

Vinylic substitution by DBN and DBU with ethyl (E)- and (Z)-3-aryl-3-chloro-2-cyanopropenoates.

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J. Chem. Research (S), 2000, 102
J. Chem. Research (M), 2000, 0430–0435

Some new 6-aryl-7-cyano-1,5-diazatricyclo[7.4.1^{9,11}.0^{5,14}]tetradeca-6,9-dien-8-ones (**4a–c**) and 6-aryl-7-cyano-1,5-diazatricyclo[7.1.2^{1,9}.0^{5,12}]dodeca-6,9-dien-8-ones (**5a–c**) have been prepared in moderate to good yields by reacting ethyl (E)- and (Z)-3-aryl-3-chloro-2-cyanopropenoates (**1a–c**) with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and DBN (1,5-diazabicyclo[4.3.0]non-5-ene).

DBU and DBN have effectively been used in the elimination of hydrohalogens yielding alkenes,¹ as catalyst in Michael-type reactions and to accelerate addition reactions, of alcohols to triple bonds.³ DBU ring opening reactions followed with rearrangement have also been reported.^{4–6} There are only a few articles describing DBU as a nucleophilic reagent.^{7–9}

Here we present the synthesis of (**4a–c**) and (**5a–c**) starting from (**1a–c**) using DBU and DBN as reagents. (Scheme 1, Table 1)

In these reactions DBU and DBN show nucleophilic character.

The synthesis is advantageous since both isomers cyclize and the troublesome separation of the isomers is avoided.

The reactions were carried out at 25°C. Only tarry products were formed at higher reaction temperatures *i.e.* at the boiling point of THF (66°C). The reaction products were identified from their ¹H, ¹³C NMR, mass spectra and HRMS. The purity of the products was verified by TLC analysis. Further evidence of the structures was achieved from the carbon proton long-range coupled spectra.

Techniques used: IR, TLC, EIMS, ¹H, ¹³C NMR.

References: 12

Table 1 Isolated yields of reaction products (**4a–c**) and (**5a–c**) in the reactions of **1a**, **1b** and **1c** with DBU and DBN.

Prod.	R	yield %	Prod.	R	yield %
4a	H	52	5a	H	65
4b	CH ₃	58	5b	CH ₃	60
4c	NO ₂	98	5c	NO ₂	65

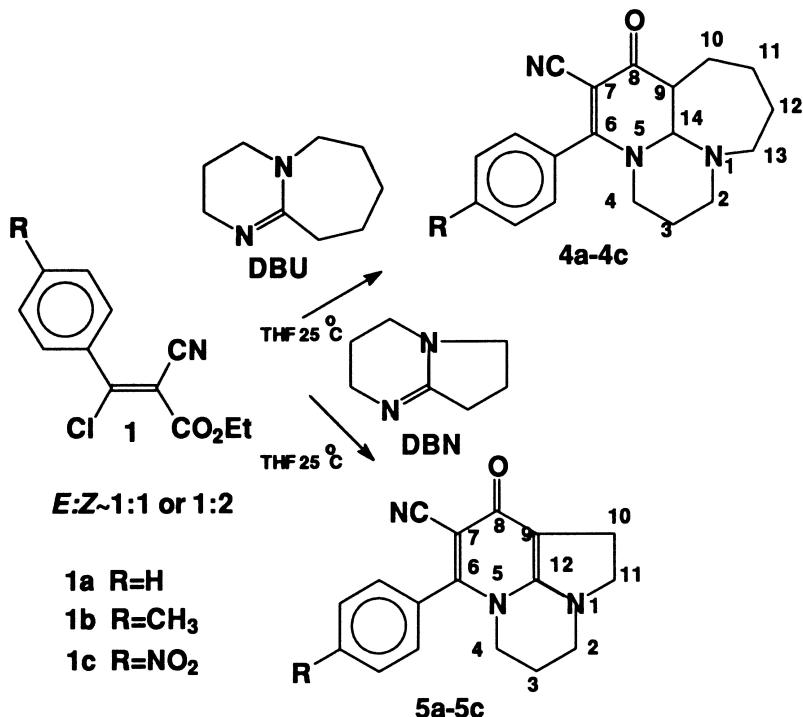
Received 25 November 1999; accepted after revision

27 January 2000

Paper 99/44

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Scheme 1

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