The Structure of 1-Cyanoallene Dimers

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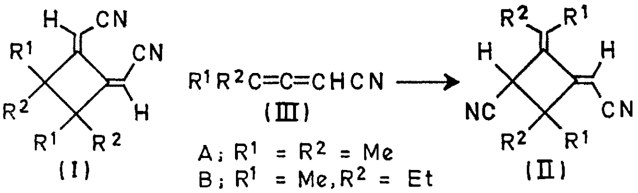
Summary Spectral evidence reveals that allenic nitriles thermally dimerize to give unsymmetrical, geminal disubstituted cyclobutanes.

SEVERAL authors[1,2] have reported that allenic nitriles dimerize to give symmetrical cyclobutane derivatives (I). We, however, report conclusive evidence which proves that the unsymmetrical analogues (IIA and B) are formed *via* a Michael cyclization. Treatment of the corresponding allenic bromides with CuCN in *NN*-dimethylformamide or the reaction of the unrearranged acetylenic alcohol with CuCN, KCN, and Cu in 48% hydrobromic acid gives the monomeric allenic nitriles (III A and B).[3]

When the distillation of crude (IIIA, 38%) was only half complete the residue solidified to give (IIA), 21%, m.p. 84—86° (cyclohexane–petroleum), *m/e* 186. The monomeric distillate which was obtained (11%, b.p. 52—53°/9 mm, *m/e* 93) slowly dimerized, even when refrigerated and protected from the light, to give the same product. The allenic nitrile (IIIB) (45%, b.p. 62°/5·5 mm, *m/e* 107) could be successfully distilled with little dimer formation, but when heated neat at 130° for 6 h it was quantitatively transformed into (IIB) (oil, not distilled, *m/e* 214). The spectral data in the Table support the suggested dimer structures which were further substantiated by satisfactory elemental analysis. The i.r. spectra indicate nitrile and double bond absorption in the dimeric products but no triple bond or allenic systems.



(I)

$R^1R^2C{=}C{=}CHCN \longrightarrow$ (III)

A; $R^1 = R^2 = Me$
B; $R^1 = Me, R^2 = Et$

(II)

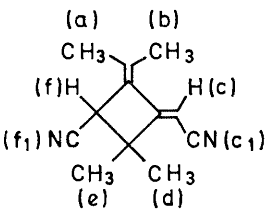
Compound	N.m.r.[a]	I.r. (ν_{max}, cm^{-1})[b]	U.v. (λ_{max}, EtOH, Å)
(IIA)	a = 1·97(d); b = 2·21(bd); c = 4·93(q); d = 1·31(m); e = 1·38(m); f = 3·35(bs) J_{fb} 1·8; J_{fa} 0·6 J_{cb} 0·1 Hz	2225, 1650, 1614, 1440, 1280	2810 (ϵ 1·5 × 10^4)
(IIB)	a = 0·86—1·35(m); b = 1·40—1·64(m); c = 2·05—2·32(m); d = 1·72—1.95(m); e(*anti*) = —4·91(s); e(*syn*) = 5·24(s); f = 3·36(bs)	2185, 2200, 1640, 1610, 1450, 1355, 1240	2835 (ϵ 2·2 × 10^4)

[a] Run as 10% solutions in CCl_4 relative to Me_4Si as an internal standard on a Jeolco, C-60HL High Resolution NMR.
[b] Run as 10% solutions in CCl_4.

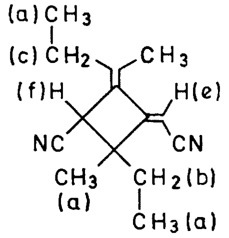
The absolute configuration of (IIA) was established by the following interpretation of the n.m.r. data. The presence of two vinyl methyl groups and two saturated methyl groups in the spectrum of (IIA) eliminates (I) and other symmetrical structures from consideration. The shifts of (a, b, c, and f) are quite normal whereas (d, e) are deshielded by approximately 0·2—0·3 p.p.m.[4,5] The best explanation is that the vinylic nitrile (c_1) is deshielding both methyl groups (d, e), while (f_1) is deshielding (e) to a lesser extent. Decoupling shows that (H_f is coupled to (a,b) by 1·8 and 0·6 Hz respectively, while (H_c) is coupled to (H_b) by 0·1 Hz; this is in agreement with published data stating that in similar cases *trans*- is greater than *cis*-coupling.[6] Furthermore, if (b) were in the same plane and on the same side of (c_1) a deshielding should be observed, but it is not. The 6-bond interaction between (H_c) and (H_b) cannot be correlated with a precedent and appears to be the first observation of this type of coupling. Finally, the absence of an isopropyl group or methylene protons in the n.m.r. eliminates all possible tautomeric compounds.

The major isomer of (IIB) exhibits protons (e) and (f) in essentially the same positions as does (IIA) for the (c) and (f) protons, although the methyl and ethyl regions of (IIB) are highly complex. This complexity and the presence of an additional vinyl hydrogen suggest a mixture of two materials due to the isomerism which can arise from two geometric centres and two optical centres in the molecule. On the basis of the observed spectral data we have suggested the *syn*- and *anti*-structures for (IIB). The extended conjugation indicated by the u.v. spectra of (IIA and B) eliminate all but structure (II) as a possibility.

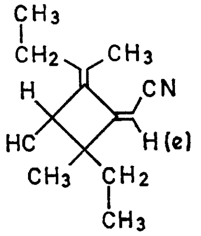
Attempted hydrolysis of the dimers (IIA and B) with sulphuric or hydrochloric acids gives only polymeric products. Reaction of either (IIA or B) with maleic anhydride or tetracyanoethylene did not give any Diels–Alder adduct and the starting materials were recovered unchanged. This is probably due to the non-planarity of the 1,2-dimethylidenecyclobutane moiety.



(IIA)



(IIB) (*anti*, 70%)



(IIB) (*syn*, 30%)

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