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

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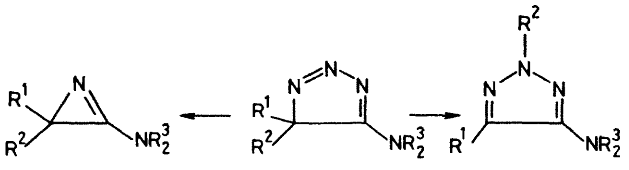
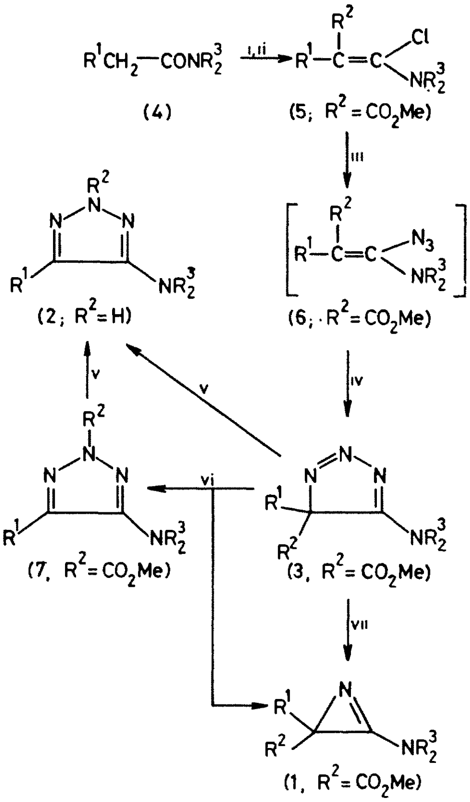
THE reaction of α-chloroenamines with sodium azide provides a convenient route to 3-amino-2*H*-azirines (**1**) or 4-amino-2*H*-1,2,3-triazoles (**2**) according to the nature of the substituents[1] Both products could arise from a 4*H*-triazole (**3**) which either loses nitrogen to give (**1**) or aromatizes to (**2**) We now report the isolation[2] of 4*H*-triazoles (**3**) and the preliminary study of their thermal and photochemical behaviour



(1) (3) (2)

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



(**a**) $R^1 = R^3 = Me$
(**b**) $R^1 = Ph$ $R^3 = Me$

SCHEME i, $COCl_2$ (3 equiv.), collidine (2 equiv.) in CH_2Cl_2, −20 °C. ii, MeONa (1 equiv.) in ether, 20 °C. iii, NaN_3 in MeCN, −20 °C. iv, −20 to +20 °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.

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 °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 °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-Chlorenamines (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.

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