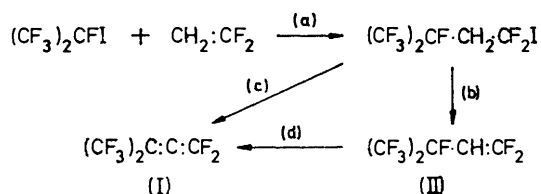


Polyhalogenoallenes. Part X.¹ An Improved Preparation of Perfluoro-(3-methylbuta-1,2-diene) and the Structure of its Dimers²

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Perfluoro-(3-methylbuta-1,2-diene), conveniently prepared by dehalogenofluorination with copper powder of perfluoro-(2-iodo- or 2-bromo-3-methylbut-2-ene), dimerises thermally to give mainly perfluoro-(3-isopropylidene-1,1-dimethyl-2-methylenecyclobutane). The reaction of perfluoro-(2-iodo-3-methylbut-2-ene) at higher pressures with copper powder gives a second dimer, perfluoro-(1-isopropylidene-2,2-dimethyl-3-methylenecyclobutane), together with variable amounts of perfluoro-(2,3,4,5-tetramethylhexa-2,4-diene). The conversion of the first dimer into the second by fluoride-initiated anionic rearrangement is described.

THE preparation of perfluoro-(3-methylbuta-1,2-diene) (I)³ (Scheme 1) exemplifies a general route to perfluoro-



SCHEME 1 Reaction conditions: (a) 190 °C; (b) powdered KOH, 20 °C; or 20% KOH aq., 35 °C; or activated charcoal, 290 °C and 10⁻² mmHg; (c) molten NaOH-KOH; (d) 75% KOH aq., 150 °C and 100 mmHg; or molten NaOH-KOH, 205 °C and 10⁻² mmHg.

1,2-dienes.⁴ Direct dehydrohalogenation of the iodo-polyfluoroalkane gave low and variable yields of the

¹ Part IX, R. E. Banks, R. N. Haszeldine, and T. Myerscough, *J.C.S. Perkin I*, 1972, 2336.

² Presented in part at the 5th European Fluorine Symposium, Aviemore, Scotland, September 1974.

³ R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. (C)*, 1969, 996.

allene (I), but stepwise dehydrohalogenation *via* the intermediate hydro-olefin (II) improved the yield of (I) to 35% (based on 2-iodoheptafluoropropane). We now report a simple two-step alternative sequence in which the allene (I) is formed conveniently and in high yield.

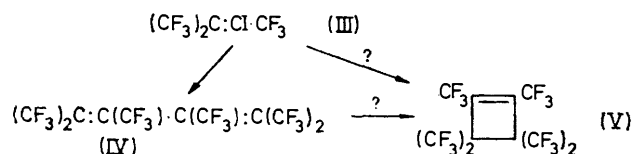
The reaction of perfluoro-(2-iodo-3-methylbut-2-ene) (III) with Ullmann copper-bronze gives a compound formulated as perfluoro-(2,3,4,5-tetramethylhexa-2,4-diene) (IV) on the basis of its mode of formation,⁵ although its spectroscopic properties did not at the time exclude specifically the isomeric cyclobutene structure (V), which could have been formed by ring closure of the diene (*cf.* ref. 6). Further investigation showed that variations in the copper-bronze used led to the appearance of a second compound, and when freshly precipitated copper powder was used at 210 °C, this second

⁴ R. E. Banks, A. Braithwaite, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. (C)*, 1968, 2593.

⁵ H. H. Evans, R. Fields, R. N. Haszeldine, and M. Illingworth, *J.C.S. Perkin I*, 1973, 649.

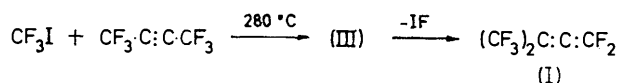
⁶ J. P. Chesick, *J. Amer. Chem. Soc.*, 1966, **88**, 4800.

compound, analysis of which agreed with $C_{10}F_{16}$ (cf. $C_{10}F_{18}$ for the coupling product), became the major product (78%). At lower temperature (80 °C) with freshly



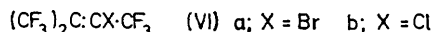
precipitated copper powder, compound (IV) was formed essentially quantitatively, and did not react with freshly precipitated copper at 210 °C to give $C_{10}F_{16}$. Formation of the allene (I) by deiodofluorination of the iodo-olefin (III) and dimerisation to give $C_{10}F_{16}$ would explain these observations.

The reaction was therefore carried out at 200 °C for only 5 min, and gave a small amount (7%) of the allene (I) (strong i.r. band at 4.91 μm and characteristic ^{19}F n.m.r. spectrum³). Further study of the reaction condi-

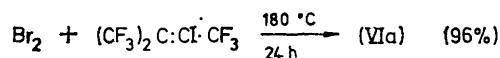


tions eventually allowed the preparation of the allene (I) in essentially quantitative yield and conversion, by passage of the iodo-olefin (III) at 1–2 mmHg through a silica tube containing freshly precipitated copper powder at 200 °C, at ca. 14 mmol h^{-1} . Under these conditions the only impurity was (III) (ca. 2%), which was readily removed by distillation.

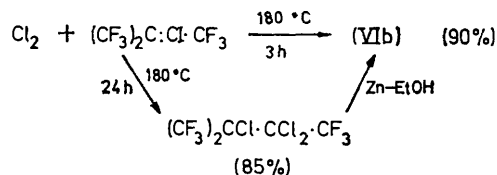
The corresponding 2-bromo- and 2-chloro-compounds (VIa and b) were required to test the scope of the novel



dehalogenofluorination reaction. Photochemical bromination of (III) gave (VIa) in only 13% yield after 7 days, but the reaction was almost quantitative at 180 °C in the dark. The chloro-compound (VIb) was prepared both



by brief thermal chlorination [to give (VIb) directly] and by dechlorination with zinc in refluxing ethanol of the perfluoro-(2,2,3-trichloro-3-methylbutane) formed in good yield after a longer reaction with an excess of chlorine.



The bromo-compound (VIa) gave the allene (I) in 30% conversion [94% yield based on consumed (VIa)] at 180 °C, but at 350 °C the conversion and yield were 96 and 95%, respectively. The chloro-compound (VIb),

recovered unchanged after passage over the copper at temperatures up to 350 °C, began to break down at 450 °C to give small amounts of silicon tetrafluoride, but the allene (I) was still not detected. Thus removal of a vinylic bromo- or iodo-substituent together with a fluoro-substituent from an adjacent perfluoroalkyl group is much easier than the corresponding dechlorofluorination.

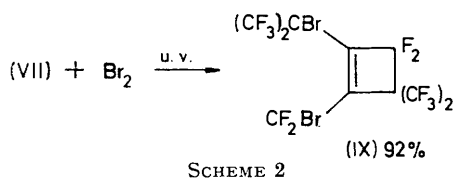
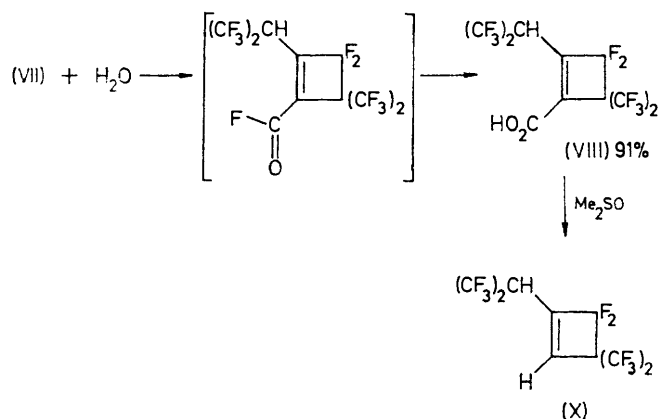
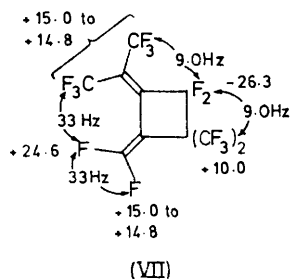
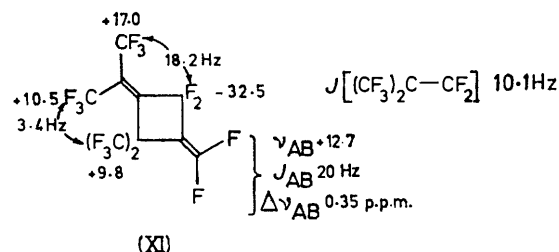
Dimerisation of the Allene (I), and Structures of the Dimers.—Although the allene (I) was not detectably dimerised in the course of its formation by flow pyrolysis even at 350 °C, after 24 h at 100 °C in a sealed tube only 1% of it survived, and five new products, in the proportions (by uncalibrated g.l.c. peak areas) 3:5:9:69:7, were detected. The solid previously reported from a small-scale dimerisation reaction³ was absent.

The major component, $C_{10}F_{16}$, showed C:C stretching bands at 5.76 and 5.92 μm , and had a ^{19}F n.m.r. spectrum showing the presence of a pair of CF_3 groups, a pair of equivalent fluorine atoms, two non-equivalent CF_3 groups, and two non-equivalent fluorine atoms. When heated with water it gave hydrogen fluoride and a white solid whose i.r. spectrum was identical with that of the solid previously obtained from the thermal reaction of the allene (I) and thought to be poly[perfluoro-(3-methylbuta-1,2-diene)].³ The mass spectrum, which was not available previously, suggested the formula $C_{10}H_2F_{14}O_2$, and this is supported by microanalytical results. Loss of OH from the molecular ion to leave $C_{10}HF_{14}O$ and the appearance of peaks at m/e 45 and 44 indicated a carboxy-group, and this was confirmed by the liberation of carbon dioxide from aqueous sodium carbonate and by strong i.r. bands at 3.37–3.60 and at 5.73 and 5.79 μm [a band at 5.80 μm had been attributed³ to C:C stretch by comparison with the known poly(perfluoroallene)]. The ^1H n.m.r. spectrum showed a singlet at δ 7.0, presumably averaged with residual water in the solvent, and a septet (8.4 Hz) at δ 5.0.

The evidence thus suggests that the major dimer has structure (VII), with the ^{19}F n.m.r. parameters shown, and that this undergoes 1,4-addition of water, followed by loss of hydrogen fluoride to give the acyl fluoride, which is then hydrolysed under the reaction conditions to the carboxylic acid (VIII) (Scheme 2). Further support for these structures comes from the bromination of (VII) to give the dibromo-compound (IX) in 92% yield, clearly showing in its ^{19}F n.m.r. spectrum signals for the two pairs of equivalent CF_3 groups, the ring difluoromethylene group, and the low-field CF_2Br group, and from decarboxylation of the acid (VIII). The acid was only sparingly soluble in deuteriochloroform, and in an attempt to improve the n.m.r. spectra a sample was dissolved in dimethyl sulphoxide. Carbon dioxide was evolved, and the reaction was shown by successive n.m.r. spectra to be 90% complete, giving compound (X) (Scheme 2) within 90 min. No deuterium was incorporated into the product (X) when the decarboxylation was carried out in [$^2\text{H}_6$]dimethyl sulphoxide, showing that the solvent is not a reactant in the decarboxylation.

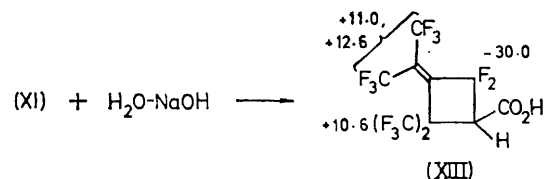
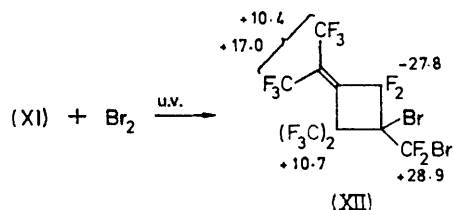
The major product of thermal dimerisation of the allene (I) was not, however, found as a product of the reaction between the iodo-olefin (III) and copper. The product of that reaction is assigned structure (XI) on the basis of microanalytical results and its mass spectrum, which gave the molecular formula $C_{10}F_{16}$, its ^{19}F n.m.r. spectrum [which showed a $(CF_3)_2C$ group, two different CF_3 groups, a ring CF_2 , and a terminal pair of vinylic fluorine atoms], and its reaction with one equivalent of bromine, to give compound (XII), in the ^{19}F n.m.r. spectrum of which the CF_3 signals remained virtually unchanged, that of the

The major product of thermal dimerisation of perfluoro-(3-methylbuta-1,2-diene) is thus firmly identified as



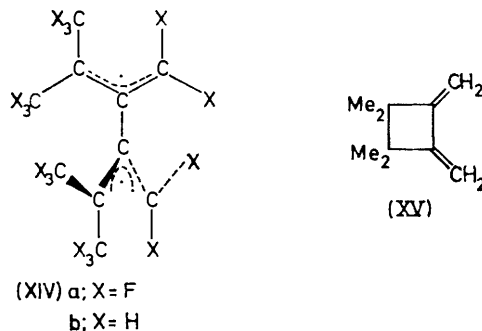
ring CF_2 group moved downfield somewhat, and the $:CF_2$ AB pattern was replaced by a low-field band due to CF_2Br . This unconjugated dimer (XI) did not react with water (150 °C; 7 days), but in the presence of sodium hydroxide gave the acid (XIII) (Scheme 3), 69% of (XI) being consumed during 48 h at 80 °C. Like its isomer (VIII), this acid was decarboxylated readily in dimethyl sulphoxide.

The dimer (XI) was also identified as one of the minor products of the thermal dimerisation of the allene (I), but the three minor products detected in that reaction remained unidentified, although two were too low boiling to be dimers.



SCHEME 3

(VII), presumably formed *via* the 'centre-to-centre' diallylic diradical (XIVa). In the dimerisation of 3-methylbuta-1,2-diene, 34% of the hydrocarbon corresponding to (VII) is formed, together with 64% of the isomer (XV) which can be formed by ring closure of (XIVb) in the opposite sense.⁷ The formation of (XI), however, an 'end-to-centre' dimer, is unusual for a substituted allene although known for allene itself. The exclusive formation of (XI) in the reaction of (III) with copper, and the lack in that reaction of any (VII), the major 'thermal dimer', suggested that the reaction sequence in sealed tubes was not simply (III) → (I)

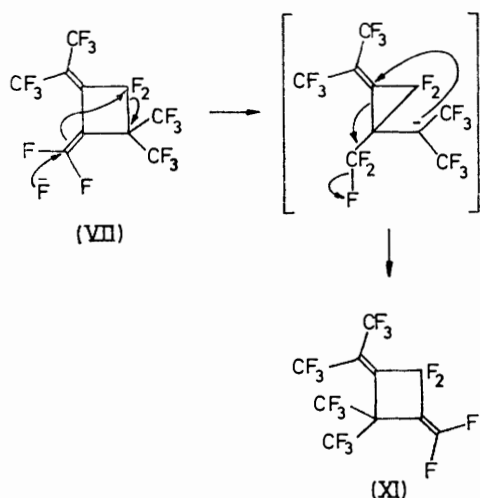


→ 'dimer' as was first thought, and several possible reaction sequences were investigated. When the allene (I) was heated in the presence of freshly precipitated

⁷ D. R. Taylor, *Chem. Rev.*, 1967, **67**, 319.

copper, the same mixture of dimers as in the normal thermal reaction was obtained, indicating that the presence of copper does not influence the thermal dimerisation. A possible route would be the formation from (III) of some vinylcopper species which could either decompose to give (I) or react with a second molecule of (III) to give (XI). Such a reaction could not, however, explain the formation of (XI), albeit in low yield, in the thermal dimerisation of (I).

The problem was clarified when it was found that although (VII) was unchanged after 15 h at 240 °C, it was converted at that temperature, in the presence of copper powder that had previously been used in the preparation of (I) (and which therefore contained copper fluoride and iodide), into a mixture of (VII) and (XI). Potassium fluoride effected the conversion more rapidly, and the reaction is thus formulated as a fluoride-ion initiated rearrangement (Scheme 4). Presumably some initial



SCHEME 4

decomposition at 80 °C provided fluoride ion to initiate the formation of (XI) in low yield, and, in accord with this, dimerisation of (I) at 70 °C gave a product containing no detectable dimer (XI).

The formation of (XI) from the formally conjugated dimer (VII) is at first sight surprising, but it has been suggested⁸ that 1,2-dimethylenecyclobutane itself has a puckered ring, so that conjugation even in that molecule must be reduced. The puckering would presumably be increased by the presence of the bulky trifluoromethyl groups, so that the loss of conjugative stabilisation may not be severe.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 grating spectrometer, mass spectra with an A.E.I. MS902 spectrometer, and n.m.r. spectra with a Perkin-Elmer R10 or Perkin-Elmer-Hitachi R20 spectrometer (60.0 MHz for ¹H, 56.46 MHz for ¹⁹F), or a Varian HA100 spectrometer (100.0 MHz for ¹H, 94.1 MHz for ¹⁹F) at 35 °C. Chemical shifts are taken as positive to low field of the reference material (trifluoroacetic acid for ¹⁹F, Me₄Si for ¹H). G.l.c.

analyses and separations were carried out on a Pye 104 instrument by using 4 or 10 m columns (i.d. 4 mm) packed with 5–10% SE 30 on Celite. Perfluoro-(2-iodo-3-methylbut-2-ene) was prepared by the reaction of trifluoroiodomethane with perfluorobut-2-yne⁹ at 280 °C in a Hastalloy-lined autoclave. Copper powder was precipitated from aqueous copper sulphate by addition of zinc dust, and was then washed successively with dilute hydrochloric acid, distilled water, and acetone, and dried *in vacuo* at 200 °C for several hours. Reactions were carried out in sealed Pyrex tubes (300 ml) unless otherwise stated.

Reaction of Perfluoro-(2-iodo-3-methylbut-2-ene) with Copper-bronze.—Perfluoro-(2-iodo-3-methylbut-2-ene) (14.5 g, 40.0 mmol) and dried (200 °C *in vacuo*; 2 h) copper-bronze (3.0 g) (*cf. ref. 5*) were heated (180 °C; 12 days) to give perfluoro-(2,3,4,5-tetramethylhexa-2,4-diene)⁵ (4.6 g, 50%) and a second product separated by preparative g.l.c. (10 m SE 30, room temperature) and identified (see Discussion section) as perfluoro-(1-isopropylidene-2,2-dimethyl-3-methylenecyclobutane) (XI) (4.2 g, 50%) (Found: C, 28.4; F, 72.0%; *M*⁺, 424. C₁₀F₁₆ requires C, 28.3; F, 71.7%; *M*, 424), b.p. 118 °C, λ_{max} 5.80 μm (C:C).

Reaction of Perfluoro-(2-iodo-3-methylbut-2-ene) with Copper Powder.—(a) At 210 °C (sealed tube). Perfluoro-(2-iodo-3-methylbut-2-ene) (2.64 g, 7.1 mmol) and copper powder (2.0 g, 30 mmol) were heated (210 °C; 2 h) to give perfluoro-(2,3,4,5-tetramethylhexa-2,4-diene) (0.180 g, 12%), compound (XI) (0.70 g, 47%), 2*H*-perfluoro-(3-methylbut-2-ene) (0.02 g, 2%), and starting material.

(b) At 80 °C (sealed tube). The iodobutene (2.05 g, 5.7 mmol) and copper powder were kept in a sealed Pyrex tube (80 °C; 10 h) to give perfluoro-(2,3,4,5-tetramethylhexa-2,4-diene) (1.20 g, 98%) and 2*H*-perfluoro-(3-methylbut-2-ene) (0.02 g, 2%).

(c) The iodobutene (9.00 g, 25.2 mmol) and copper powder (6.0 g, 90 mmol), kept at 200 °C (5 min) then cooled, gave perfluoro-(3-methylbuta-1,2-diene) (0.36 g, 7% based on initial olefin), identified by comparison of its spectra with those of an authentic³ sample, perfluoro-(2,3,4,5-tetramethylhexa-2,4-diene)⁵ (3.85 g, 72%), compound (XI) (0.70 g, 13%), and two minor unidentified compounds.

(d) At 200 °C *in a flow system*. A silica tube (14 mm i.d.) was loosely packed with copper powder (30 g) over a length of 50 cm and heated over this length in a furnace; one end was attached *via* a trap at -196 °C to a vacuum pump, and an ampoule containing the iodobutene (5.0 g, 13.9 mmol) was attached to the other. The tube was heated *in vacuo* (200 °C; 1 h), and then the iodo-olefin was allowed to vaporise into the tube (1 h). The contents of the -196 °C trap were distilled to give starting material (0.10 g, 2%) and perfluoro-(3-methylbuta-1,2-diene) (I) (2.80 g, 97% based on olefin consumed).

Dimerisation of Perfluoro-(3-methylbuta-1,2-diene).—The allene (I) (10.0 g, 47 mmol) was kept *in vacuo* in a sealed tube (100 ml capacity; 24 h at 100 °C), to give compounds (I) (0.30 g, 3%) and (XI) (0.80 g, 8%), perfluoro-(3-isopropylidene-1,1-dimethyl-2-methylenecyclobutane) (VII) (7.8 g, 78%) (Found: C, 28.1; F, 72.2%; *M*⁺, 424. C₁₀F₁₆ requires C, 28.3; F, 71.7%; *M*, 424), b.p. 124 °C, separated from the mixture by g.l.c., and three minor unidentified components.

Reaction of the Dimer (VII) with Water.—The dimer (VII) (1.00 g, 2.5 mmol) and water (0.10 g, 6 mmol) were kept *in*

⁸ J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, 1970, **15**, 281.

⁹ C. G. Krespan, *J. Amer. Chem. Soc.*, 1961, **83**, 3434.

vacuo at 80 °C (24 h) to give a solid product (1.01 g) which, on sublimation *in vacuo* at 50 °C, gave pure 3,3-difluoro-4,4-bistrifluoromethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)cyclobut-1-enecarboxylic acid (VIII) (0.91 g, 91%) (Found: C, 28.6; H, 0.8; F, 63.2%; M^+ , 420. $C_{10}H_2F_{14}O_2$ requires C, 28.6; H, 0.5; F, 63.3%; M , 420), m.p. 134 °C, λ_{max} 5.73 and 5.79 (C:O) and 5.92 μm (C:C), as white crystals.

Reaction of the Dimer (VII) with Bromine.—The dimer (VII) (0.37 g, 0.87 mmol) and bromine (0.14 g, 0.87 mmol) were sealed *in vacuo* in a silica n.m.r. tube and irradiated (Hanovia UVS 500 medium-pressure mercury lamp; 12 h) to give 1-(bromodifluoromethyl)-2-(1-bromo-2,2,2-trifluoro-1-trifluoromethylethyl)-3,3-difluoro-4,4-bistrifluoromethylcyclobutene (IX) (0.47 g, 92%) (Found: C, 20.6; F, 51.6. $C_{10}Br_2F_{16}$ requires C, 20.9; F, 52.1%), b.p. 181 °C, λ_{max} 6.02 μm (C:C), m/e (highest value) 503/505 ($M^+ - Br$).

Reaction of the Dimer (XI) with Water.—The dimer (XI) (2.12 g, 5.0 mmol) and water (0.2 g, 12 mmol) were unchanged after 7 days *in vacuo* at 150 °C. After addition of sodium hydroxide (0.04 g, 1.0 mmol) the reactants were kept at 80 °C (2 days) to give starting material (XI) (0.71 g, 31%), and, after extraction (CHCl₃) and removal of solvent, 2,2-difluoro-4,4-bistrifluoromethyl-3-(2,2,2-trifluoro-1-trifluoromethylethylidene)cyclobutanecarboxylic acid [1.03 g, 76% based on (XI) consumed] (Found: C, 28.7; H, 0.6; F, 62.9. $C_{10}H_2F_{14}O_2$ requires C, 28.6; H, 0.5; F, 63.3%), m.p. 24 °C, b.p. 146 °C, λ_{max} 5.70 (C:O) and 5.86 μm (C:C), m/e (highest value) 403 ($M^+ - OH$). The acid liberated carbon dioxide when added to dimethyl sulphoxide to give a product tentatively identified (Found: M^+ , 376. Calc. for $C_9H_2F_{14}$: M , 376; breakdown pattern similar to that of the acid) as 1,1-difluoro-3,3-bis(trifluoromethyl)-2-(2,2,2-trifluoro-1-trifluoromethylethylidene)cyclobutane.

Reaction of the Dimer (XI) with Bromine.—The dimer (XI) (0.16 g, 0.35 mmol) and bromine (0.05 g, 0.35 mmol) were irradiated (see above) (12 h), to give 1-bromo-1-(bromodifluoromethyl)-2,2-difluoro-4,4-bistrifluoromethyl-3-(2,2,2-trifluoro-1-trifluoromethylethylidene)cyclobutane (0.19 g, 91%) (Found: C, 20.6; F, 51.9. $C_{10}Br_2F_{16}$ requires C, 20.9; F, 52.1%), b.p. 178 °C, λ_{max} 5.99 μm (C:C), m/e (highest value) 453/455 ($M^+ - CF_2Br$).

Perfluoro-(2-chloro-3-methylbut-2-ene) (VIb).—(a) *From perfluoro-(2,2,3-trichloro-3-methylbut-2-ene)*. Perfluoro-(2,2,3-trichloro-3-methylbut-2-ene)⁵ (3.38 g, 10.0 mmol) dissolved in anhydrous ethanol (20 ml) was added slowly (1 h) to a stirred mixture of refluxing ethanol (10 ml) and activated zinc dust (10.0 g). After a further hour at reflux the mixture was fractionally distilled, and the material boiling up to 56 °C was washed, dried, and fractionated *in vacuo* to give perfluoro-(2-chloro-3-methylbut-2-ene) (VIb) (1.9 g, 71%) (Found: C, 22.2%; M^+ , 266. C_5ClF_9 requires C, 22.5%; M , 266), b.p. 56 °C, λ_{max} 6.10 μm (C:C).

(b) *From perfluoro-(2-iodo-3-methylbut-2-ene)*. Perfluoro-(2-iodo-3-methylbut-2-ene) (3.0 g, 8.4 mmol) and dry chlor-

ine (2.38 g, 34 mmol) were heated *in vacuo* (180 °C, 3 h) to give perfluoro-(2-chloro-3-methylbut-2-ene) (2.0 g, 90%), identical with that described above.

Perfluoro-(2-bromo-3-methylbut-2-ene) (VIa).—(a) *Thermal*. Perfluoro-(2-iodo-3-methylbut-2-ene) (3.00 g, 8.4 mmol) and bromine (2.51 g, 15.7 mmol) were kept *in vacuo* (180 °C, 24 h). The excess of bromine was removed (Hg), and the product fractionated *in vacuo* to give perfluoro-(2-bromo-3-methylbut-2-ene) (VIa) (2.6 g, 96%) (Found: C, 19.8; F, 54.5%; M^+ , 310. C_5BrF_9 requires C, 19.3; F, 55.0%, M , 310), b.p. 85 °C, λ_{max} 6.13 μm (C:C).

(b) *Photochemical*. Perfluoro-(2-iodo-3-methylbut-2-ene) (3.00 g, 8.4 mmol) and bromine (2.69 g, 16.8 mmol) were irradiated *in vacuo* (tungsten lamp; 7 days) to give, after treatment with mercury, perfluoro-(2-bromo-3-methylbut-2-ene) (0.39 g, 15%) and starting material (2.5 g, 82%).

Flow Pyrolysis of Perfluoro-(2-bromo- and 2-chloro-3-methylbut-2-ene).—Perfluoro-(2-bromo-3-methylbut-2-ene) (2.7 g, 8.7 mmol) was pyrolysed in the apparatus described above (180 °C; 30 min) to give starting material (1.85 g, 68%) and the allene (I) (0.55 g, 97% based on bromo-olefin consumed). When the pyrolysis was repeated (3.80 g, 12.2 mmol; 350 °C; 1 h), distillation gave starting material (0.15 g, 4%) and the allene (I) (2.35 g, 95% based on bromo-olefin consumed). Similar pyrolysis of perfluoro-(2-chloro-3-methylbut-2-ene) (2.20 g, 8.2 mmol) at 200 °C (30 min) gave unchanged olefin (2.20 g, 100%).

The pyrolysis was repeated with identical results at 250, 300, and 350 °C. After pyrolysis at 450 °C (30 min) the olefin (2.12 g, 97%) was recovered, together with a small amount of silicon tetrafluoride.

Reaction of Perfluoro-(3-methylbuta-1,2-diene) with Copper.—The diene (1.74 g, 4.1 mmol) and fresh copper powder were kept *in vacuo* (150 °C, 24 h). The product (1.51 g, 87%) was shown by g.l.c. to be a mixture of compounds (VII) (76%) and (XI) (12%), and two other more volatile and one less volatile unidentified components.

Thermal Reactions of the Dimer (VII).—(a) *Alone*. The dimer (2.1 g, 5.0 mmol) was unchanged after being kept *in vacuo* (100 ml tube; 240 °C; 15 h).

(b) *With used copper powder*. The dimer (VII) (2.1 g, 5.0 mmol) and copper powder [previously used for the preparation of (I)] (2 g) were kept *in vacuo* (100 ml tube; 240 °C; 66 h). The product (1.8 g, 86%) was shown by g.l.c. (2 m SE 30; room temperature) to be a mixture of the dimer (XI) and starting material, with g.l.c. peak areas in the ratio 5:2. The i.r. spectrum of the vapour also showed the presence of traces of silicon tetrafluoride.

(c) *With potassium fluoride*. The dimer (VII) (1.3 g, 3.1 mmol) and dried potassium fluoride (1.0 g, 17 mmol) were kept *in vacuo* in a Pyrex reaction tube (250 °C; 18 h). The product was shown by g.l.c. and i.r. spectroscopy to be entirely the dimer (XI) (1.15 g, 89%).