Allenes. Part XXV.[1] Cyclobutane Dimers of 1-Cyanoallenes

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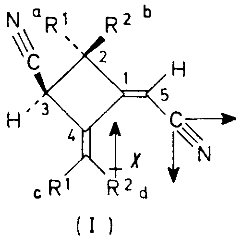
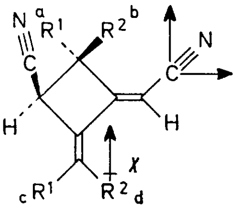
The synthesis of 2,2-dialkyl-3-cyanomethylene-4-dialkylmethylenecyclobutanecarbonitriles by dimerisation of allenic nitriles is described. Spectroscopic and dipole moment data provide conclusive evidence for the structure of the dimers.

GENERAL methods for the synthesis of allenic nitriles have already been described.[2,3] In a preliminary communication[2] we noted that 4-methylpenta-2,3-dienenitrile and 4-methylhexa-2,3-dienenitrile slowly dimerises on keeping at room temperature but the structure of the dimers was incorrectly formulated as 1,1,2,2-tetra-alkyl-3,4-biscyanomethylenecyclobutane.[4] When n.m.r. and dipole moment data became available we were able to show[5] that an unusual head-to-tail dimerisation had taken place, giving cyclobutanes of structure (I). A recent report[6] also suggested a head to tail dimerisation based on n.m.r. evidence but an *anti*-structure was suggested whereas evidence presented here suggests a *syn*-structure for the main isomers formed.

Allenic nitriles may be distilled *in vacuo* at bath temperatures of <100° with little or no dimerisation but with external heating to >100° some dimer formation always takes place (15—30%). Purification of the non-volatile residue permits isolation of the cyclobutane derivatives but these are best prepared by the quantitative conversation of monomer to dimer by heating under nitrogen at temperatures >100° for 2—4 h. However, slow formation of dimer at room temperature or lower temperature produced relatively more *syn*-isomer whereas formation of the dimer by heating the cyanoallene at 100—130° produced relatively more *anti*-isomer.



(I)



(II)

All the dimers [$R^1 = R^2 =$ Me; $R^1 =$ Me (or Et), $R^2 =$ Et (or Me); $R^1 = R^2 =$ Et] showed similar i.r. and u.v. spectra and common features in the n.m.r. spectra. They all showed two C≡N stretch bands for saturated and unsaturated nitrile, two C=C stretch bands for the $R_2C=C$ and C=CCN double bonds in the i.r. and an intense maximum at 282 nm in the u.v. spectrum corresponding to the dialkylidenenitrile chromophore ($R_2C=C-C=C-CN$). Signals in the n.m.r. spectrum showed one olefinic proton (split into two signals for the dimethyl-diethyl and tetraethyl substituted dimers for *syn*- and *anti*-isomers) and one proton α to a cyano-group. This shows conclusively that all three dimers possess the same carbon skeleton and this can only be reconciled with structure (I) or its stereoisomers.

The crystalline tetramethyl dimer (I; $R^1 = R^2 =$ Me) obtained in 70% yield shows six signals, four of which correspond to four magnetically different methyl groups: Me_a, τ 8·7, has normal deshielding due to the β-CN substituent, Me_d, τ 8·6, is deshielded by a *syn*-CN group, Me_c, τ 8·01, is deshielded by CN, and Me_d, τ 7·75, is more strongly deshielded by the C=C–CN group. The two remaining signals are due to single protons, the multiplet at τ 6·57 being ascribed to 1-H coupled mainly to Me_d and the singlet at τ 5·0 to the olefinic proton.

A liquid dimeric fraction was isolated from the mother liquors of the *syn*-dimer which had been formed at 100°. This was believed to be a 1 : 1 mixture of the *syn*- and *anti*-stereoisomers, and this was strongly supported by spectroscopic data. The n.m.r. spectrum, besides showing the six signals due to the crystalline *syn*-dimer, gave additional signals at τ 8·45 and 8·38 corresponding to Me_a and Me_b in structure (II), both deshielded by the proximity of an *anti*-CN group and hence both shifted 12·5 Hz downfield compared with the signal of the corresponding methyl groups in the *syn*-isomer. The intensity of the 3H signals at τ 8·07 were in the ratio 3 : 1 as both Me_c and Me_d were magnetically equivalent in the *anti*-isomer which accounted for half the proton signal at τ 8·01. A new olefinic proton signal appeared at τ 4·67 of equal intensity to the signal at τ 5·0 ascribed to the *syn*-isomer. Dipole moment data further supported this assignment. The crystalline *syn*-compound gave μ 3·84 D whereas the liquid 1 : 1 *syn–anti*-mixture gave a somewhat higher dipole moment 4·61 D as expected from the following considerations. The induced dipole X of the 4-dialkylmethylene group is in the

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[1] Part XXIV, J. C. Cowie, P. D. Landor, and S. R. Landor, *J.C.S. Perkin I*, 1972, 720.

[2] P. M. Greaves, S. R. Landor, and D. R. J. Laws, *Chem. Comm.*, 1966, 321.

[3] P. M. Greaves, S. R. Landor, and D. R. J. Laws, *J. Chem. Soc.*, 1968, 991.

[4] These were based on u.v. evidence and analogy with the great majority of (2 + 2) cycloaddition reactions of allenes which were known to give products derived from head-to-head, tail-to-tail dimerisation, *cf.* J. R. McClenon, Ph.D. Thesis, University of California, 1964.

[5] P. M. Greaves, Ph.D. Thesis, Durham University, 1967.

[6] G. R. Hansen, K. W. Ratts, and J. T. Marvel, *Chem. Comm.*, 1970, 918.

same direction as the vertical component of the *anti*-cyano-group in isomer (I) but in the opposite direction to the vertical component of the *syn*-cyano-group in the isomer (II). Separation of *syn*- and *anti*-isomers could not be achieved by wet column or dry column chromatography, t.l.c., or g.l.c.

Similarly the tetraethyl dimer ($R^1 = R^2 = Et$), formed by keeping the corresponding cyanoallene at 5° for seven months (only 10% of monomer had dimerised) proved to contain more of the *syn*-isomer (I; $R^1 = R^2 = Et$) (*syn* : *anti* ratio 3 : 2) as shown by integration of peaks at τ 4·61 and 5·0 whereas the same dimer formed at 120—130° contained mainly *anti*-isomer (II; $R^1 = R^2 = Et$) (*syn* : *anti* ratio 15 : 85). I.r. and u.v. evidence (see Table 1) show that the two tetraethyl isomers had the same basic skeleton as that of their tetramethyl analogues. A detailed analysis of the n.m.r. spectrum is more difficult; both mixtures (containing either predominantly *syn*- or predominantly *anti*-isomer) showed several overlapping triplets for the methyl groups between τ 9·17 and 8·73. The product from the low temperature dimerisation, containing more of the *syn*-isomer, showed a complex 8H multiplet between τ 8·53 and 7·2 due to all four methylene groups being in different magnetic surroundings, two peaks for the ring proton at τ 6·53 and 6·47 (ratio 3 : 2) corresponding to *syn*- and *anti*-compound, and the olefinic proton at τ 5·0 and 4·63 in the same ratio. The product from the higher temperature dimerisation, containing 85% *anti*-isomer, showed three overlapping quartets for the methylene groups of the *anti*-isomer at τ 8·20 (2H), 8·07 (2H), and 7·70 (4H) which were superimposed on the small signals of the multiplet due to 15% of the *syn*-isomer present, a 1H signal for the ring proton at τ 6·53 and 6·47 (ratio 15 : 85), and the signal for the olefinic proton at τ 5·0 and 4·63 in the same ratio. These were evidence for the presence of the *syn*- and *anti*-form in that proportion. The dipole moment of the 85% *anti*-isomer was found to be 5·28 D, in reasonable agreement with the prediction that the *anti*-compound should have a higher dipole moment than the *syn*-isomer, the induced dipole *X* of the 4-diethylmethylene being in the same direction as the vertical component of the *anti*-cyano-group.

TABLE 1

Spectroscopic data for cyclobutane dimers

R^1	R^2	$\nu_{max.}$/cm^{-1} [a]				$\lambda_{max.}$/nm	ε/l mol^{-1} cm^{-1}	τ [b]
Me	Me	2240	2218	1660	1630	282	11,300	8·67 (3H, s), 8·60 (3H, s), 7·73 (3H, s), 6·57 (1H, m), 5·0 (1H, s)
Me	Me	2240	2218	1650	1620	282	11,400	8·67 (1·2H, s), 8·60 (1·2H, s), 8·47 (1·8H, s), 8·40 (1·8H, s), 8·03 (4·5H, s), 7·73 (1·5H, s), 6·57 (1H, m), 5·0 (0·4H, s), 4·67 (0·6H, s) [c]
Me	Et	2238	2215	1650	1620	282	19,700	9·2—7·6 (16H, m), 6·55 (1H, s), 5·0 (0·75H, s), 4·67 (0·25H, s)
Me	Et	2238	2215	1650	1620	282	20,100	9·2—7·6 (16H, m), 6·58 (1H, s), 5·0 (0·56H, s), 4·67 (0·44H, s)
Et	Et	2240	2218	1650	1620	282	18,200	9·17—8·73 (12H, m), 8·53—7·20 (8H, m), 6·53 (0·58H, s), 6·47 (0·42H, s), 5·0 (0·58H, s), 4·63 (0·42H, s)
Et	Et	2240	2216	1650	1620	282	18,400	9·15—8·75 (12H, m), 8·20 (2H, q), 8·07 (2H, q), 7·7 (4H, q), 6·53 (0·15H, s), 6·47 (0·85H, s), 5·0 (0·15H, s), 4·63 (0·85H, s)

[a] For 30% $CHCl_3$ solutions. [b] Position of signals may very slightly with the concentration of the solution, *e.g.* for the dimethyl-diethyl dimer a 3·4% solution gave signals at τ 5·0 and 4·67 whereas a 12·1% solution gave signals at τ 5·02 and 4·68. [c] 2:3 *syn*:*anti* mixture.

Formation of the dimethyl-diethyl substituted dimer ($R^1 = Me$; $R^2 = Et$) at 100° for 2·5 h gives a mixture of *syn*- (I) and *anti*-isomers (II) of *syn* : *anti* ratio 56 : 44 as indicated by integration of the signals at τ 5·0 and 4·67, whereas dimerisation at 5° for 21 months gave a product (90% dimerised) with *syn* : *anti* ratio 3 : 1. Each *syn*- or *anti*-form could exist as four different stereoisomers; the protons of methyl and ethyl groups gave rise to complex multiplets which were not analysed. Although t.l.c. or dry column chromatography gave four bands the first three on elution had identical n.m.r spectra, and certainly no separation of *syn* and *anti*-isomers was achieved. The fourth band, on elution gave a strong absorption at 3400—3600 cm^{-1} in the i.r. spectrum indicating hydration of the conjugated double bond. Corresponding hydrated compounds were also isolated from the tetramethyl or tetraethyl substituted dimers after chromatography on alumina.

In recent years a number of investigations of the mechanism of allene dimerisation have been reported and discussed in terms of concerted or two stage (2 + 2) cycloadditions.[7] As far as we are aware the dimerisation of the 1-cyanoallene reported here is only the second example of a quantitative unsymmetrical (2 + 2) addition (the first example being the unsymmetrical dimerisation of 1,1-diphenylallene[8]) although there have been previous reports of mixtures of symmetrical and unsymmetrical dimers being formed. Conrotatory or disrotatory perpendicular joining of the 2- and 2′-positions of the allenes, anticlockwise rotation round the 2,2′-bond (rather than the more usual clockwise rotation) of the vertical allene unit due to repulsion of cyanide groups

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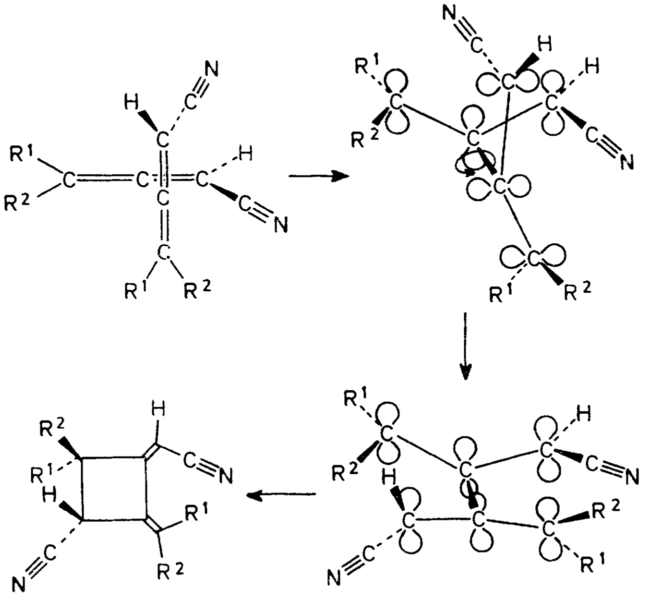
[7] See references and discussion in J. E. Baldwin and R. H. Fleming, *Topics Current Chem.*, 1970, **15**, 281.

[8] P. Baltrome, D. Pitea, A. Marzo, and M. Simonetta, *J. Chem. Soc.* (*B*), 1967, 71.

followed by disrotatory or conrotatory ring closure would account for the formation of the *syn*- and *anti*-forms of the dimers. Low temperature preferential formation of the *syn*-isomer and higher temperature preferential formation of the *anti*-isomer appear to be both kinetically controlled as the reverse reaction to the perpendicular intermediate is too slow at 100—130° to be significant (the *syn*-isomers were not significantly transformed to *anti*-isomers on heating under the conditions under which the *anti*-isomers are preferentially formed).



Mascio and Jacobs [9] suggest that the inward position of substituents on the allene is preferred to the outward position in the (2 + 2) cycloaddition. If this is correct the two cyanide groups prefer the inward position and the *syn*-isomers would be preferentially formed. It follows that the activation energy for the formation of the *anti*-isomer would be higher than that for *syn*-isomer. Hence formation of the *anti*-isomer is favoured at higher temperature. The orientation of approach of the two perpendicular allene molecules (CN group inward or outward) at the first stage of the (2 + 2) cycloaddition determines the configuration of the product.

EXPERIMENTAL

3-*Cyanomethylene*-4-*isopropylidene*-2,2-*dimethylcyclobutanecarbonitrile*.—1-Cyano-3-methylbuta-1,2-diene (5 g, 0·056 mol) was heated at 100° for 45 min under nitrogen, the reaction being monitored by i.r. absorption. The disappearance of the band at $\nu_{max.}$ 1950 cm^{-1} (C=C=C) showed completion of the dimerisation. After most of the product had crystallised at 0° the liquid fraction was pipetted out and the crystals were washed with and recrystallised from isohexane to give plates of the *syn*-isomer of the *nitrile* (3·52 g, 70%), m.p. 84° (Found: C, 77·5; H, 7·6; N, 14·9. $C_{11}H_{14}N_2$ requires C, 77·4; H, 7·6; N, 15·0%), $\nu_{max.}$ 2240 (C≡N), 2218 (conj. CN), 1660 (C=C), and 1630 (C=C–C≡N) cm^{-1}, $\lambda_{max.}$ (EtOH) 282 nm (ε 11,300), τ ($CDCl_3$) 5·0 (1H, s, CHCN). Fractional crystallisation of the liquid fraction in isohexane gave more of the *syn*-isomer (0·5 g). Removal of the solvent from the combined mother liquors gave a mixture of the *syn*- (50%) and *anti*-isomer (50%) (0·5 g, 10%), $\nu_{max.}$ 2240 (C≡N), 2218 (conj. CN), and 1660, 1650, and 1620 cm^{-1}, $\lambda_{max.}$ (EtOH) 282 nm (ε 11,400), τ ($CDCl_3$) 5·0 (0·4H, s, CHCN) and 4·67 (0·6H, s, CHCN). An attempt to separate the isomers by column chromatography failed; however the last fraction (0·1 g) (eluted with ethanol) showed $\nu_{max.}$ 3600—3400 (OH), 2220 (C≡N), 1760, 1665, and 1630 cm^{-1}, $\lambda_{max.}$ (EtOH) 216 nm (ε 1640), and was probably a hydration product.

3-*Cyanomethylene*-2-*ethyl*-2-*methyl*-4-(1-*methylpropylidene*)-*cyclobutanecarbonitrile*.—(*a*) 1-Cyano-3-methylpenta-1,2-diene (5 g, 0·046 mol) was heated under nitrogen at 100° for 2·5 h, the reactions being monitored by i.r. absorption as in the previous experiment. The n.m.r. spectrum of the product showed it to be a mixture of *syn*- and *anti*-isomers (56 : 44). Chromatography on alumina or silica gel (dry column) did not effect separation of the isomers, although it gave a purer product (Found: C, 79·2; H, 8·1; N, 13·1. Calc. for $C_{14}H_{18}N_2$: C, 78·6; H, 8·4; N, 13·1%), $\nu_{max.}$ 2238 (C≡N), 2215 (C=C–C≡N), 1650 (C=C), and 1620 (C=C–C≡N) cm^{-1}, $\lambda_{max.}$ (EtOH) 282 nm (ε 20,100), τ ($CDCl_3$) 5·0 (0·56H, s, CHCN), and 4·67 (0·44H, s, CHCN).

(*b*) 1-Cyano-3-methylpenta-1,2-diene was kept at 5° for 21 months. The product (90%), after purification, consisted of a mixture of *syn*- and *anti*-isomers (3 : 1), τ 5·0 (0·75H, s, CHCN) and 4·67 (0·25H, s, CHCN).

3-*Cyanomethylene*-2,2-*diethyl*-4-(1-*ethylpropylidene*)*cyclobutanecarbonitrile*.—(*a*) 1-Cyano-3-ethylpenta-1,2-diene (6 g, 0·05 mol) was heated under nitrogen at 120—130° for 3 h, the reaction being monitored by i.r. absorption as described above. The n.m.r. spectrum of the product showed it to be a mixture of *syn*- and *anti*-isomers (15 : 85) (Found: C, 79·4; H, 9·1; N, 11·4. Calc. for $C_{16}H_{22}N_2$: C, 79·3; H, 9·1; N, 11·6%), $\nu_{max.}$ 2240 (C≡N), 2216 (C=C–C≡N), 1650 (C=C), and 1620 (C=C–CN) cm^{-1}, $\lambda_{max.}$ (EtOH) 282 nm (ε 18,000), τ ($CDCl_3$) 5·0 (0·15H, s, CHCN) and 4·61 (0·85H, s, CHCN).

(*b*) 1-Cyano-3-ethylpenta-1,2-diene was kept at 5° for 7 months. The product (10% dimer) after purification consisted of a mixture of *syn*- and *anti*-isomers. (3 : 2), τ 5·0 (0·60H, s, CHCN) and 4·61 (0·40H, s, CHCN).

(*c*) The product from (*b*) was heated at 120—130° for 3 h. The n.m.r. spectrum was identical to that of the starting material.

(*d*) The product from (*a*) was heated at 200° for 25 min. A dark oil resulted which, apart from small amounts of impurity, showed no change in the n.m.r. spectrum.

The electric dipole moments were determined [10] from dielectric constant and specific volume measurements on dilute solutions in benzene at 25·0 °C. The distortion polarisation was assumed to be equal to the molar refraction to Na(D) radiation and obtained from the summation of bond refractions. The polarisation data and dipole moments (μ) are recorded in Table 2; the symbols have their usual meanings.

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[9] O. J. Mascio and T. L. Jacobs, *Tetrahedron Letters*, 1969, 2867.

[10] C. W. N. Cumper, A. A. Foxton, J. F. Read, and A. I. Vogel, *J. Chem. Soc.*, 1964, 430.

TABLE 2

Polarisation data and dipole moments (μ) in benzene solution at 25·0 °C

Isomer $R^1 = R^2 = Me$	α	β	P_T (cm^3)	R_D (cm^3)	μ(D)
(I)	$6{\cdot}38_5$	−0·183	356·2	54·4	3·84
50% (I), 50% (II)	$9{\cdot}21_2$	−0·020	488·3	54·4	4·61
(II) (calculated)					5·27
$R^1 = R^2 = Et$					
(I) (calculated)					4·1
60% (I), 40% (II)	$5{\cdot}89_3$	−0·107	520·5	73·0	4·68
15% (I), 85%(II)	$7{\cdot}54_7$	−0·145	642·7	73·0	5·28
(II) (calculated)					5·5

APPENDIX

In order to predict electric dipole moments for the *syn*- and *anti*-isomers assumptions have to be made. (*a*) A recent investigation [11] of the electric dipole moments of various organic nitriles demonstrated that their moments varied by *ca.* 0·7 D depending upon conjugation, conformation, and the presence of β-alkyl groups in an acrylonitrile skeleton. We take the dipole moment of the unconjugated nitrile group to be 3·61 D (as in $CH_2{=}CH{\cdot}CH_2{\cdot}CN$) and that of the conjugated nitrile as 4·06 D (as in $Me_2C{=}CH{\cdot}CN$). (*b*) It is also assumed that the cyclobutane ring is planar, with the C(1)·CN direction 56° to the plane of the cyclobutane and a C(1) · · · C(3)=C(5)·CN bond angle of 57·5°, as in acrylonitrile.[12] Vector addition of these two group moments gives a predicted dipole moment of 4·54 D. This value would be decreased slightly by the moment X induced in the $R^1R^2C{=}C$ group in the *syn*-isomer (I) but correspondingly increased in the *anti*-isomer (II), the induced moments being greater in the tetraethyl dimers. If the angle at C(1) is decreased by 10° *or* if the C(5)·CN direction was only 47° to the bisector of C(2)C(1)C(4), due to non-planarity of the ring, then the predicted moment would only be decreased by 0·2 D. The experimental results (Table 2) are sensitive to the isomer composition, as indicated by the n.m.r. results, but are seen to be in full accord with the values predicted for the *syn*- and *anti*-isomers.

[2/2075 *Received, 4th September,* 1972]

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[11] C. W. N. Cumper, S. K. Dev, and S. R. Landor, *J.C.S. Perkin II*, 1972, 557.

[12] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, 1959, **30**, 777.