

The Preparation of 1-Cyanoallenes

By P. M. GREAVES, S. R. LANDOR, and D. R. J. LAWS

(*Fourah Bay College, The University College of Sierra Leone, and Woolwich Technical College, London, S.E.18*)

WE now report a number of new methods for the preparation of cyanoallenes which have been evolved in our laboratories.

Most tertiary acetylenic alcohols are readily converted into cyanoallenes by treatment with cuprous cyanide (1.5 equivalents), a trace of

copper, potassium cyanide (1 equivalent), and hydrobromic acid (48% ; 2.5 equivalents) for 3 days. A small quantity of acetylenic alcohol is recovered but no bromoallenes¹ are obtained. Concentrated hydrochloric acid in place of hydrobromic acid gives mainly recovered acetylenic alcohol but with

¹ D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Letters*, 1963, 483.

a large excess of hydrochloric acid (5 equivalents) lower yields of cyanoallenes together with equal quantities of chloroallenes² are obtained. Other

acids (H₂SO₄, HCO₂H, CH₃CO₂H) gave no conversion into cyanoallenes.

In view of these observations the reaction is best explained by the slow formation of acetylenic chloride or bromide which then undergoes a fast conversion into allenic cyanide through a cuprous cyanide π -complex. However, acetylenic halides under the same conditions give considerably lower yields and more by-products. Sterically hindered and polysubstituted cyanoallenes cannot be obtained by the above method but are readily obtained from bromoallenes¹ by treatment with anhydrous cuprous cyanide at 100–120°. Under these conditions lower homologues with a suitably placed proton eliminate hydrogen cyanide to give enynes.³

Monoalkylbromoallenes, from secondary acetylenic alcohols, give monoalkyl-1-cyanoallenes in good yield on heating with anhydrous cuprous cyanide in dimethylformamide at 60°. 1-Cyanoallenes show ν_{\max} 2220–2250 (C \equiv N), 1950–1960 (C=C=C), and 725–765 cm⁻¹ (H-C-CN) and λ_{\max} 207 m μ ($\epsilon \sim 10,000$).

All previous attempts⁴ to prepare cyanoallenes started with halogenoacetylenes and gave poor yields of mixtures of acetylenes and allenes.

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TABLE

$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C}=\text{C} \\ \diagup \\ \text{R}^2 \end{array} \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CN} \end{array}$		
R ¹	R ²	% yield
Et	H	60 ^c
Pr	H	60 ^c
Me	Me*	30 ^a
		22 ^b
Me	Et†	51 ^a
		31 ^b
Et	Et	75 ^a
		18 ^b
Me	Bu [†]	40 ^a
Me	Bu [†]	60 ^c
Pr [†]	Pr [†]	60 ^c
Bu [†]	Bu [†]	60 ^c
‡Bu [†]	Bu [†]	90 ^c

^a Acetylenic alcohol, HBr, CuCN, KCN, Cu, for 3 days; ^b acetylenic alcohol, HCl, CuCN, KCN, Cu for 10–15 hr.; [†] allenic bromide, CuCN. * Dimerises⁵ on keeping to 1,1,2-tetramethyl-3,4-di(cyanomethylene)cyclobutane, m.p. 85°, λ_{\max} 281 m μ , (ϵ 11,420); ν_{\max} 2252, 2235, 1680, 1650 cm⁻¹ † dimerises⁵ on keeping to 1,2-diethyl-1,2-dimethyl-3,4-di(cyanomethylene)cyclobutane, b.p. 180°/1 mm., λ_{\max} 282 m μ , (ϵ 18,300); ν_{\max} 2250, 2260, 1660, 1630 cm⁻¹.

² Cf. Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, 1959, 24.

³ Under basic conditions 1-halogenoallenes undergo α -elimination to allenic carbenes and only traces of enynes are formed, cf. Allenes, Part IX, S. R. Landor and P. F. Whiter, *J. Chem. Soc.*, 1965, in press.

⁴ Cf. J. H. Wotiz and E. S. Hudah, *J. Org. Chem.*, 1954, 19, 1580; L. I. Smith and J. S. Swenson, *J. Amer. Chem. Soc.*, 1957, 79, 2962; K. Schlogl and K. Orgler, *Monatsh.*, 1959, 90, 306; P. Kurtz, H. Gold, and H. Disselnkotter, *Annalen*, 1959, 624, 1. A recent preliminary report by Y. Pasternak and G. Peiffer, *Compt. rend.*, 1964, 259, 1142 described the preparation of two cyanoallenes from acetylenic bromides but gives no yields.

⁵ Cf. Dimerisation of allenes, P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 1963, 2707; W. J. Ball and S. R. Landor, *ibid.*, 1962, 2298; T. C. Jacobs and W. L. Petty, *J. Org. Chem.*, 1963, 28, 1360.