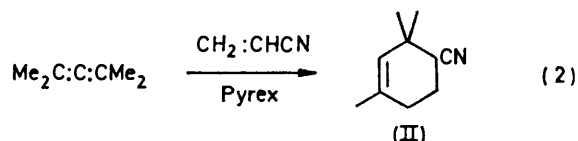
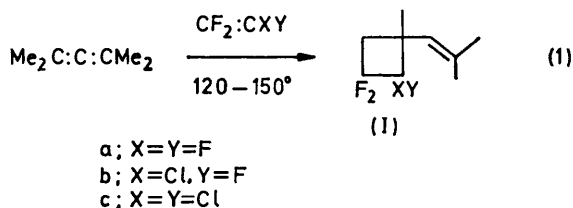


Allene Cycloadditions. Part IV.¹ Reactions of Tetramethylallene with Unsymmetrically Substituted Olefins

By David R. Taylor* and D. Bruce Wright, Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Cycloadditions between tetramethylallene and chlorotrifluoroethylene, 1,1-dichlorodifluoroethylene, and acrylonitrile occur in Pyrex vessels only after isomerisation of the hydrocarbon to 2,4-dimethylpenta-1,3-diene, and the adducts formed are a 47 : 53 mixture of *cis*- and *trans*-2-chloro-2,3,3-trifluoro-1-methyl-1-(2-methylprop-1-enyl)-cyclobutane, 2,2-dichloro-3,3-difluoro-1-methyl-1-(2-methylprop-1-enyl)cyclobutane, and 4-cyano-1,3,3-trimethylcyclohexene, respectively. N.m.r. analysis indicates that the cyclobutanes are puckered, with a marked preference for their 2-methylprop-1-enyl groups to be situated equatorially.

We have previously reported² that 2,4-dimethylpenta-2,3-diene (afterwards named tetramethylallene to avoid confusion with the isomeric 1,3-diene) reacts with tetrafluoroethylene to give a (2-methylprop-1-enyl)cyclobutane [equation (1); X = Y = F]. Details of similar reactions of this allene with two unsymmetrically substituted fluoro-olefins [equation (1); X = Cl, Y = F or Cl], and of its reaction with acrylonitrile which proceeds differently [equation (2)], are now presented.³



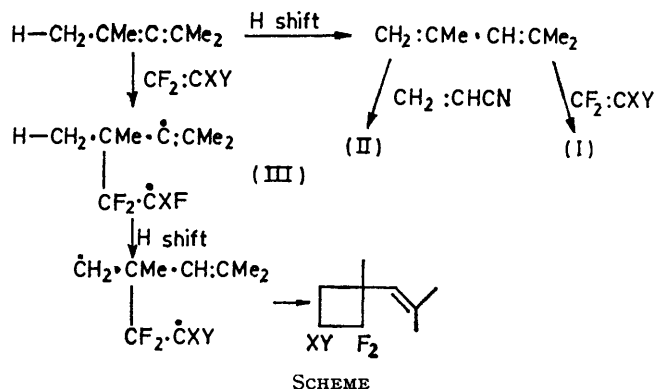
These reactions can only be rationalised, to our view, on the basis of an initial isomerisation of tetramethylallene to 2,4-dimethylpenta-1,3-diene, which then undergoes either [2 + 2] or [4 + 2] cycloaddition according to the olefinic component's preference. The alternative mechanism, in which hydrogen migration occurs in a diradical intermediate (III) is excluded by the results here reported, since it predicts products of opposite orientation (see Scheme).

A reaction between tetramethylallene and acrylo-

¹ Part III, D. R. Taylor, M. R. Warburton, and D. B. Wright, *J.C.S. Perkin I*, 1972, 1365.

² D. R. Taylor, M. R. Warburton, and D. B. Wright, *J. Chem. Soc. (C)*, 1971, 385.

nitrile in a steel reactor containing alkali was reported recently;⁴ cycloaddition and concurrent ene-reaction proceeded without rearrangement under those conditions.



Reaction of Tetramethylallene with Fluoro-olefins.—The cycloaddition between tetramethylallene and chlorotrifluoroethylene proceeds to complete consumption of the allene after 72 h at 150°. By-products consisted of the dimers of the olefin (15%) and of the allene (18%), and a C₇H₁₂ hydrocarbon (10%) which proved to be 2,4-dimethylpenta-1,3-diene and not recovered tetramethylallene.

The 1 : 1 adduct was isolated by low-pressure distillation as a liquid, b.p. 175 °C; it is formed in 80% yield. Of the various structures considered, straightforward [2 + 2] cycloadducts of the type obtained from 1,1-dimethylallene⁵ were excluded by the ¹H n.m.r. spectrum, which displays a vinylic resonance (τ 4.6) and

³ D. R. Taylor and D. B. Wright, *Chem. Comm.*, 1968, 434.

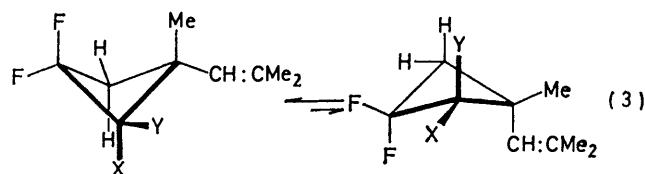
⁴ J. C. Martin, P. L. Carter, and J. L. Chitwood, *J. Org. Chem.*, 1971, **36**, 2225.

⁵ D. R. Taylor and D. B. Wright, *J. Chem. Soc. (C)*, 1971, 391.

a 3H-resonance due to a single non-allylic methyl group (τ 8.6). The detailed features of the ^1H and ^{19}F spectra are discussed below. However, a general comparison of its ^{19}F spectrum with those of the $\text{CF}_2\cdot\text{CFCl}$ -isoprene adducts completely analysed by Ernst,⁶ is sufficient for its unambiguous identification as (Ib), and quite excludes a reversed orientation of addition because of the evident proximity of the CH_2 and CF_2 groups. The ^{19}F spectrum also shows that an approximately equimolar mixture of two isomers is present, which was confirmed by g.l.c. analysis. Since both isomers contain the $\text{CH}_2\cdot\text{CF}_2\cdot\text{CFCl}$ grouping, on spectroscopic grounds, they are evidently the *cis*- and *trans*-isomers of (Ib), with the Cl-(2-methylprop-1-enyl) *trans*-isomer predominating slightly (53 : 47).

An analogous 1 : 1 adduct (Ic), b.p. 202 °C, was obtained in 93% yield from the reaction of tetramethylallene with 1,1-dichlorodifluoroethylene. Its n.m.r. data could be fully analysed on the basis of structure (Ic) since, geometrical isomerism being absent, the spectra are somewhat simpler. Particularly valuable were comparisons with the published spectra of related adducts⁷⁻⁹ of this fluoro-olefin.

The spectra of compounds (Ib) and (Ic), discussed in more detail below, indicate that the ring inversion equilibrium [equation (3)] favours those conformers with 'equatorial' 2-methylprop-1-enyl groups, presumably on steric grounds.



cis - (Ib) X=Cl, Y=F

trans - (Ib) X=F, Y=Cl

(Ic) X=Y=Cl

The structures of the adducts (I), and the detection of the conjugated isomer of the allene in one product mixture, very strongly suggest that the penta-1,3-diene is an intermediate. This was confirmed by treating 2,4-dimethylpenta-1,3-diene with chlorotrifluoroethylene under the same conditions, when a mixture of *cis*- and *trans*-(Ib) was again obtained, in 75% yield.

Surface acidity of the Pyrex reactor appears to be responsible, at least in part, for the spontaneous isomerisation of tetramethylallene in the presence of fluoro-olefins. Thus, when the allene was treated with chlorotrifluoroethylene under otherwise identical conditions, but in a reactor which had been pre-treated with ethanolic KOH to eliminate acid sites, 80% of the allene was converted to its dimer (tetramethyl-1,2-di-isopropylidene-cyclobutane), much more olefin was recovered, and the

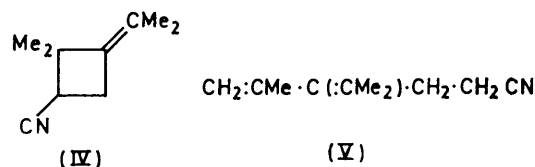
⁶ R. R. Ernst, *Mol. Phys.*, 1969, **16**, 241.

⁷ M. Takahashi, D. R. Davis, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1962, **84**, 2953.

⁸ J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 3884.

yield of (Ib) fell sharply. The fact that (Ib) was still formed after such de-acidification of the reactor must be attributed to (i) decomposition of the fluoro-olefin on glass, giving traces of hydrogen halides, (ii) some interaction between the reactants which assists the symmetry-disallowed 1,3-hydrogen shift, or (iii) persistent surface acidity. In solution, isomerisation of tetramethylallene to the penta-1,3-diene is known to be acid-catalysed.¹⁰

Reaction of Tetramethylallene with Acrylonitrile.—Since our work was completed,³ the reaction between tetramethylallene and acrylonitrile has been re-investigated by Martin and his co-workers.⁴ Whereas our procedure gives (II) (95%; see Experimental section), theirs (stainless steel reactor containing K_2CO_3) gave the cycloadduct (IV) and the ene-adduct (V).



We suggest two possible causes for the different pathways: surface acidity of our Pyrex reactor, which would lead to the formation of the penta-1,3-diene and a Diels-Alder reaction with acrylonitrile to give (II), and/or traces of water in the acrylonitrile which was purified only by distillation. We have recently shown that in a suitably deactivated reactor, polar aprotic solvents such as acetonitrile only cause the isomerisation of tetramethylallene if catalytic amounts of water are added.¹¹

N.m.r. analysis of our 1 : 1 adduct (II) shows that it contains neither (IV) nor (V), and g.l.c. analysis also failed to indicate the presence of other isomers. Our n.m.r. data precisely concur with those reported for a sample of (II) obtained from the Diels-Alder reaction of 2,4-dimethylpenta-1,3-diene with acrylonitrile.⁴

N.m.r. Analysis of the Fluoro-olefin Adducts (Ib and c).—Both adducts were analysed at 60 and 100 MHz for ^1H and at 56.4 and 94.1 MHz for ^{19}F , in CCl_4 solution. It should be noted that these spectra arise from time-averaging in rapid conformational equilibria, albeit equilibria which lie well towards one side [equation (3)].

The simpler of the two adducts (Ic) lacks geometrical isomerism although it has an asymmetric centre; its spectra are treated first (data in Table 1). Its ^1H spectrum displays the characteristic bands of a 2-methylprop-1-enyl group, with nearly equal *cis* and *trans* couplings ($^4J_{\text{HH}}$ 1.2–1.4 Hz). An additional 3H-doublet ($^5J_{\text{HF}}$ 2.0 Hz) is assigned to the ring methyl group, the cross-ring coupling to the axial fluorine being close to reported values.⁷ The remaining ^1H resonance is a complicated multiplet due to the ring methylene group, which constitutes the XY portion of an ABXY system

⁹ J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 3891.

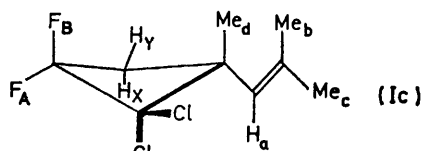
¹⁰ P. Prempre, Ph.D. Thesis, U.C.L.A., 1967, *Diss. Abs.*, 1967, **27**, 3463.

¹¹ H. A. Chia and D. R. Taylor, unpublished results.

and appears as a 14-line (two lines of the expected 16 are masked) doublet of doublets of doublets of doublets,

TABLE 1

N.m.r. data for the $\text{CF}_2\text{:CCl}_2$ adduct (Ic) in CCl_4



Band	δ (p.p.m.) ^a	Multiplicity ^b	Assignment	Coupling constants $ J /\text{Hz}$
¹ H-1	5.38	7-line qq	=CH _a	$J_{a,b} = J_{a,c} = 1.3 \pm 0.1$
¹ H-2	2.63	16-line dddd	CH _X H _Y ^c	$J_{XY} 13.0 \pm 0.2,$ $J_{XA} 9.0 \pm 0.5,$ $J_{XB} 20.0 \pm 0.2,$ $J_{YA} 2.5 \pm 0.5,$ $J_{YB} 14.5 \pm 0.2$
¹ H-3	1.72	d	=CMe _a (or b)	
¹ H-4	1.59	d	=CMe _b (or a)	
¹ H-5	1.39	d	Me _d	$J_{d,b} 2.0 \pm 0.2$
¹⁹ F-1	15.9	dd	F _A	
¹⁹ F-2		dd		
¹⁹ F-3	22.3	ddq	F _B	$J_{AB} 188 \pm 2$
¹⁹ F-4		ddq		

^a δ Values for ¹⁹F are relative to external $\text{CF}_3\text{:CO}_2\text{H}$, positive when upfield. ^b d = Doublet, q = quartet. ^c $\delta_{XY} 0.22,$ $\delta_X 2.74,$ and $\delta_Y 2.52$ p.p.m.

with the expected couplings to the *vic*-fluorines. The downfield proton ($\delta_X 2.74$ p.p.m.) is assigned to the axial position on the grounds of its greater *trans* $^3J_{\text{HF}}$

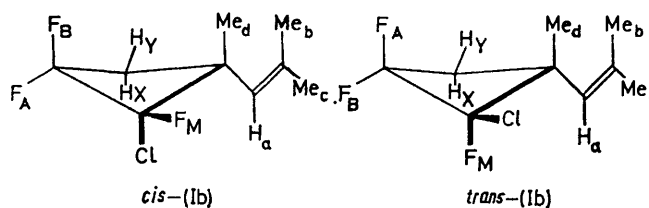
22.3 p.p.m.) are further resolved into doublets of doublets of quartets ($J_q = {}^5J_{\text{FH}} 2.0$ Hz). The high-field fluorine must therefore be axially disposed, as must the methyl group diagonally opposite to it.

The ¹⁹F spectrum (Table 2) of the mixture of *cis*- and *trans*-isomers of (Ib) displays ten bands, analysed as two overlapping 'AB-systems' (in reality the AB portions of two ABMXY systems), due to their CF₂ groups, and two high-field bands, due to their CFCl groups. The principal isomer gives rise to bands 3–6 and 10, and hence has the smaller value of δ_{AB} (4 p.p.m.); it is therefore considered to be the *trans*-isomer (Cl *trans* to CH:CMe₂), because in that isomer the chlorine lies almost equidistant from the vicinal fluorines. The minor isomer, *cis*-(Ib), produces bands 1, 2, and 7–9, and has a much larger δ_{AB} value (16 p.p.m.) presumably because its chlorine is axially placed and so approaches one fluorine more closely than the other. At high resolution, bands 7 and 8, and less clearly bands 3 and 4, show quartet splitting (${}^5J_{\text{FH}} 2$ Hz); they are therefore believed to stem from axial fluorines (F_B in *cis*-(Ib), F_A in *trans*-(Ib)) coupled, as in (Ic), to the axial methyl group. Bands 1, 2, 5, and 6 do not display such 2 Hz coupling, and appear as 6-component multiplets from which accurate coupling constants could not be deciphered, in the absence of spin-decoupling facilities.

Unfortunately, the ¹H spectrum of (Ib), even at 100 MHz, yielded little useful information, since it proved impossible to determine the contribution of the individual

TABLE 2

¹⁹F N.m.r. data for the $\text{CF}_2\text{:CFCl}$ adduct (Ib) in CCl_4



Band	Shift/Hz ^a	Multiplicity ^b	Isomer ^c	δ (p.p.m.) ^d	Assignment	J/Hz
1	1593	dt	<i>cis</i>	18.0	F _A	
2	1792	dt	<i>cis</i>			
7	3087	dtq	<i>cis</i>	33.8	F _B	$J_{AB} 199 \pm 1$ $J_{Bd} 2.0 \pm 0.2$
8	3286	dtq	<i>cis</i>			
9	3980	brs	<i>cis</i>			
3	2222	tq	<i>trans</i>	42.3	F _M	
4	2424	tq	<i>trans</i>	24.9	F _A	$J_{Ad} 2.0 \pm 0.5$
5	2646	dtm	<i>trans</i>	28.9	F _B	$J_{AB} 202 \pm 1$
6	2849	dtm	<i>trans</i>			
10	4585	brd	<i>trans</i>	48.7	F _M	

^a Determined at 94.1 MHz. ^b s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ^c Integration showed *trans* : *cis* = 1:1. ^d Positive when upfield of external $\text{CF}_3\text{:CO}_2\text{H}$.

coupling (20 Hz). A strong resemblance of the ¹H spectrum of (Ic) to that of the $\text{CF}_2\text{:CCl}_2$ adduct of α -methylstyrene⁷ greatly assisted the interpretation.

The ¹⁹F spectrum of (Ic) is the AB portion of the ABXY system. Each component of the low-field fluorine's resonances ($\phi_A 15.9$ p.p.m.) appears as a doublet of doublets (due to *cis* and *trans* coupling to the vicinal protons), whereas those of the high-field fluorine (ϕ_B

isomers. Nevertheless, the methylene portion generally resembles that of the less complicated adduct (Ic), and the similarity of the spectra to those of $\text{CF}_2\text{:CFCl}$ adducts of olefins and dienes fully analysed by Ernst⁶ leaves little doubt about the structures. The spectra of these puckered cyclobutanes differ sharply from those of the alkylidencyclobutanes obtained from 1,1-dimethylallene,⁵ which are planar.

EXPERIMENTAL

General experimental procedures, spectroscopic techniques, and the preparation of 2,4-dimethylpenta-2,3-diene (tetramethylallene) were described in Part I.² Chlorotrifluoroethylene (Societe d'Electrochimie d'Ugine) and 1,1-dichlorodifluoroethylene (a gift from Professor Haszeldine) were purified by trapwise fractional condensation *in vacuo*, and acrylonitrile was purified by distillation. 2,4-Dimethylpenta-1,3-diene was prepared in 90% yield by treating tetramethylallene with undried acetonitrile at 170° and was purified by distillation.

Reaction of Tetramethylallene with Chlorotrifluoroethylene.—Chlorotrifluoroethylene (3.5 g, 30 mmol), tetramethylallene (3.0 g, 29 mmol), and Terpene B polymerisation inhibitor² (0.2 g) were kept at 150° for 72 h in a sealed, dry, untreated, Pyrex tube (300 ml), to give chlorotrifluoroethylene (17% recovery) and a liquid (5.8 g) shown by g.l.c. (2 m Apiezon L at 130°) to consist of (i) 1,2-dichlorohexafluorocyclobutane (7%, 0.4 g, 15% on olefin consumed), (ii) 2,4-dimethylpenta-1,3-diene (5%, 0.3 g, 10% on tetramethylallene), (iii) 1,2-di-isopropylidenecyclobutane (9%, 0.54 g, 18% on tetramethylallene), all identified by comparison with authentic samples, and (iv) an unknown substance (74%, 4.3 g). The liquid mixture was distilled and a fraction, b.p. 59–61° at 12 mmHg, collected and identified spectroscopically and by g.l.c. (6 m Carbowax 20M at 150°) as a 53 : 47 mixture of *cis*- and *trans*-2-chloro-2,3,3-trifluoro-1-methyl-1-(2-methylprop-1-enyl)cyclobutane (Ib) (the major isomer has Cl *trans* to 2-methylprop-1-enyl) (20 mmol, 80% based on olefin consumed), a liquid, b.p. 175°, n_D^{20} 1.4310, [Found: C, 51.5; H, 6.0; Cl, 15.8; F, 26.0%; *M*, 212 (mass spectrum). Calc. for C₉H₁₂ClF₃: C, 51.0; H, 5.7; Cl, 16.7; F, 26.8%; *M* (for ³⁵Cl), 212], ν_{\max} (capillary film) 3010s, 2953s, 2900m, 1678w, 1640w, 1450s, 1430s, 1381s, 1314vs, 1226vs, 1172m, 1142s, 1104vs, 1068s, 1002s, 972vs, 942s, 925s, 910m, 901m, 865m, 858m, 844w, 815m, 772w, 710m, 670s, and 652s cm⁻¹, *m/e* (rel. int., assignment) 212/214 (12%, C₉H₁₂ClF₃), 197/199 (56, C₈H₉ClF₃), 177 (37, C₉H₁₂F₃), 161 (10), 148 (10, C₇H₁₀ClF), 145 (20), 113 (12), 109 (7), 97 (13), 96 (100, C₇H₁₂), 95 (14), 93 (7), 91 (10, 82 (8), 81 (97, C₂F₃), 79 (12), 77 (13), 76 (8), 70 (8), 69 (14), 67 (14), and 65 (12), with metastable ions at 107.7 and 68.4; ¹H δ 5.4–5.5 (1H, m), 2.5 (2H, m), 1.6 (3H, m), 1.5 (3H, m), and 1.3 (3H, m); ¹⁹F data, Table 2. A small-scale reaction in a Pyrex tube pretreated by washing it with KOH–EtOH, then EtOH, and drying *in vacuo*, gave g.l.c.-determined product yields as follows: 2,4-dimethylpenta-2,3-diene (11% recovery), chlorotrifluoroethylene (75% recovery), 1,2-dichlorohexafluorocyclobutane (10% on olefin consumed), the *cis*- and *trans*-isomer mixture (Ib) (81% on olefin consumed), and 1,2-di-isopropylidenecyclobutane (80% on allene consumed).

Reaction of Tetramethylallene with 1,1-Dichlorodifluoroethylene.—1,1-Dichlorodifluoroethylene (4.0 g, 30 mmol), tetramethylallene (3.0 g, 29 mmol), and Terpene B (0.3 ml), kept at 120° for 72 h in a sealed Pyrex tube (200 ml), gave CF₂CCl₂ (8%) and a liquid mixture (6.4 g), shown by g.l.c. (2 m Apiezon L at 175°) to consist of 1,1,2,2-tetrachloro-

tetrafluorocyclobutane (2%), 1,2-di-isopropylidenecyclobutane (4%), and an unknown substance (94%, 6.0 g). The unknown was isolated by preparative g.l.c. (6 m SE301, 200°) as a liquid, b.p. 202.5° at 764 mmHg (decomp.), n_D^{18} 1.4541, and identified spectroscopically as 2,2-dichloro-3,3-difluoro-1-methyl-1-(2-methylprop-1-enyl)cyclobutane (Ic) (26 mmol, 93% based on olefin consumed) [Found: C, 47.7; H, 5.3; F, 16.9%; *M*, 228 (mass spectrum). C₉H₁₂Cl₂F₂ requires C, 47.4; H, 5.3; F, 16.7%; *M* (for ³⁵Cl), 228], with the following spectroscopic data: ν_{\max} (capillary film) 2995s, 2980s, 2940s, 2921s, 2879m, 2864w, 2740w, 1652w, 1645w, 1500w, 1451s, 1430s, 1388m, 1380s, 1349w, 1298vs, 1262s, 1225s, 1215w, 1182w, 1151s, 1140vs, 1131vs, 1092w, 1080m, 1060s, 997vs, 984vs, 968vs, 896vs, 880vs, 846s, 830vs, 825vs, 700m, 683w, and 635s cm⁻¹, *m/e* (rel. int., assignment) 224/226/228 (4%, C₉H₁₂F₂Cl₂), 211/213/215 (11, C₈H₉F₂Cl₂), 193/195 (21, C₉H₁₂F₂Cl), 145 (15, C₈H₁₁F₂), 97 (9), 96, (100, C₇H₁₂), and 81 (63), n.m.r. data in Table 1.

Reaction of Tetramethylallene with Acrylonitrile.—Acrylonitrile (1.49 g, 28 mmol), tetramethylallene (2.7 g, 28 mmol), and Terpene B (0.2 ml), kept at 150° for 24 h in an untreated Pyrex tube (200 ml), gave a mixture (3.48 g) shown by g.l.c. (2 m Apiezon L at 150°) to consist of acrylonitrile (14%, 0.5 g, 34% recovery), 2,4-dimethylpenta-1,3-diene (9%, 0.3 g, 11%), and an unknown substance (77%, 2.7 g). Distillation gave a fraction, b.p. 90–92° at 10 mmHg, identified spectroscopically as 4-cyano-1,3,3-trimethylcyclohexene (18 mmol, 95% on olefin), n_D^{20} 1.4690 (lit.,¹² b.p. 105–108° at 18 mmHg, n_D^{20} 1.4705), ν_{\max} 2245 (C:N) and 1690 (C:C) cm⁻¹, δ 1.10 (6H, s, CMe₂), 1.60 (3H, s, :CMe), 1.9–2.4 (5H, m, ring CH's), and 5.12 (1H, s, :CH). Any 5-cyanocyclohexane (or other isomers) passed undetected on g.l.c.

Reaction of 2,4-Dimethylpenta-1,3-diene with Chlorotrifluoroethylene.—Chlorotrifluoroethylene (0.70 g, 6.0 mmol), 2,4-dimethylpenta-1,3-diene (0.60 g, 6.2 mmol), and Terpene B (0.05 g), kept at 150° for 72 h in a sealed Pyrex tube (50 ml) gave, after removal of recovered fluoro-olefin (38%), a liquid (0.9 g), shown by g.l.c. (2 m Apiezon L at 135° and 2 m SE30 at 120°) and i.r. analysis to contain *cis*- and *trans*-2-chloro-2,3,3-trifluoro-1-methyl-1-(2-methylprop-1-enyl)cyclobutane (Ib) (g.l.c. estimated yield, 75% on olefin consumed), by comparison with authentic samples.

Reaction of 2,4-Dimethylpenta-1,3-diene with Acrylonitrile.—2,4-Dimethylpenta-1,3-diene (1.35 g) and acrylonitrile (0.7 g), kept at 170° for 24 h in a sealed Pyrex tube (200 ml), gave starting materials (25% recovery) and 4-cyano-1,3,3-trimethylcyclohexene (88% on olefin consumed), identical by g.l.c. and i.r. analysis with authentic material prepared from tetramethylallene.

We thank the S.R.C. for financial support.

[2/1907 Received, 11th August, 1972]

¹² I. N. Nazarov and M. V. Mavrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 1068.