

Polyhalogenoallenes. Part 11.¹ The Preparation of some New Perfluoro-1,2-dienes and their Reactions with Nucleophiles²

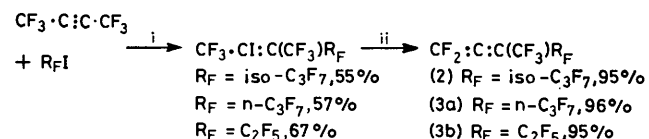
By Paul W. L. Bosbury, Roy Fields, and Robert N. Haszeldine,* The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Perfluoro(3,4-dimethylpenta-1,2-diene), perfluoro(3-methylhexa-1,2-diene), and perfluoro(3-methylpenta-1,2-diene) are readily prepared, almost quantitatively, by copper-induced de-iodofluorination. With methanol containing a small amount of methoxide ion, the dimethylpenta-1,2-diene gives almost exclusively 2-methoxyperfluoro(3,4-dimethylpenta-1,3-diene), which undergoes spontaneous ring closure at room temperature. Under similar conditions the other two allenes give mixtures of the 1 : 1-adducts, formed by nucleophilic attack at C-2 and proton abstraction at C-3, and the *cis*- and *trans*-isomers of the 2-methoxy-1,3-dienes. The *cis*-dienes undergo more rapid ring closure than the *trans*-dienes. With caesium fluoride, the dimethylpenta-1,2-diene gives a low yield of 2*H*-perfluoro(3,4-dimethylpent-2-ene) by fluoride ion attack on the terminal :CF₂ group and abstraction of a proton, but the major products are formed by fluoride ion attack at C-2 and expulsion of the tertiary fluorine from C-4, followed by cyclisation or further rearrangement of the 1,3-diene.

OUR recent¹ two-step preparation of perfluoro(3-methylbuta-1,2-diene) (1) suggested a general route to allenes containing the C:C:CF₂ group, and the preparation of three new perfluoro-1,2-dienes, and their reactions with some nucleophiles, are now reported.

Perfluoroiodo-alkanes R_FI reacted with perfluorobut-2-yne at elevated temperatures to give the corresponding mixtures of *cis*- and *trans*-iodo-olefins CF₃·Cl:C(CF₃)R_F (R_F = iso-C₃F₇,³ n-C₃F₇,³ or C₂F₅) in good yields. Passage of the *cis*-*trans* mixtures over freshly precipitated copper powder at 200 °C (*cf.* ref.1) has now been found to give the 1,2-dienes (2) and (3a, b) almost quantitatively (Scheme 1). All showed the characteristic strong i.r. band at 4.91 μm for the C:C:CF₂ asymmetric stretching mode, and the expected ¹⁹F n.m.r. absorptions. Weak long-range F-F coupling from the terminal :CF₂ to the CF₃·CF₂ group (⁶J_{FF} = 1 Hz) was observable in the spectrum of allene (3b), but could not

be detected for (2) or (3a). In contrast to perfluoropropadiene,⁴ perfluoropenta-1,2-diene,⁵ and the allene (1),^{1,6} these compounds showed little tendency to



SCHEME 1 Reagents: i, 240—270 °C; ii, freshly precipitated copper powder, 200 °C

dimerise at room temperature, and long reaction times and/or elevated temperatures could be used without major losses.

Reactions with Nucleophiles.—(a) *Methanol or methoxide ion.* Simple perfluoroallenes react readily with methanol. Thus perfluoropropadiene gives 1,1,3,3-tetrafluoro-3-methoxypropene at -24 to -20 °C,⁷ and per-

¹ Part X. P. W. L. Bosbury, R. Fields, R. N. Haszeldine, and D. Moran, *J.C.S. Perkin I*, 1976, 1173.

² Presented at the 5th European Symposium on Fluorine Chemistry, Aviemore, September 1974, and in part at the Centenary Symposium, A.C.S., New York, 1976, and the 3rd Euchem Conference on Fluorine Chemistry, Menton, 1976.

³ R. Fields, R. N. Haszeldine, and I. Kumadaki, to be published, *cf.* A. N. Bell, R. Fields, R. N. Haszeldine, and I. Kumadaki, *J.C.S. Chem. Comm.*, 1975, 866.

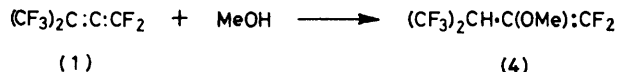
⁴ T. L. Jacobs and R. S. Bauer, *J. Amer. Chem. Soc.*, 1959, **81**, 606.

⁵ R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc., (C)*, 1968, 2593.

⁶ R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. (C)*, 1969, 966.

⁷ D. R. Taylor, unpublished results, cited in R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc., (C)*, 1969, 454.

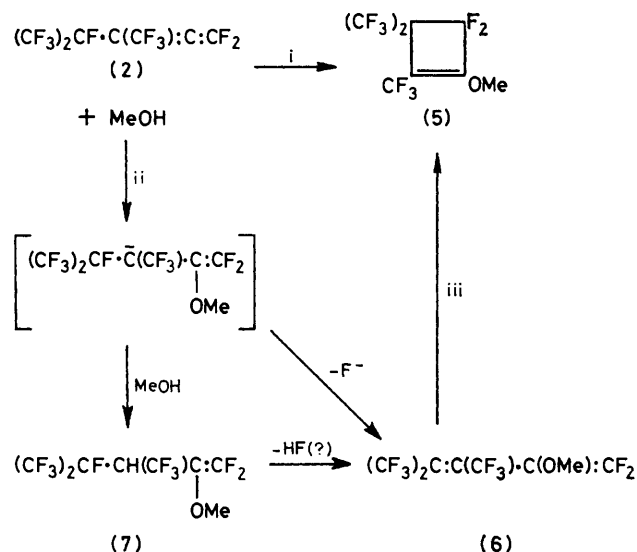
fluoro(3-methylbuta-1,2-diene) gives the adduct (4) virtually quantitatively on warming to room temperature.⁵



The allene (2), however, reacted only slowly with methanol at room temperature, but after 3 weeks a 95% yield of the cyclobutene (5) was obtained (Scheme 2). In the presence of a trace of sodium methoxide, however, (2) and methanol reacted exothermically at room temperature to give the diene (6). The spontaneous conversion of the diene (6) into the cyclobutene (5) was conveniently followed by ¹⁹F n.m.r. spectroscopy, the diene having a half-life of *ca.* 16 h. A minor (1%) product was shown by g.l.c./m.s. to have *M*⁺ at *m/e* 344, and fragment ions at *m/e* 313, 263, and 175 as expected for the 1:1 adduct (7); whether this adduct was rapidly dehydrofluorinated under the reaction conditions to give the diene (6), or whether (6) was formed independently, by loss of fluoride ion from the intermediate carbanion could not be determined.

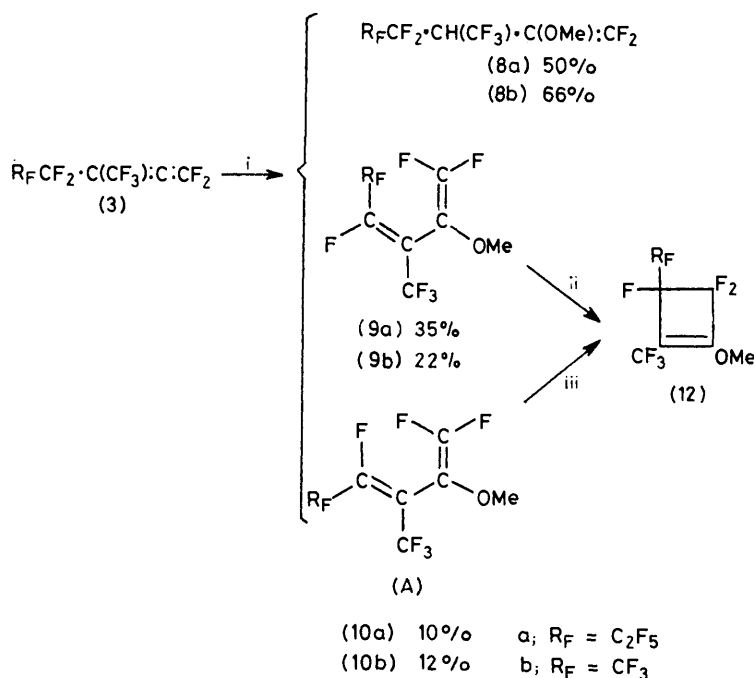
The reaction of neutral methanol with the allene (3a) was faster (10% in 12 h) than with (2) and, again, the presence of a trace of sodium methoxide resulted in an exothermic reaction. The products, the adduct (8), and the *cis*- and *trans*-dienes (9a) and (10a), were fully

vinylic C₂F₅ group, which are thus identified as being *cis* to each other in the isomer having the *trans*-configuration (10a). The other isomer showed no detectable coupling between the corresponding groups, as expected



SCHEME 2 Reagents: i, Room temp., three weeks; ii, trace MeO⁻, room temp.; iii, room temp.

for CF₃ and C₂F₅ groups *trans*-disposed about the double bond of the *cis*-diene (9a) (Scheme 3).⁸ The adduct



SCHEME 3 Reagents: i, MeOH, trace MeO⁻, room temp.; ii, room temp., a, 29 days, 93% conversion; b, 32 days, 66% conversion; iii, room temp., a, 18 months, 18% conversion; b, 2 months, no detectable change. The yields given are percentages of total products formed. The yields of each component isolated by preparative g.l.c. are given in the Experimental section

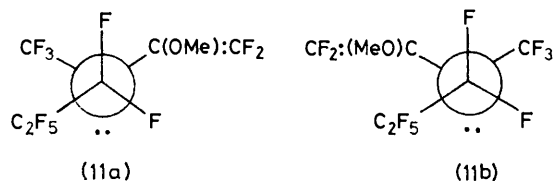
characterised. The assignment of stereochemistry to the dienes rests on the large (19 Hz) coupling between the vinylic CF₃ group (A) and the CF₂ group of the

(8a) showed no loss of hydrogen fluoride on storage, suggesting that in this reaction at least the dienes are

⁸ G. V. D. Tiers, *J. Phys. Chem.*, 1962, **66**, 1192.

formed by a route which does not involve an adduct as intermediate.

The isomer ratio for the two dienes (9a) : (10a) = 7 : 2 is in accord with an unfavourable $\text{CF}_3\text{-C}_2\text{F}_5$ *gauche* interaction in the carbanion (11a) leading to the diene

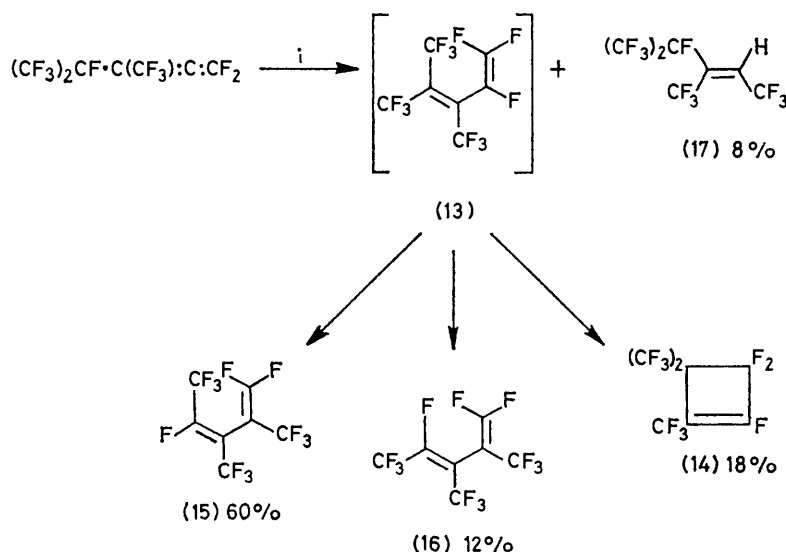


(10a), compared with the $\text{C}_2\text{F}_5\text{-[C(OMe):CF}_2\text{]}$ *gauche* interaction in carbanion (11b) leading to the diene (9a).

No product corresponding to the cyclobutene (5) was detected in the reaction mixture, but the *cis*-diene (9a) isomerised (half-life at 20 °C = 7½ days) on storage to

the 210—213 Hz geminal F-F coupling in the n.m.r. spectrum] more slowly (half-life 20½ days at room temperature) than the *cis*-diene (9a), but the *trans*-diene was not detectably changed after two months' storage.

(b) *Fluoride ion*. Perfluoro(3-methylbuta-1,2-diene) (1) is partly isomerised by fluoride ion to perfluoro(3-methylbuta-1,3-diene) (perfluoroisoprene).⁵ With caesium fluoride at 50 °C, the allene (2) gave a mixture of products (*ca.* 8 : 1 : 1 ratio by g.l.c. peak areas) instead of the expected perfluoro(3,4-dimethylpenta-1,3-diene) (13). The major g.l.c. fraction proved to be a mixture of perfluoro(2,3,3-trimethylcyclobutene) (14) (18% yield), presumably formed by cyclisation of the diene (13), and *cis*-perfluoro(2,3-dimethylpenta-1,3-diene) (15), formed in 60% yield. The other g.l.c. fractions were identified spectroscopically as the *trans*-diene (16) and the mono-olefin (17) (Scheme 4). The latter could arise by reaction of the initial carbanion, formed by fluoride



SCHEME 4 Reagents: i, CsF, 50°C. The yields given are percentages of total products. The yields of each component isolated are given in the Experimental section

give (12a) in 93% yield after 29 days. The *trans*-diene (10a) also gave (12a) on storage, but much more slowly, 82% of (10a) remaining after 18 months at room temperature.

The reaction of the allene (3b) with methanol and a trace of methoxide gave a mixture of the adduct (8b) and the *cis*- and *trans*-dienes (9b) and (10b) in which the adduct clearly predominated. Again there was no evidence of loss of hydrogen fluoride from the adduct, and the dienes were produced in more nearly equal proportion [(9b) : (10b) = 2.3 : 1] compared with (9a) and (10a), presumably reflecting the more nearly equal $\text{CF}_3\text{-CF}_3$ *vs.* $\text{CF}_3\text{-[C(OMe):CF}_2\text{]}$ *gauche* interactions. Diene formation under these conditions is clearly favoured, compared with adduct formation, by the presence of secondary, or, better still, a tertiary fluorine at C-4. The *cis*-diene (9b) isomerised to the cyclobutene (12b) [readily recognised, as was cyclobutene (12a), by

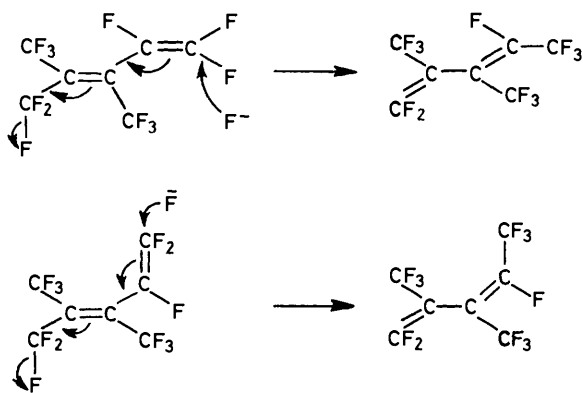
ion attack on the terminal :CF_2 group of (2), with hydroxylic centres on the glass surface, but the two dienes (15) and (16) were presumably formed by further isomerisation of (13) initiated by fluoride ion attack at the terminal :CF_2 group.

The cyclisation of per- and poly-fluoro-1,3-dienes to the corresponding cyclobutenes is a well known reversible reaction. In contrast to the hydrocarbon butadiene-cyclobutene system, perfluorocyclobutene is more stable than the diene⁹ by some 11.7 kcal mol⁻¹, but this difference is only 0.4 kcal mol⁻¹ for perfluoro(2,3-dimethylcyclobutene) compared with its open-chain isomer.¹⁰ The activation energies for the ring-opening reactions are 47.1 and 46 kcal mol⁻¹ respectively, both reactions being unimolecular. The spontaneous room-

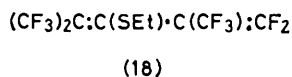
⁹ E. W. Schlag and W. B. Peatman, *J. Amer. Chem. Soc.*, 1964, **86**, 1676.

¹⁰ J. P. Chesick, *J. Amer. Chem. Soc.*, 1966, **88**, 4800.

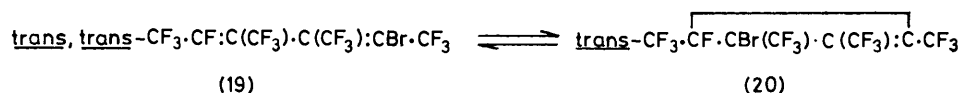
temperature cyclisations of the dienes (6), (9a,b), (10a), and (13) observed in the present work imply both a



greater stability difference for the cyclobutenes compared with the isomeric dienes than was found for perfluoro(2,3-dimethylcyclobutene), and also a considerable decrease in the activation energy for cyclisation. Thus if $\log A = 14$, as found for the perfluorobutadiene-perfluorocyclobutene reaction, the activation energies for ring closure of (6), (9a,b), and (10a) are all in the range 25–30 kcal mol⁻¹. Compounds (10a) and (10b), in which the R_F group is *cis* to the CF₃ group, cyclise more slowly than their isomers with R_F *trans* to the CF₃ group, suggesting that relief of the R_F:CF₂ 1,4-interaction in the diene is important. Mesomeric electron release by the methoxy-group at C-2 may also be important since it seems unlikely that the difference in steric effect between a CF₃ and MeO group in this position could account for such a drop in activation energy. Russian workers have recently¹¹ noted the cyclisation, under rather more vigorous conditions than those used here, of the thioethyl compound (18), formed



in the reaction of ethanethiol with perfluoro(tetramethylallene), and Miller and his co-workers¹² have observed the thermal equilibrium at 100–150 °C between the *trans,trans*-diene (19) and the cyclobutene (20). In this case, the extra bulk of the terminal :CBr-CF₃ group, compared with the :CF₂ group in (6), (9), and (10), may also be important in view of the observation that cyclisation of (19) (CF₃ *cis* to CF₃) is



easier than that of the *cis,trans*- or *trans,cis*-isomers, in contrast to our observation that the dienes (9) cyclise more readily than dienes (10).

¹¹ N. S. Mirzabekyants, M. D. Bargamova, Yu. A. Cheburkov, and I. L. Knunyants, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 1974, 2451.

EXPERIMENTAL

Activated copper powder was prepared as described previously.¹ All reactions were carried out in sealed tubes *in vacuo*. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer, n.m.r. spectra on a Perkin-Elmer R10 at 60.0 MHz (¹H) or 56.46 MHz (¹⁹F) at 35 °C or a Varian HA100 spectrometer at 100.0 and 94.1 MHz, with positive shifts to low field of tetramethylsilane or trifluoroacetic acid respectively, and mass spectra on an A.E.I. MS902 spectrometer.

Preparation of 2-Iodoperfluoro(3-methylpent-2-ene).—Pentafluoroiodoethane (4.92 g, 20 mmol) and perfluorobut-2-yne (3.24 g, 20 mmol), kept at 240 °C (170 h), gave 2-iodoperfluoro(3-methylpent-2-ene) (5.02 g, 67% based on reactants consumed) (Found: C, 18.2; F, 50.8%; *M*⁺, 408. Calc. for C₆F₁₁I: C, 17.7; F, 51.2%; *M*, 408), b.p. 115 °C, i.r. 6.27 μm (C=C), shown by g.l.c. (4m SE 30; 50 °C) and its ¹⁹F n.m.r. spectrum to be a mixture of *cis*- and *trans*-isomers in the ratio of 1 : 1, together with pentafluoroiodoethane (0.44 g, 9%) and perfluorobut-2-yne (0.27 g, 9%). 2-Iodoperfluoro(3-methylhex-2-ene) and 2-iodoperfluoro(3,4-dimethylpent-2-ene), prepared similarly, were characterised by comparison with known samples.³

Preparation of Perfluoro(1,2-dienes).—(a) *Perfluoro(3,4-dimethylpenta-1,2-diene)* (2).—2-Iodoperfluoro(3,4-dimethylpent-2-ene) (5.07 g, 11.1 mmol) was passed as vapour at 200 °C (1 h) through a silica tube packed with activated copper powder to give unchanged iodo-olefin (0.16 g, 3%) and *perfluoro(3,4-dimethylpenta-1,2-diene)* (2) (3.19 g, 95% based on iodo-olefin consumed) (Found: C, 26.6; F, 72.6%; *M*⁺, 312. C₇F₁₂ requires C, 26.9; F, 73.1%; *M*, 312), b.p. 54 °C, i.r. 4.91 μm (C=C=C); ¹⁹F n.m.r. +12.9 [3] (d 19.8 of t 3.7 of sept 2.0), -1.3 [6] (q 2.0 of t 0.6), -16.5 [2] (q 3.7 of d 1.4 of sept 0.6), and -114.2 p.p.m. [1] (q 19.8 of t 1.4 Hz).

(b) *Perfluoro(3-methylhexa-1,2-diene)* (3a). 2-Iodoperfluoro(3-methylhex-2-ene) (4.12 g, 9.0 mmol) was pyrolysed as in (a) to give unchanged olefin (0.20 g, 5%) and *perfluoro(3-methylhexa-1,2-diene)* (3a) (2.58 g, 96% based on iodo-olefin consumed) (Found: C, 26.2; F, 73.1%; *M*⁺, 312), b.p. 53 °C, i.r. 4.91 μm (C=C=C); ¹⁹F n.m.r. +13.1 [3] (q 5.9 of t 3.5), -4.6 [3] (t 10.5), -16.5 [2] (q 3.5 of t 3.5), -33.8 [2] (broad), and -51.0 p.p.m. [2] (q 5.9 Hz).

(c) *Perfluoro(3-methylpenta-1,2-diene)* (3b). 2-Iodoperfluoro(3-methylpent-2-ene) (4.07 g, 10.0 mmol) was pyrolysed as in (a) to afford unchanged iodo-olefin (0.26 g, 7%), and *perfluoro(3-methylpenta-1,2-diene)* (3b) (2.33 g, 95% based on consumed olefin) (Found: C, 27.8; F, 72.0%; *M*⁺, 262. C₆F₁₀ requires C, 27.5; F, 72.5%; *M*, 262), b.p. 40 °C, i.r. 4.91 μm (C=C=C); ¹⁹F n.m.r. +12.8 [3] (t 8.1 of q 3.0 of t 3.0), -9.2 [3] (q 3.0 of t 1.2 of t ~1), -17.2 [2] (t 4.2 of q 3.0 of q ~1), and -38.0 p.p.m. [2] (q 8.1 of t 4.2 of q 1.2 Hz).

Reaction of Methanol with Perfluoro-1,2-dienes.—(a) *With perfluoro(3,4-dimethylpenta-1,2-diene)*. (i) Perfluoro(3,4-dimethylpenta-1,2-diene) (0.90 g, 2.9 mmol) and anhydrous

¹² W. T. Miller, R. J. Hummel, and L. F. Pelosi, *J. Amer. Chem. Soc.*, 1973, **95**, 6850.

methanol (0.10 g, 3.1 mmol), shaken at 20 °C (24 h), gave >90% recovery of starting materials. After 21 days at 5 °C the major product was 1-methoxyperfluoro(2,3,3-trimethylcyclobutene) (5) (0.86 g, 91%) (Found: C, 29.6; H, 1.1; F, 64.0%; M^+ , 324. $C_8H_3F_{11}O$ requires C, 29.7; H, 0.9; F, 64.5%; M , 324), b.p. 128 °C; i.r. (C=C) 5.80 and 5.87 μm ; ^{19}F n.m.r. +18.1 [3] (poorly resolved), +10.0 [6] (t 10.2 of q 3.6) and -35.5 p.p.m. [2] (sept 10.2 of q 4.0 Hz); ^1H n.m.r. +3.77 p.p.m.* (s). A minor product (ca. 1%) was tentatively identified by g.l.c./mass spectrometry as 1,1,4,5,5,5-hexafluoro-2-methoxy-3,4-bis(trifluoromethyl)-pent-1-ene (Found: M^+ , 344. Calc. for $C_8H_4F_{12}O$: M , 344).

(ii) Perfluoro(3,4-dimethylpenta-1,2-diene) (1.64 g, 5.1 mmol), anhydrous methanol (0.17 g, 5.2 mmol), and sodium methoxide (ca. 0.05 g) at 20 °C (10 min) gave 2-methoxyperfluoro(3,4-dimethylpenta-1,3-diene) (6) (1.60 g, 98%) (Found: C, 29.7; H, 1.0; F, 64.3%; M^+ , 324. $C_8H_3F_{11}O$ requires C, 29.7; H, 0.9; F, 64.5%; M , 324); i.r. (C=C) 5.71 and 6.05 μm ; ^{19}F n.m.r. +17.0 [3] (q 12 further split), +16.0 [6] (complex multiplets), -19.5 [1] (d 66 Hz), and -29.5 p.p.m. (broadened doublet 66 Hz); ^1H n.m.r. +3.44 p.p.m.* (d 2.5 Hz).

(b) With perfluoro(3-methylhexa-1,2-diene). Perfluoro(3-methylhexa-1,2-diene) (1.0 g, 3.2 mmol) and anhydrous methanol (0.11 g, 3.3 mmol) at 20 °C (12 h) gave unchanged starting materials (ca. 90%). Addition of sodium methoxide (0.05 g) gave (5 min) a mixture separated by g.l.c. (4m S.E. 30; 60 °C) to give, in order of elution; (i) perfluoro(3-methylhexa-1,2-diene) (0.03 g, 3%); (ii) cis-2-methoxyperfluoro(3-methylhexa-1,3-diene) (9a) (0.18 g, 17%) (Found: M^+ , 324. $C_8H_3F_{11}O$ requires M , 324); ^{19}F n.m.r. +14.5 [3] (d 23), -7.1 [3] (mult), -19.6 [1] (d 59), -27.3 [1] (q 23 of t 11), -28.6 [1] (d 59), and -42.7 p.p.m. [2] (d 11 Hz with further splitting); ^1H n.m.r. +3.25 p.p.m. (s); (iii) trans-2-methoxyperfluoro(3-methylhexa-1,3-diene) (10a) (0.06 g, 6%) (Found: C, 29.7; H, 1.2; F, 64.9%; M^+ , 324. $C_8H_3F_{11}O$ requires C, 29.7; H, 0.9; F, 64.5%; M , 324); i.r. (C=C) 5.68 and 5.95 μm ; ^{19}F n.m.r. +19.3 [3] (d ~19 of t ~19), -7.3 [3] (complex), -20.1 [1] (d 52 of q 6), -24.0 [1] (broad complex mult), -28.5 [1] (d 52 of d 14), and -41.9 p.p.m. [2] (q ~19 of d 10 Hz); ^1H n.m.r. +3.22 p.p.m. (s); and (iv) 1,1,4,4,5,5,6,6,6-nonafluoro-2-methoxy-3-trifluoromethylhex-1-ene (8a) (0.39 g, 30%) (Found: C, 28.2; H, 1.1; F, 66.1%; M^+ , 344. $C_8H_4F_{12}O$ requires C, 27.9; H, 1.2; F, 66.3%; M , 344), b.p. 115 °C; i.r. (C=C) 5.66 μm ; ^{19}F n.m.r. +14.3 [3] (d ~9 of t ~9 with further splitting), -4.3 [3] (t 11.2), -19.8 [1] (d, 64.5 with further splitting), -33.7 [1] (d 64.5 Hz further split), -36.6 [2] (broad), and -50.3 p.p.m. [2] (unresolved), ^1H n.m.r. +3.46 [3] (d 2.7 Hz) and +3.69 p.p.m. [1] (very broad).

(c) With perfluoro(3-methylpenta-1,2-diene). Perfluoro(3-methylpenta-1,2-diene) (1.58 g, 6.0 mmol) and anhydrous methanol (0.20 g, 6.2 mmol), shaken at 20 °C (18 h), gave a mixture separated by g.l.c. (4m S.E. 30; 40 °C) to afford, in order of elution, (i) perfluoro(3-methylpenta-1,2-diene) (0.24 g, 15%); (ii) cis-2-methoxyperfluoro(3-methylpenta-1,3-diene) (9b) (0.27 g, 16%) (Found: C, 30.4; H, 1.2; F, 62.7%; M^+ , 274. $C_7H_3F_9O$ requires C, 30.7; H, 1.1; F, 62.4%; M , 274), b.p. 85 °C; i.r. (C=C) 5.64 and 5.88 μm ; ^{19}F n.m.r. +14.1 [3] (d 21 of q ~2), +5.6 [3] (d 6 of q ~2), -19.7 [1] (d 56), -29.5 [1] (d 56), and -31.1 p.p.m.

(q 21 of q 6 Hz); ^1H n.m.r. +3.16 p.p.m. (s); (iii) a mixture (0.77 g, 44%) (Found: C, 28.5; H, 1.7; F, 64.3%; M^+ , 294. $C_7H_4F_{10}O$ requires C, 28.6; H, 1.4; F, 64.6%; M , 294), b.p. 95 °C, identified as 1,1,4,4,5,5,5-heptafluoro-2-methoxy-3-trifluoromethylpent-1-ene (8b) (85%); i.r. (C=C) 5.68 μm ; ^{19}F n.m.r. +14.0 [3] (broadened d ~11 of t ~11), -8.1 [3] (s), -20.0 [1] (d 68), -34.2 (d 68), and -41.3 p.p.m. [2] (J_{AB} 286 Hz, ΔAB 2.9 p.p.m.); ^1H n.m.r. +3.38 [3] (d 2.8 Hz) and +3.2 to +3.7 p.p.m.* [1] (broad), together with a compound (15%) identified by its n.m.r. spectra as trans-2-methoxyperfluoro(3-methylpenta-1,3-diene) (10b); ^{19}F n.m.r. +18.2 [3] (d 11.5 of q 11.5), +8.2 [3] (q 11.5 of d 6.0), -20.0 [1] (broad), and -38.0 p.p.m. [1] (q 11.5 of q 6.0 Hz) (the peak for the other vinylic fluorine was not detected); ^1H n.m.r. +3.27 p.p.m.* (s).

Reaction of Perfluoro(3,4-dimethylpenta-1,2-diene) with Caesium Fluoride.—Perfluoro(3,4-dimethylpenta-1,2-diene) (1.51 g, 4.8 mmol) and caesium fluoride (0.05 g, 0.3 mmol) at 50 °C (24 h) gave a mixture (1.50 g) separated by g.l.c. (4m S.E. 30; 20 °C) into (i) a 3:1 mixture of cis-perfluoro(2,3-dimethylpenta-1,3-diene) (15) and perfluoro(2,3,3-trimethylcyclobutene) (14) (0.75 g, 50%) (Found: C, 26.7; F, 73.1%; M^+ , 312. Calc. for C_7F_{12} : C, 26.9; F, 73.1%; M , 312); i.r. (C=C) 5.71 and 5.88 μm ; ^{19}F n.m.r. (15) +15.5 [3] (d 17 of d ~12 further split), +13.5 [3] (d 21.0 of complex mults), +7.2 [1] (broadened q [7]), +6.1 [3] (complex), +5.5 [1] (unresolved), and -27.3 p.p.m. [1] (q 21.0 of q 7 Hz with further splitting); and (14) +12.6 [3] (d 9.6 of sept 3.0 of t 3.0), +9.2 [6] (t 9.8 of q 3.0 of d ~2), -16.8 [1] (complex multiplet), and -36.8 p.p.m. [2] (sept 9.8 of d ~6 of q 3.0 Hz); (ii) trans-perfluoro(2,3-dimethylpenta-1,3-diene) (0.12 g, 8%) (16) (Found: M^+ , 312), i.r. 5.71 and 5.92 μm ; ^{19}F n.m.r. +16.5 [3] (q 11.0 of d 11), +15.0 [3] (unresolved), +8.0 (q 11.0 of d 6.0), +6.9 [1] (broadened q 18 Hz), +5.7 [1] (unresolved mult), and -25.1 p.p.m. [1] (unresolved); and (iii) a compound identified spectroscopically as trans-2H-perfluoro(3,4-dimethylpent-2-ene) (17) (0.08 g, 5%) (Found: M^+ , 332. Calc. for C_7HF_{13} : M , 332); i.r. 5.95 μm ; ^{19}F n.m.r. +16.5 [3] (q ~13 of d ~9), +16.0 [3] (broad multiplet), +2.8 [6] (q 5.0 of d 5.0 Hz), and -102.3 p.p.m. [1] (unresolved).

Isomerisation of Polyfluoro-1,3-dienes.—(a) 2-Methoxyperfluoro(3,4-dimethylpenta-1,3-diene). The diene (0.91 g, 2.8 mmol) was kept at 20 °C and the ^1H and ^{19}F n.m.r. spectra were recorded after 6, 28, and 72 h showing 30, 62, and 100% conversion into 1-methoxyperfluoro(2,3,3-trimethylcyclobutene) (5).

(b) cis-2-Methoxyperfluoro(3-methylhexa-1,3-diene). The diene (0.12 g, 0.4 mmol) was kept at 20 °C (45 days) to give 1-methoxyperfluoro(3-ethyl-2-methylcyclobutene) (12a) (0.12 g, 100%) (Found: C, 29.7; H, 1.2; F, 64.6%; M^+ , 324. $C_8H_3F_{11}O$ requires C, 29.7; H, 0.9; F, 64.5%; M , 324); i.r. (C=C) 5.85 and 5.92 μm ; b.p. 131 °C; ^{19}F n.m.r. +16.7 [3] (unresolved), -5.3 [3] (d ~12 of d ~10 further split), -34.9 and -38.5 [2] (J_{AB} 213 Hz), -45.7 [2] (unsymmetrical multiplet), and -87.5 p.p.m. [1] (broad); ^1H n.m.r. +3.75 p.p.m. (s).

(c) trans-2-Methoxyperfluoro(3-methylhexa-1,3-diene). After 18 months at 20 °C the trans-diene gave a mixture of starting material (82%) and (12a) (18%).

(d) cis-2-Methoxyperfluoro(3-methylpenta-1,3-diene). After 16 months at 20 °C the cis-diene (0.13 g, 0.4 mmol) gave 1-methoxyperfluoro(2,3-dimethylcyclobutene) (12b) (0.13 g, 100%) (Found: C, 30.4; H, 1.4; F, 62.1%; M^+ , 274. $C_7H_3F_9O$ requires C, 30.7; H, 1.4; F, 62.4%; M , 274);

* Measured from external neat benzene ($\delta = +6.53$) and converted to SiMe_4 reference.

b.p. 117 °C; i.r. (C:C) 5.81 and 5.92 μm ; ^{19}F n.m.r. +16.3 (q ~ 10 of d ~ 10 Hz with further splitting); ^1H n.m.r. [3] (unresolved), +1.5 [3] (t ~ 10 of q ~ 3.5 of d ~ 3.5), +3.75 p.p.m. (s).
-38.2 and -39.7 [2] (J_{AB} 210), and -93.5 p.p.m. [1]

[7/1147 Received, 1st July, 1977]
