# SYNTHESES OF THIAZOLES AND THIAZINES FROM ALLENES

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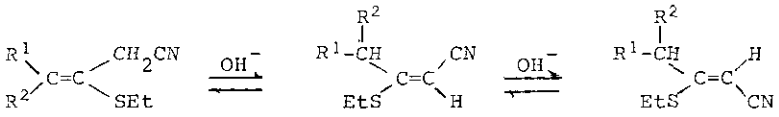
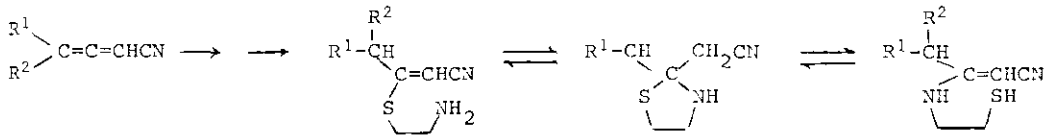
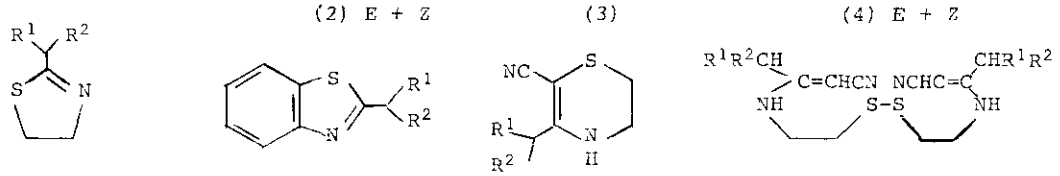
Thiazoles and thiazines can be synthesised in good yield from readily available allenic and acetylenic nitriles[1]. A detailed study of the mechanism has shown that both types of nitrile add thiols at the Michael position in the presence of catalytic base. 2,3-Dienenitriles give first unconjugated nitriles(1) and then conjugated adducts (2, E and Z) on heating with base whereas acetylenic nitriles give only conjugated adducts (2, E and Z). If a second nucleophile is present as in amminoethanethiol further heating results in 5-exotrig ring closure to give the thiazolidine (3) but this opens again to give the more stable N-adduct(4). Distillation of S- or N-adducts (2 or 4) or mixtures of both gives good yields of 2-substituted thiazolines(5) or benzthiazoles(6).



(1) (2) E (2) Z



(2) E + Z (3) (4) E + Z



(5) (6) (7) (8)

Refluxing S- or N-adducts (2 and 4) with excess sodium ethoxide in ethanol for 24 hours gave, 2,3-dihydro-6-cyano-5-alkyl-4,H-1,4-thiazines (7) in about 90% yield. This constitutes a new general method for the synthesis of dihydro-1,4-thiazines involving an interesting oxidation step to disulphide (8).

The assignation of the structures of all intermediates and heterocycles and proposed mechanisms will be discussed.