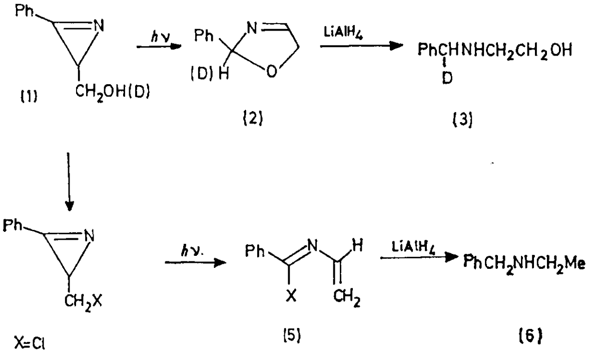
A Novel Photochemical Rearrangement of 2-Hydroxymethyl-2*H*-azirine Derivatives to *N*-Vinylimines

By Albert Padwa,* Jerald K. Rasmussen, and Alan Tremper
(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)

Summary Irradiation of a series of 2-hydroxymethyl-2*H*-azirine derivatives which contain good leaving groups affords *N*-vinylimines *via* a novel 1,4-substituent shift.

We have previously reported that arylazirines undergo irreversible ring opening on electronic excitation to give nitrile ylides as reactive intermediates.[1] The initially generated 1,3-dipoles can be intercepted with a variety of dipolarophiles to form five-membered rings.[1,2] More recently, we have become interested in the intramolecular photoreactions of 2*H*-azirines and have found that 2-alkenyl substituted 2*H*-azirines undergo ready intramolecular cycloadditions, the reactions providing clean transformations for the synthesis of five-membered nitrogen containing heterocycles.[3] We now report some unusual intramolecular reactions which occur on photolysis of certain derivatives of 2-hydroxymethyl-3-phenyl-2*H*-azirines. These reactions are more striking than the internal cycloadditions because they involve a novel 1,4-substituent shift.



(4a); X=Cl
(4b); X=Br
(4c); X=OC(O)Me
(4d); X=OC(O)Ph
(4e); X=OSiMe$_3$
(4f); X=OMe

2-Hydroxymethyl-3-phenyl-2*H*-azirine (**1**),† readily available from cinnamoyl alcohol *via* the iodine azide route,[4] gave 2-phenyl-3-oxazoline (**2**) when irradiated in benzene solution with a 450-W Hanovia lamp. Support for structure (**2**) was provided by the oxidation of (**2**) with dichlorodicyanoquinone (DDQ) to 2-phenyloxazole. Irradiation of (**1**) in benzene which had been saturated with D_2O gave the oxazoline (**2**) mono-deuteriated at position 2 only. The location of the deuterium atom was verified by reduction of $[^2H_1]$-(**2**) with lithium aluminum hydride to $[^2H_1]$-*N*-benzylethanolamine (**3**). The photochemical results are easily rationalized by the initial formation of a nitrile ylide intermediate which subsequently transfers a proton from the neighbouring hydroxyl group and then collapses to the oxazoline (**2**).

The azirine (**1**) provided an easy entry into other substituted 2*H*-azirine derivatives (**4**). 2-Chloromethyl-3-phenyl-2*H*-azirine (**4a**) was prepared by the reaction of (**1**) with *tris*-(dimethylamino)phosphine in carbon tetrachloride. Azirines (**4c**—**4e**) were readily prepared by treatment of (**1**) with acetyl chloride–triethylamine, benzoyl chloride–pyridine, and trimethyl chlorosilane–triethylamine respectively. Reaction of (**1**) with methanesulphonyl chloride–triethylamine followed by treatment of the mesylate with lithium bromide in ether solution gave (**4b**). The corresponding methyl ether (**4f**) was prepared from 1-phenyl-3-methoxy-prop-1-ene *via* the iodine azide route.

On irradiation of benzene solutions of the azirines (**4a**)—(**4d**), an unexpected rearrangement occurred producing the azabutadienes (**5a**)—(**5d**) in essentially quantitative yield. The structures of the imines (**5**) were assigned on the basis of their n.m.r. spectra, and further established by lithium aluminum hydride reduction to *N*-ethylbenzylamine (**6**). A marked feature of the photoreactions was the extreme cleanliness of the rearrangement (>95% yield). In contrast to this, photolysis of the trimethylsiloxy derivative (**4e**) produced only polymeric materials while the methyl ether (**4f**) afforded a mixture of *exo*- and *endo*-(2,6-dimethoxymethyl)4,5-diphenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene (**7**).

The results indicate that the migrating substituent (X) must be a reasonably good leaving group in order for the rearrangement to occur. An equally good explanation is that the migration is the result of neighbouring group participation. The lack of migration for OMe and $OSiMe_3$ can be attributed to the small size of the migrating group leaving it being unable to bridge the linear 3 atom unit of the $-\overset{-}{C}{=}\overset{+}{N}{=}C-$ dipole, whereas the larger halogens are able to do so, as are the acyloxy-groups. Involvement of a nitrile ylide intermediate in the above rearrangements was demonstrated by carrying out the photolysis of (**4c**) in the presence of the very reactive dipolarophile methyl trifluoroacetate.[5] Under these conditions, the formation of (**5c**), which is produced in high yield in the absence of a trapping reagent, is entirely suppressed. The only product isolated was the 3-oxazoline (**8**). Assignment of the 3-oxazoline structure rather than the isomeric 2-oxazoline structure was made on the basis of the i.r. spectrum ($\nu_{C=N}$ 1630 cm^{-1}) and by comparison with the n.m.r. spectra of model compounds.[5,6]

The formation of the 1,3-diazabicyclohexene system (**7**) from irradiation of (**4f**) can be interpreted in terms of 1,3-dipolar addition of the nitrile ylide (**9**) across the C–N double bond of the starting azirine. Other accounts describing the cycloaddition of 1,3-dipoles with azirines have appeared in the literature and provide a good chemical analogy for this reaction.[7] The fact that a dimer is formed from the irradiation of (**4f**) suggests that the methoxy substituent is such a poor migrating group that the nitrile ylide intermediate prefers to undergo cycloaddition with unreacted starting material rather than undergo a 1,4-substituent shift.

We thank the National Institutes of Health for financial support.

(*Received*, *22nd September* 1975; *Com.* 1077.)

---

† All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given later.

[1] A. Padwa and J. Smolanoff, *J. Amer. Chem. Soc.*, 1971, **93**, 548; A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *ibid.*, 1972, **94**, 1395; 1973, **95**, 1945, 1954; *Pure Appl. Chem.*, 1973, **33**, 269; A. Padwa and S. Wetmore, *J. Org. Chem.*, 1973, **38**, 1333; 1974, **39**, 1396; *J. Amer. Chem. Soc.*, 1974, **96**, 2414.

[2] A. Padwa, D. Dean, and J. Smolanoff, *Tetrahedron Letters*, 1972, 4087; N. Gakis, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1972, **55**, 748; H. Giezendanner, M. Marky, B. Jackson, H. J. Hansen, and H. Schmid, *ibid.*, p. 745; B. Jackson, M. Marky, H. J. Hansen, and H. Schmid, *ibid.*, p. 919.

[3] A. Padwa and P. H. J. Carlsen, *J. Amer. Chem. Soc.*, 1975, **97**, 3862; A. Padwa, J. Smolanoff, and A. Tremper, *ibid.*, p. 4682.

[4] F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, 1967, **89**, 2077.

[5] A. Orahovats, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, 1974, **57**, 2626.

[6] P. Claus, P. Gilgen, H. J. Hansen, H. Heimgartner, B. Jackson, and H. Schmid, *Helv. Chim. Acta*, 1974, **57**, 2173.

[7] A. L. Logothetis, *J. Org. Chem.*, 1964, **29**, 3049; V. Nair, *J. Org. Chem.*, 1968, **33**, 2121; *Tetrahedron Letters*, 1971, 4831.