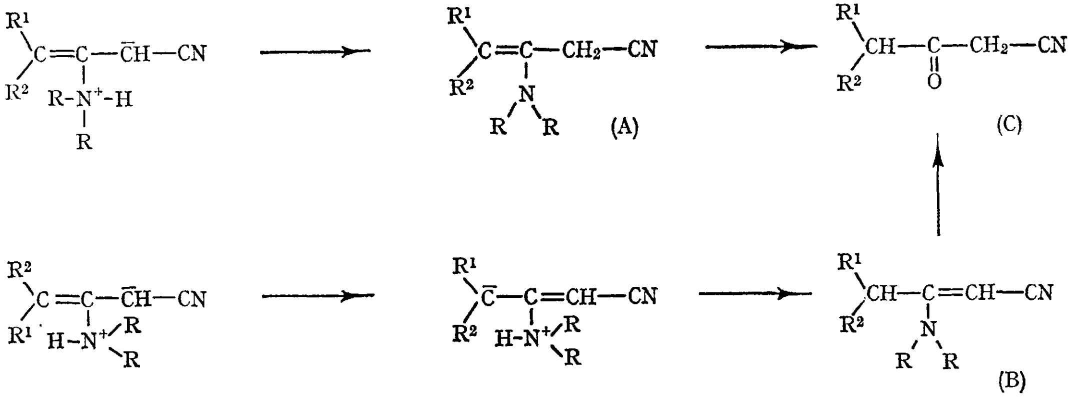
Enamines from Allenes

By P. M. GREAVES and S. R. LANDOR

(*Department of Chemistry, Fourah Bay College, The University College of Sierra Leone, Freetown, Sierra Leone*)

THE reactions of enamines[1] have come into prominence in recent years, particularly the alkylation reactions developed by Stork. While enamines derived from cyclic ketones are readily available few simple enamines derived from aliphatic ketones have been described in the literature. We here report the formation of enamines by addition of amines to 1-cyanoallenes, general methods for the preparation of which have recently been described.[2] The addition of amines to 1-cyanoallenes results in a fast exothermic reaction which is virtually completed after a few minutes when allenes with small alkyl substituents are used but may require some heating where large alkyl substituents are present. Enamines are usually obtained in 80—90% yield. Addition may take place at the 1,2- or 2,3-double bond and this can to some extent be regulated by choice of the amine used in the reaction. Diethylamine gives mainly 1,2-addition whereas piperidine affords mostly the 2,3-addition product.

Both types of enamine are stable under the reaction conditions employed and do not isomerise. They are therefore formed by different mechanistic pathways which may be formulated as in the reaction Scheme.



REACTION SCHEME

A 90° rotation round the C-1–C-2 bond is necessary before delocalisation of the anion can occur and (B) can be formed. The detailed mechanistic implications of this reaction will be discussed elsewhere.

Both types of enamine, (A) and (B), hydrolyse quantitatively to the same β-keto-nitrile[3] (C) and this constitutes a new method of synthesis of β-keto-nitriles. 1-Cyanoalk-2-en-2-amines (A) show ν_{max} 2250—2280 (CN), 1650—1670 cm.$^{-1}$ (C=C) and λ_{max} 203—204 mμ (ε, 6000) $\lambda_{shoulder}$ 232—244mμ (ε, 1000) whereas 1-cyanoalk-1-en-2-amines (B) show ν_{max} 2210 (C=N), 1575—1580 cm.$^{-1}$ (C=C), λ_{max} 275—285 mμ (ε, 20,000). Further studies on the scope of these reactions and their applications are in progress.

TABLE

Cyanide		Amine	Yield of A	Yield of B
R^1	R^2			
H	Pr^i	Et_2NH	—	90%
Me	Me	Et_2NH	75%	—
Me	Me	$[CH_2]_5NH$	8%	78%
Me	Et	Et_2NH	72%	17%
Me	Et	$[CH_2]_5NH$	8%	81%
Et	Et	Et_2NH	70%	*
Et	Et	$[CH_2]_5NH$	*	66%
Me	Bu^t	Et_2NH	*	43%
Me	Bu^t	$[CH_2]_5NH$	58%	23%
Pr^i	Pr^i	Et_2NH	16%	54%

* Not isolated pure

(*Received, April 25th,* 1966; *Com.* 268.)

---

[1] J. Szmuszkovicz, *Adv. Org. Chem.*, 1963, **4**, 1.

[2] P. M. Greaves, S. R. Landor, and D. R. J. Laws, *Chem. Comm.*, 1965, 321.

[3] β-Keto-nitriles have previously been prepared by Claisen ester type of condensation of nitriles having reactive α-methylene groups and either esters (J. B. Dorsch and S. M. McElvain *J. Amer. Chem. Soc.*, 1932, **54**, 2960 and subsequent papers) or nitriles (*e.g.*, A. Dornow, I. Kulilcke, and F. Baxmann, *Chem. Ber.*, 1949, **82**, 254.) See also 2-cyanoalkanones prepared from enamines (M. E. Kuehne, *J. Amer. Chem. Soc.*, 1959, **81**, 5400.