

Synthesis and Reactivity of 4*H*-Triazoles

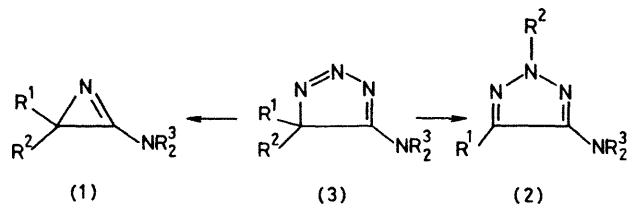
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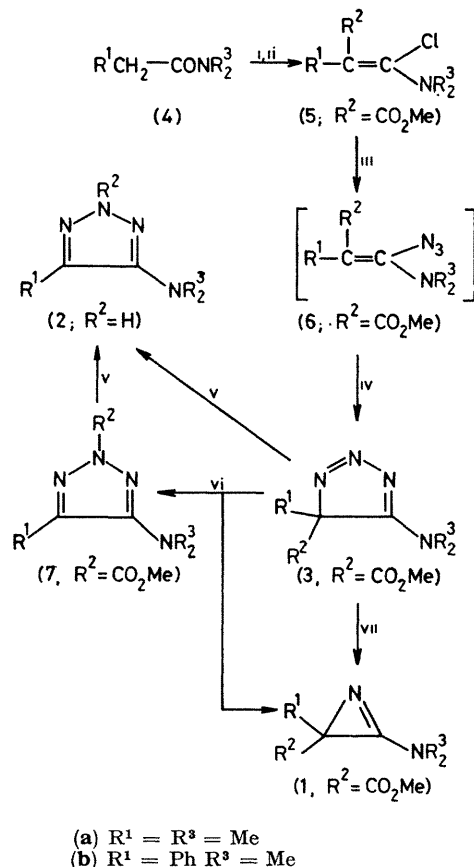
Summary 4*H*-Triazoles, formed from sodium azide and α -chloroenamines bearing methoxycarbonyl- and alkyl-groups at the β -position, give, on thermolysis, aromatic triazoles and/or 3-amino-2*H*-azirines, and on photolysis only azirines

matizes to (2) We now report the isolation² of 4*H*-triazoles (3) and the preliminary study of their thermal and photochemical behaviour

THE reaction of α -chloroenamines with sodium azide provides a convenient route to 3-amino-2*H*-azirines (1) or 4-amino-2*H*-1,2,3-triazoles (2) according to the nature of the substituents¹ Both products could arise from a 4*H*-triazole (3) which either loses nitrogen to give (1) or aro-



Tertiary amides (4) were readily converted into α -chloroenamines (5)³ by treatment with an excess of phosgene in the presence of collidine, followed by reaction with 1 equiv. sodium methoxide. Yields are 80% for (5a) and 72% for (5b). The reaction of (5) with sodium azide in acetonitrile did not give the expected 3-amino-2*H*-azirines



SCHEME i, $COCl_2$ (3 equiv.), collidine (2 equiv.) in CH_2Cl_2 , $-20^\circ C$. ii, $MeONa$ (1 equiv.) in ether, $20^\circ C$. iii, NaN_3 in $MeCN$, $-20^\circ C$. iv, -20 to $+20^\circ C$. v, KOH in CH_3OH , reflux. vi, Refluxing toluene or on distillation (0.1 torr). vii, High pressure lamp, 500 W, Pyrex filter, benzene.

but rather the 4*H*-triazoles (3a) and (3b) in 93% and 90% yields, respectively.

The assignment of 4*H*-triazole structures to (3a) and (3b) is based upon a comparison of their spectroscopic properties, in particular ^{13}C n.m.r. spectra, with those of the aromatic 2*H*-1,2,3-triazole (7a). The structure of (3a) was further confirmed by an X-ray diffraction analysis.⁴

Saponification of (3a) and (3b) was accompanied by decarboxylation and gave the aromatic triazoles (2a) and (2b) in 85 and 93% yields, respectively.

The 4*H*-triazole (3a) remained unchanged after 22 h in refluxing toluene. However, on heating neat at $80^\circ C$ (0.1 torr), it was converted into a mixture of 3-amino-2*H*-azirine (1a) and the 2*H*-1,2,3-triazole (7a) in a ratio of 1:3. Evidence for these structures rests upon spectroscopic data and the conversion of (7a) into (2a) on alkaline hydrolysis. The structural assignment of (7a) and, particularly, the position of the methoxycarbonyl-group was confirmed by an X-ray diffraction analysis.⁴ The 4*H*-triazole (3b) was much less stable; loss of nitrogen and cyclization to the 3-amino-2*H*-azirine (1b) was the sole result of thermolysis of (3b) in refluxing toluene (0.14 mol l^{-1} , 24 h). Distillation *in vacuo* [$125^\circ C$ (0.1 torr)] also yielded (1b) quantitatively.

Both the 4*H*-triazoles (3a) and (3b) are stable under the conditions previously described for the preparation of 3-amino-2*H*-azirines. This observation allows us to reject the hypothesis that (3) is the precursor of both (1) and (2) under such conditions.

The photolysis of both (3a) and (3b) in benzene provides an excellent method of preparation of the 2-substituted-3-amino-2*H*-azirines (1a) and (1b) which were formed in 85 and 93% yields, respectively.

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¹ M. Rens and L. Ghosez, *Tetrahedron Lett.*, 1970, 3765; L. Ghosez in 'Medicinal Chemistry,' Vol. V, ed. J. Mathieu, Elsevier Scientific Publishing Company, Amsterdam, Oxford, New York, 1977, p. 363; H. Heimgartner, *Chimia*, 1979, **33** 111; M. Henriet, M. Houtekie, B. Téchy, R. Touillaux, and L. Ghosez, *Tetrahedron Lett.*, 1980, 223.

² A synthesis of a 5-amino-4*H*-triazole has been claimed by K. Hohenlohe-Oeringen, *Montash Chem.*, 1958, B89, 557. However, spectroscopic data do not differentiate between the proposed structure or the tautomeric imine.

³ α -Chloroenamines (5) were first described by R. Buyle and H. G. Viehe, *Tetrahedron*, 1968, **24**, 4217; 1969, **25**, 3447. Yields were rather poor. Our procedure is based on the experimental modification proposed by G. Winters, N. Di Maha, E. Oppico, and C. Nathansahu, *Il Farmaco*, 1975, **30**, 620.

⁴ J. P. Declercq, G. Germain, R. Touillaux, M. Van Meersehe, C. Bernard, and L. Ghosez, *Acta Crystallogr.*, submitted for publication.