

## Novel Synthesis of Imidazolines and Imidazoles by Michael Addition to Allenic or Acetylenic Nitriles

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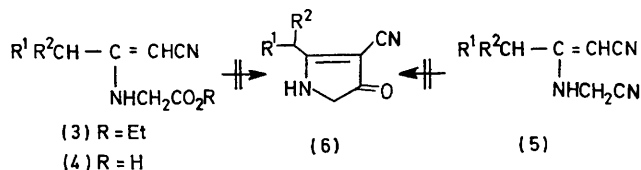
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**Summary** The synthesis of imidazolines and imidazoles by double Michael addition of ethylene- or phenylenediamines to allenic or acetylenic nitriles is described; enamino nitriles from  $\alpha$ -amino-acids, -esters, and -nitriles did not give pyrrolone derivatives.

MICHAEL addition of amines to the central carbon atom of allenic nitriles gives first unconjugated (1) and then conjugated enamino nitriles (2) in near quantitative yield.<sup>1</sup>



Experiments with a deuterioamine and kinetic data indicate that the nucleophile adds to the 2,3-double bond



and this is followed by a fast equilibration of unconjugated and conjugated nitrile. This reaction has now been applied to the synthesis of heterocycles.

Surprisingly, the conjugated enamino nitriles (3), (4), and (5) obtained by Michael additions of  $\alpha$ -amino-esters,  $\alpha$ -amino-acids, and  $\alpha$ -amino-nitriles could not be cyclised to pyrrolone derivatives (6) under a variety of standard conditions.<sup>†</sup>

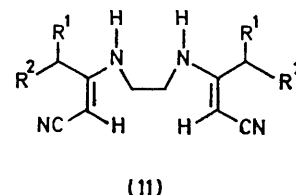
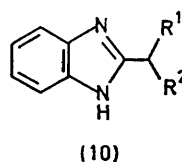
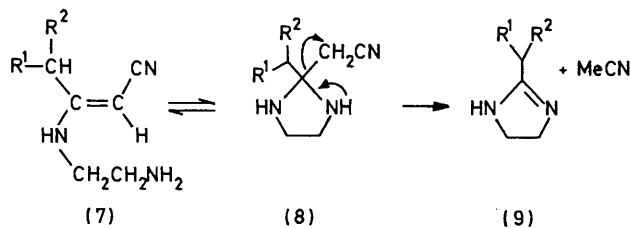
<sup>†</sup> (a) Acid- or base-catalysed conditions for ester (3), (b) dicyclohexylcarbodi-imide or *via* the corresponding acid chloride for the acid (4), and (c) under Ziegler conditions for the dinitrile (5).

<sup>‡</sup> R<sup>1</sup> = Me, Et, Pr, Ph; R<sup>2</sup> = H, Me, Et, all adducts and heterocycles (9) had satisfactory elemental analyses and spectral properties in accord with the assigned structures.

<sup>§</sup> Identified by comparison with an authentic sample.

<sup>1</sup> Z. T. Fomum, P. M. Greaves, P. D. Landor, and S. R. Landor, *J.C.S. Perkin I*, 1973, 1108.

<sup>2</sup> R. L. Bol'shedvorskaya, G. A. Pavlova, L. D. Gavrilov, N. V. Alekseeva, and L. I. Vereshchagin, *Zhur. org. Khim.*, 1972, 8, 1879 describe a similar bis-adduct from an allenic ketone and ethylenediamine.



However, the conjugated 1:1 Michael adducts (7) from ethylenediamine and allenic nitriles or acetylenic nitriles (with a range of alkyl substituents) cyclise readily to give > 80% of 2-alkylimidazolines (9).<sup>‡</sup> This is rationalised by postulating a second Michael addition with formation of the unstable imidazolidine (8) which on distillation eliminates acetonitrile<sup>§</sup> and thus displaces the equilibrium to the right.

Similarly *o*-phenylenediamines gave 2-alkylbenzimidazoles (10). Addition of ethylenediamine to excess of the allenic nitrile gave the 1:2 bis-adducts (11).<sup>2</sup>

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