. Molecular models clearly show that a severe interaction exists between the C-1 phenyl group of the azepine ring with the adjacent naphthyl group in the transition state for ring flipping. This steric interaction would be expected to result in a large energy barrier for ring inversion and thereby accounts for the high conformational stability of 6 when compared to benzazepine 2.

The above transformations can best be accounted for by assuming C-C bond cleavage of the azirine ring. Intramolecular reorganization of the nitrile ylide followed by a 1,5-sigmatropic hydrogen shift of the initially formed 7-membered ring readily rationalizes the formation of the final product.

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References

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1. Photochemical Transformations of Small Ring Heterocyclic Compounds. LIII. For LII see A. Padwa, J. Smolanoff, and A. Tremper, Tetrahedron Letters, 1973.

2. Satisfactory analytical data were collected for all compounds described herein.

3. A. Mannschreck, G. Rissmann, F. Vogtle, and D. Wild, Chem. Ber., 100, 335 (1967).

4. Structure 4, mp 171-172°; ir (KBr) 5.70, 5.88 and 6.22μ; UV (95% ethanol) 258, 292, and 312 nm (ε 23,800, 22,000, and 18,000); nmr ($CDCl_3$) τ 6.94 (s,3H), 6.36 (s,3H), 6.08 (d, 1H, J = 4.0Hz), 4.20 (1H,s), 4.10 (1H, dd, J = 10 and 4.0Hz), 3.40 (1H, d, J = 10Hz), 2.4-3.1 (m,9H).

5. Structure 5, ir (neat) 2.95μ; UV (95% ethanol) 258 nm (ε 9400); nmr ($CDCl_3$) τ 6.50 (2H,m), 4.92 (1H, dt, J = 12 and 3.0Hz), 3.60 (1H, dt, J = 12 and 1.0Hz), 2.7-3.4 (m,9H).

6. Structure 6; mp 148-149°; ir (KBr) 6.24μ; UV (95% ethanol) 224, 238, and 255 nm (ε 32,000, 35,900, and 31,800); m/e 269 (base); nmr (100 MHz) τ 7.20 (1H, ddd, J = 18.0, 6.0 and 2.0 Hz), 6.75 (dd, 1H, J = 18.0 and 6.0 Hz), 3.92 (dt, 1H, J = 10.0 and 6.0Hz), 3.48 (1H, d, J = 10.0Hz), 2.6-3.4 (m,11H).

7. Structure 8; mp 114-115°; ir (KBr) 6.30μ; UV (95% ethanol) 240, 250, 290, and 305 nm (ε 45,000, 38,200, 7,100, and 4,900); m/e 269 (base); nmr (100 MHz) τ 5.50-7.0 (2H, broad signal), 3.80 (1H, dt, J = 10.0 and 6.0 Hz), 2.0-3.0 (m, 1H).