Pyrazole Addition to Δ^1-Azirines. Structure of Purported 2:1 Adducts of Δ^1-Azirines with *sym*-Tetrazines

By RUDI E. MOERCK and MERLE A. BATTISTE*
(*Department of Chemistry, University of Florida, Gainesville, Florida* 32611)

Summary The previously unestablished structure of purported 2:1 adducts isolated from the reaction of Δ^1-azirines with *s*-tetrazines is now shown to be identical with the aziridine derivatives resulting from thermally promoted addition of pyrazoles to Δ^1-azirines.

A NUMBER of reagents, including Grignard reagents, $LiAlH_4$, alkoxides, and tertiary amine hydrochlorides,[1] react with the π-bond of Δ^1-azirines to give aziridines. In contrast, primary and secondary amines give complex mixtures of products.[2]

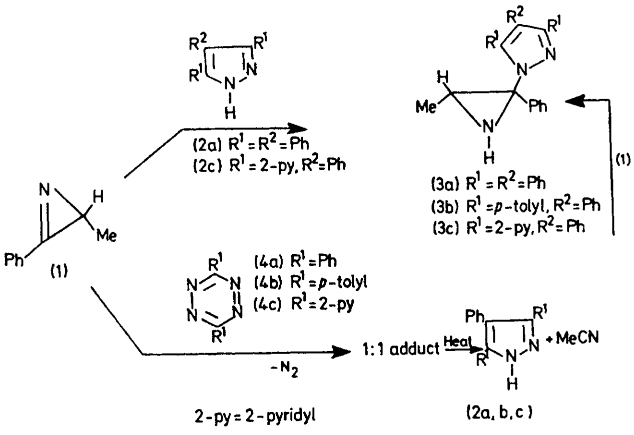
We now report that Δ^1-azirines undergo thermally promoted addition reactions with pyrazoles to afford novel aziridine derivatives in good yield. Reaction of the azirine (**1**) with triphenylpyrazole (**2a**) in refluxing toluene solution afforded the crystalline aziridine (**3a**), m.p. 144—145° [δ ($CDCl_3$) 7·60—6·80 (20H, m, ArH), 3·31 (1H, q, *J* 6·0 Hz), 1·63br (1H, s, exchanges with D_2O), and 0·98 (3H, d, *J* 6·0 Hz)] in 61% yield after silica gel chromatography.† Tentative stereochemical assignment is strongly supported by comparison with aziridines of similar structure.[3] Assignment of structure (**3a**) is further supported by its mass spectrum [M^+, *m/e* 427·2068; M^+-(**2a**) 131·0736].

Analogously, reaction of the azirine (**1**) with the pyrazole (**2c**) in refluxing toluene afforded the 1:1 adduct (**3c**), m.p. 164—165°, in 80% yield.

---

† Satisfactory elemental analyses were obtained for all new compounds. The i.r. and n.m.r. spectra were in agreement with the assigned structures. The yields represent isolated amounts.

These results are of particular interest in regard to a recent report of the reaction of Δ^1-azirines with *sym*-tetrazines,[4] which reportedly afforded novel 2 : 1 adducts ($-N_2$, $-$MeCN) 'of uncertain structure,' along with various amounts of 2*H*- and 6*H*-1,2,4-triazepines (1 : 1 adducts $-N_2$),‡ and pyrazoles. It was suggested that these 2 : 1 adducts may possess a triazocine structure; however, independent work in our laboratory has clearly shown the aziridine (**3a**) to be identical to the reported 2 : 1 adduct formed in the reaction of the azirine (**1**) with diphenyl-*s*-tetrazine (**4a**) in refluxing toluene (Scheme). Under milder conditions, only traces of (**3a**) were detected, the major isolated products being triazepine and the pyrazole (**2a**). A separate experiment established that the pyrazole (**2a**) arises from thermal fragmentation of the triphenylmethyltriazepine with extrusion of MeCN. The aziridines (**3b**) and (**3c**) were isolated in good yield from reaction of the azirine (**1**) with the tetrazines (**4b**) and (**4c**), respectively, in refluxing toluene. We therefore conclude that the purported 2 : 1 adducts do not possess a triazocine structure, but simply arise from reaction of the Δ^1-azirines with the corresponding pyrazoles formed as secondary products under the conditions of the cycloaddition reactions.



SCHEME

Financial support by the National Science Foundation is gratefully acknowledged.

(*Received*, 16*th July* 1974; *Com.* 870.)

---

‡ A detailed treatment of the structural features of the 1,2,4-triazepine system in solution and in the crystalline state will be presented elsewhere.

[1] M. J. Hatch and D. J. Cram, *J. Amer. Chem. Soc.*, 1953, **75**, 38; N. J. Leonard, and B. Zwanenburg, *ibid.*, 1967, **89**, 4456; A. Hassner and F. W. Fowler, *ibid.*, 1968, **90**, 2875; *Tetrahedron Letters*, 1967, 1545; A. Hassner, *Angew. Chem. Internat. Edn.*, 1968, **7**, 643; S. Sato, *Bull. Chem. Soc. Japan*, 1968, **41**, 1440.
[2] G. Smolinsky and B. I. Fever, *J. Org. Chem.*, 1966, **31**, 1423.
[3] N. S. Narasimhan, H. Heimgartner, H. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1973, **56**, 1351; R. Martino, M. J. Abeba, and A. Lattes, *Tetrahedron Letters*, 1973, 433; K. Kotera, S. Miyazaki, H. Takahashi, T. Okada, and K. Kitahonoki, *Tetrahedron*, 1968, **24**, 3681.
[4] D. J. Anderson and A. Hassner, *J.C.S. Chem. Comm.*, 1974, 45.