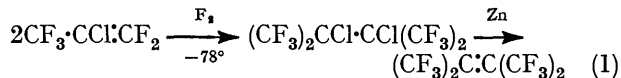


Fluoro-olefins. Part VIII.¹ Preparation and Some Reactions of Perfluoro-2,3-dimethylbut-2-ene and of Some Tristrifluoromethyl Ethylenes

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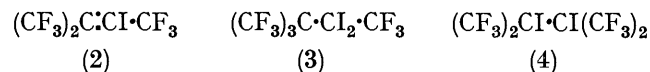
A single-stage preparation of perfluoro-2,3-dimethylbut-2-ene involves the high-temperature reaction of trifluoroiodomethane with perfluorobut-2-yne. Hexafluoro-2-iodo-3-trifluoromethylbut-2-ene, formed at lower temperature from the butyne and trifluoroiodomethane, gives perfluoro-2-methylbut-2-ene by reaction with fluoride ion, and 2*H*-perfluoro-3-methylbut-2-ene by reduction with zinc and hydrochloric acid. The high reactivity with nucleophiles expected for these olefins from purely electronic considerations is markedly reduced, apparently by steric hindrance; apart from perfluoro-2-methylbut-2-ene, the olefins reacted with methanol only in the presence of base. The iodo-olefin reacts with copper-bronze at high temperatures to give a coupled product formulated as perfluoro-2,3,4,5-tetramethylhexa-2,4-diene.

PERFLUORO-2,3-DIMETHYLBUT-2-ENE was first prepared by Miller and his co-workers² *via* fluorination and dimerisation of 2-chloropentafluoropropene, followed by dechlorination of the dichlorobutane. A more convenient synthesis and some reactions of the perfluoro-



butene (1), and the preparation and reactions of a number of olefins containing three vinylic trifluoromethyl groups are now reported. While this work was in progress, the butene was reported³ to be one of the products of the decomposition of bis(trifluoromethyl)diazomethane or of the corresponding diazirine, and also to be formed by base-catalysed desulphurisation of tetrakis(trifluoromethyl)thiiran.

The free-radical reaction of trifluoroiodomethane with perfluorobut-2-yne takes place readily both under u.v. irradiation⁴ and thermally⁵ at 250° to give hexafluoro-2-iodo-3-trifluoromethylbut-2-ene (2). Further addition to the iodobutene (2) was expected to be slow, because of the considerable steric hindrance, and to

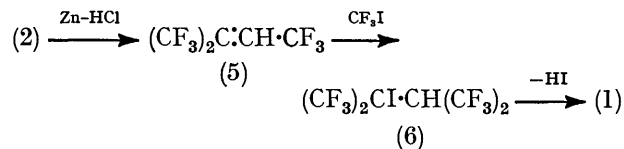


give the geminal di-iodo-compound (3), rather than, or as well as, the vicinal di-iodo-compound (4) required for deiodination to perfluoro-2,3-dimethylbut-2-ene (1).

¹ Part VII, R. E. Banks, L. E. Birks, M. Bridge, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1970, 2539.

² W. T. Miller, R. L. Ehrenfeld, J. M. Phelan, M. Prober, and S. K. Reed, *Ind. Eng. Chem.*, 1947, **39**, 401; W. T. Miller, 'Preparation, Properties and Technology of Fluorine and Organic Fluoro Compounds,' ed. C. Slesser and S. R. Schramm, McGraw-Hill, 1951, p. 567.

Since the reaction of the iodo-compound (2) with zinc and concentrated hydrochloric acid readily affords the corresponding hydro-olefin (5), an alternative route to (1) was the reaction of compound (5) with trifluoroiodomethane to give an adduct (6) which could give the required product (1) on dehydroiodination.



Trifluoroiodomethane failed to react with the olefin (5) however, either thermally or under u.v. irradiation at temperatures up to 180°, and neither the iodo-compound (6) nor the butene (1) was obtained. The reactants were largely recovered, together with small amounts of hexafluoroethane. In contrast, the butene (1) was obtained in good yield in a single step when perfluorobut-2-yne and 2 mol equiv. of trifluoroiodomethane were kept at 350° in an autoclave. This experimentally simple reaction presumably involves either attack by the second trifluoromethyl radical at the $\cdot\text{CI}\cdot\text{CF}_3$ group of (2), probably with loss of I· from the intermediate radical, or 'normal' attack by a trifluoromethyl radical followed either by thermal deiodination of (3) or loss of I· from the intermediate radical without formation of (3) and rearrangement of the carbene so formed by migration of a trifluoromethyl group (Scheme 1), which is known⁶ to be

³ D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1965, **87**, 657; 1966, **88**, 3617.

⁴ R. N. Haszeldine, unpublished results.

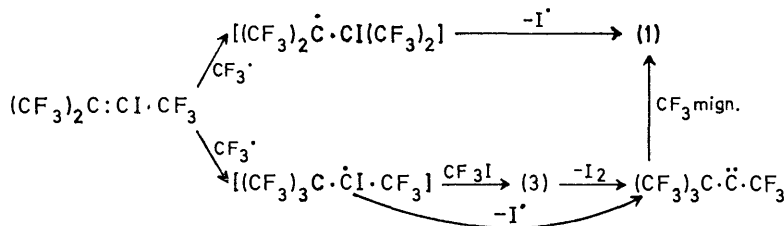
⁵ C. G. Krespan, *J. Amer. Chem. Soc.*, 1961, **83**, 3434.

⁶ R. Fields and R. N. Haszeldine, *Proc. Chem. Soc.*, 1960, 22; *J. Chem. Soc.*, 1964, 1881.

preferred to fluorine migration. The high temperature required for appreciable formation of the butene (1) precluded attempts to trap the suggested carbene.

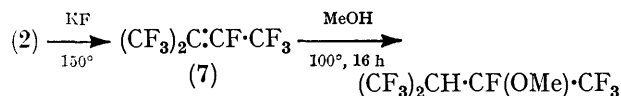
Reactions of Perfluoro-2,3-dimethylbut-2-ene and the 1,1,1,4,4,4-Hexafluoro-2-trifluoromethylbut-2-enes.—The high reactivity towards nucleophiles expected for the

compound (8). The highly exothermic reactions between dimethylamine and compounds (1) and (5) could not be controlled under the conditions investigated (see Experimental section). Here the group X is a poor leaving group (CF₃ or H), and presumably elimination of F⁻ from one of the adjacent trifluoromethyl groups

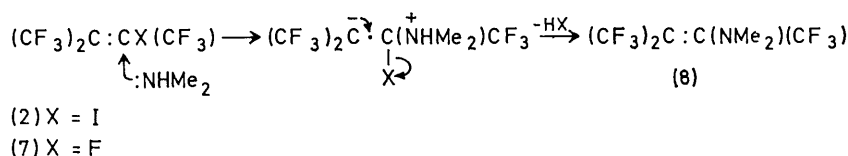


SCHEME 1

olefin (1), with its four vinylic trifluoromethyl substituents, and for the olefins (2), (5), and (7) [which was readily prepared in good yield from the iodo-olefin (2) and anhydrous potassium fluoride] by virtue of their multiple substitution with highly electron-attracting groups, is apparently markedly diminished by steric hindrance to approach by the nucleophile. Thus although perfluoroisobutene reacts readily with methanol in the absence of base,⁷ only the fluoro-olefin (7) reacted with methanol in the absence of base, and this required elevated temperature for a reasonably rapid reaction. In the presence of trimethylamine,



olefins (1) (which gave a deep yellow solution with the amine at -78° , presumably due to a charge-transfer

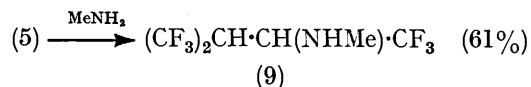


complex) and (5) gave the corresponding methoxybutanes (CF₃)₂CH·C(OMe)(CF₃)₂ and (CF₃)₂CH·CH(OMe)(CF₃) in 62 and 84% yield, respectively. The iodo-olefin (2) did not react with methanol alone, but gave a complex mixture of products with triethylamine. The olefin (5) also reacted readily with water under these conditions to give the hydroxybutane (CF₃)₂CH·CH(OH)(CF₃) in 79% yield [cf. the reaction of (1) with water⁸].

Nitrogen nucleophiles also reacted readily with the olefins (1), (2), (5), and (7). Both the fluoro-olefin (7) and the iodo-olefin (2) gave the same dimethylamino-

olefin [e.g. (CF₃)₂C(NMe₂)·C(CF₃)·CF₂], which undergoes further reaction with the nucleophile more rapidly than does the original olefin and hence leads to complex products. However, the olefin (5) reacted smoothly with the less basic methylamine, and gave the 1 : 1 adduct (9) in good yield.

Radical addition was also relatively selective. Photochemical chlorination of the olefins (1), (2), (5), and (7) took place readily and gave the expected dichloro-compounds in good yields with the olefins (1) and (7). With the olefin (5), as well as the expected dichloro-compound (10), formed in 28% yield, the trichlorobutane (12) was formed (39%) (Scheme 2). The iodo-olefin (2) also gave the trichlorobutane (12) when irradiated in the presence of chlorine. No trace of the expected dichloroiodo-compound (13) was found. Reaction in the dark at 180° (24 h) gave a similar result, but when a short reaction time (3 h) was used⁹ the chloro-olefin (11) was formed in good yield, either by an addition-



bromide failed, and the olefin (5) did not react photochemically with trifluoroiodomethane even at high

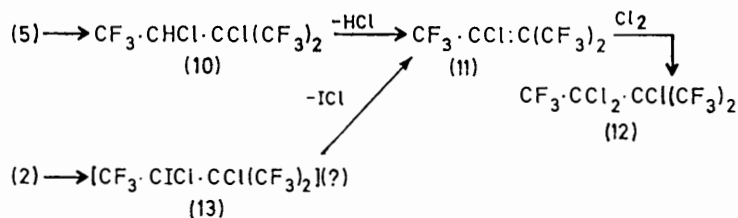
⁷ I. L. Knunyants, L. S. German, and B. L. Dyatkin, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, 1353 (*Chem. Abs.*, 1957, 51, 8037f).

⁸ W. J. Middleton and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1964, 86, 4948.

⁹ R. Fields, R. N. Haszeldine, and D. Moran, unpublished results.

temperatures, presumably because the attacking radicals are larger and less reactive than photochemically generated chlorine atoms. As expected, even the hydroolefin (5) was resistant to electrophilic attack by hydrogen bromide in the presence of Lewis acid catalysts.

Hydrogenation over palladium on alumina proceeded smoothly at 20–50° with the olefins (5) and (7) to give



SCHEME 2

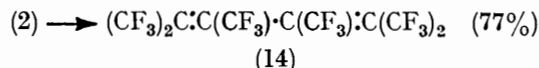
the expected dihydro-adducts, but (5) also gave a low yield of an olefin presumably formed by alumina-initiated dehydrofluorination. Identical products resulted when the iodo-olefin (2) was hydrogenated under the same mild conditions although the reaction was slower, but perfluoro-2,3-dimethylbut-2-ene resisted hydrogenation under these conditions.

Modified Courtauld molecular models suggested that polymerisation of the olefins (1), (5), and (7) would be difficult, but that copolymerisation with (*e.g.*) tetrafluoroethylene should be more sterically favourable. In the event, attempts at both polymerisation [*e.g.* for (1) with benzoyl peroxide, azobisisobutyronitrile, di-*t*-butyl peroxide, sodium sulphite–persulphate;¹⁰ for (5) and (7) with the sulphite–persulphate system] and co-polymerisation [olefins (1), (5), and (7), each with an excess of tetrafluoroethylene and the sulphite–persulphate system, and (1) with ethyl vinyl ether and benzoyl peroxide] were unsuccessful; the fluoroalkyl olefin was recovered essentially quantitatively in each experiment, and only polytetrafluoroethylene was formed when tetrafluoroethylene was present. Attempts to bring about cycloco-dimerisation of perfluoro-2,3-dimethylbut-2-ene with a range of olefins, and with trifluoronitrosomethane, were also unsuccessful, and the olefin (1) was again recovered essentially quantitatively. In contrast, reaction with diazomethane gave the expected Δ^1 -pyrazoline in high yield; the less reactive 1,3-dipoles, 2,2,2-trifluorodiazooethane and ethyl diazoacetate, did not react, however, again suggesting the importance of steric hindrance in the reactions of this olefin, since it has been shown¹¹ that in the series C_2H_4 , $\text{CF}_3 \cdot \text{CH} : \text{CH}_2$, $\text{CF}_3 \cdot \text{CH} : \text{CH} \cdot \text{CF}_3$, where steric hindrance is much less severe, the trifluoromethyl group markedly activates the double bond to 1,3-dipolar addition.

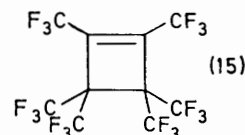
Reaction of Hexafluoro-2-iodo-3-trifluoromethylbut-2-ene with Copper-bronze.—When the iodo-olefin (2) was heated with copper-bronze, the highly hindered diene

(14) was formed in good yield. The structure has been assigned from spectroscopic and analytical results and from the method of formation, but the possibility of isomerisation under the reaction conditions to the cyclobutene (15) (*cf.* the interconversion of perfluoro-2,3-dimethylbuta-1,3-diene and perfluoro-1,2-dimethylcyclobutene¹²) cannot be completely excluded. The

u.v. spectrum of (14) shows the same position of maximum absorption as that of perfluoro-2,3-dimethylbut-2-ene, suggesting that conjugation of the double bonds is



not important. A modified Courtauld model of the diene suggests that the molecule will be virtually locked in a conformation with the planes of the two π -bonds almost perpendicular, so that conjugation would be negligible. Attempts to distinguish chemically between



the two possible structures (14) and (15) by hydrogenation, oxidation, and chlorination were frustrated by the failure of the compound to react appreciably.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 21 spectrometer with sodium chloride optics, mass spectra with an A.E.I. MS2b spectrometer, and n.m.r. spectra with a Perkin-Elmer R10 spectrometer at 60.0 (¹H) or 56.46 (¹⁹F) MHz. Chemical shifts are reported with positive values to low field of external benzene (neat liquid) (for ¹H) or external trifluoroacetic acid (¹⁹F). Molecular weights were measured by mass spectrometry (designated M^+) or by Regnault's method (designated M). All irradiations were performed with a Hanovia UVS 500 medium-pressure arc lamp, with the reactants contained in silica tubes.

Preparation of Perfluoro-2,3-dimethylbut-2-ene (1).—Tri-fluoroiodomethane (137 g, 0.70 mol) and hexafluorobut-2-yne (47.7 g, 0.295 mol) were heated (5 days; indicated temp. 350°) in a Hastalloy-lined autoclave (150 ml) to give

¹⁰ S. Dixon, D. R. Rexford, and J. S. Rugg, *Ind. Eng. Chem.*, 1957, **49**, 1687.

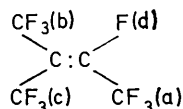
¹¹ J. H. Atherton and R. Fields, *J. Chem. Soc. (C)*, 1968, 1507.

¹² J. P. Chesick, *J. Amer. Chem. Soc.*, 1966, **88**, 4800.

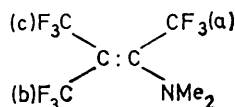
hexafluoroethane (10.0 g), trifluoroiodomethane (5.7 g, 4%), perfluoro-2,3-dimethylbut-2-ene (64.8 g, 73%) (Found: C, 24.2; H, 0.2%; M , 298. Calc. for C_6F_{12} : C, 24.0; H, 0.0%; M , 300), b.p. 53.5° (lit.,² 55°), ^{19}F n.m.r. δ +16.5 p.p.m. (singlet), λ_{max} 205 nm (ϵ ca. 300), and $\bar{\nu}$ (C:C) (Raman) 1670w cm^{-1} ; traces of hexafluoro-2-iodo-3-trifluoromethylbut-2-ene and four other unidentified components were detected in the still-pot residue.

Reactions of Hexafluoro-2-iodo-3-trifluoromethylbut-2-ene (2).—(a) *With zinc and hydrochloric acid.* The iodobutene (11.0 g, 31 mmol) (prepared by the photochemical⁴ or thermal⁵ reaction of trifluoroiodomethane with perfluoro-but-2-yne), granulated zinc (10.0 g), and methylated spirit (10 ml) were stirred and heated under reflux while conc. hydrochloric acid (50 ml) was added, and then for a further 1 h, volatile material being trapped at -78° . Fractional condensation *in vacuo* gave 2*H*-perfluoro-3-methylbut-2-ene (5) (6.80 g, 95%) (Found: C, 25.8; H, 0.5%; M , 231. Calc. for $C_5H_7F_9$: C, 25.9; H, 0.4%; M , 232), b.p. 32°, ^{19}F n.m.r. δ +16.0 and +9.8 p.p.m. (complex bands, intensity ratio 2:1), 1H n.m.r. δ -0.3 p.p.m. (complex), $\bar{\nu}$ (C:C) 1747 m and 1701 m cm^{-1} .

(b) *With potassium fluoride.* Anhydrous potassium fluoride (9.0 g, 0.15 mol) was heated *in vacuo* (200°; 3 h) in a Dreadnought glass tube (350 ml), the iodobutene (12.75 g, 35.6 mmol) was condensed in, and the mixture was heated (150°; 7 days) to give, after fractional condensation *in vacuo*, perfluoro-2-methylbut-2-ene (7) (6.32 g, 71%) (Found: C, 23.9; H, 0.0%; M , 250. C_5F_{10} requires C, 24.0; H, 0.0%; M , 250), b.p. 29.0–29.5°, ^{19}F n.m.r. δ (a) +8.7 [q (12.4 Hz) of d (3.0 Hz) of q (1.4 Hz)], (b) +16.2 [d (27.4 Hz) of q (8.4 Hz) of q (1.4 Hz)], (c) +17.6 [q (12.4 Hz) of d (8.1 Hz) of q (8.4 Hz)], (d) -23.3 p.p.m. [q (27.4 Hz) of q (8.1 Hz) of q (3.0 Hz)], in the ratio 3:3:3:1 assigned to the groups shown, $\bar{\nu}$ (C:C) 1704 cm^{-1} .



(c) *With dimethylamine.* The iodobutene (2.4 g, 6.7 mmol) and dimethylamine (0.30 g, 6.7 mmol) were sealed together in a Pyrex tube at -196° , and allowed to warm to room temperature. An exothermic reaction gave a white solid and a volatile mixture which contained ca. 50% of the iodobutene. Further treatment of the mixture with an excess of dimethylamine and fractional condensation of the volatile products *in vacuo* gave 2-dimethylaminohexafluoro-3-trifluoromethylbut-2-ene (8) (1.65 g, 90%) (Found: C, 30.9; H, 2.5; N, 4.9%; M , 275. $C_7H_6F_9N$ requires C, 30.5; H, 2.2; N, 5.1%; M , 275), ^{19}F n.m.r. δ (a) +14.2 (q, 14.1 Hz), (b) +19.7 (q, 9.2 Hz), (c) +24.5 p.p.m. [q (14.1 Hz) of q (9.2 Hz) of equal intensities assigned to the groups shown, 1H n.m.r. δ -3.85 br p.p.m. (s), $\bar{\nu}$ (C:C) 1667 cm^{-1} .



(d) *With hydrogen.* Hydrogen was bubbled through the iodobutene (7.2 g, 20.0 mmol) and the mixed vapours were passed at room temperature through a tube containing

palladium on alumina to give the unchanged iodobutene (4.0 g, 56%), 1,1,1,4,4,4-hexafluoro-2-trifluoromethylbutane (1.61 g, 79% based on iodobutene consumed) (Found: C, 26.4; H, 1.3%; M , 234. $C_5H_3F_9$ requires C, 25.6; H, 1.3%; M , 234), ^{19}F n.m.r. δ +9.5 [t (9.9 Hz) of septets (3.5 Hz) of d (1 Hz), $CF_3 \cdot CH_2$] and +7.4 p.p.m. [d (7.5 Hz) of q (3.5 Hz), $(CF_3)_2CH$] with the intensity ratio 1:2, 1H n.m.r. δ -3.5 [complex, $(CF_3)_2CH$] and -4.1 p.p.m. [q (9.9 Hz) of d (5.5 Hz), CF_3CH_2] in the ratio 1:2, and an unidentified compound (0.29 g) with strong $\bar{\nu}$ (C:C) at 1724 cm^{-1} .

(e) *With copper-bronze.* The iodobutene (5.0 g, 14.0 mmol) and dried (200° *in vacuo*; 2 h) copper-bronze were heated (200°; 24 h), to give perfluoro-2,3,4,5-tetramethylhexa-2,4-diene (14) (2.5 g, 77%) (Found: C, 26.2; H, 0.2%; M^+ 462. $C_{10}F_{18}$ requires C, 26.0; H, 0.0%; M , 462), b.p. 105°, ^{19}F n.m.r. δ +18.7 and +17.2 p.p.m. (broad, intensity ratio 1:2), $\bar{\nu}$ (C:C) 1653 cm^{-1} , λ_{max} 205 nm (ϵ ca. 1400).

(f) *With chlorine.* The olefin (7.16 g, 20.0 mmol) and chlorine (5.68 g, 81 mmol) were irradiated (tungsten lamp; 3 days) to give a solid identified chemically and spectroscopically as 2,2,3-trichlorohexafluoro-3-trifluoromethylbutane (12) (4.7 g, 77% based on olefin consumed) (Found: M^+ , 336, 338, 340, 342 and fragment ions. Calc. for $C_6Cl_3F_9$: M 336, 338, 340, 342), ^{19}F n.m.r. δ +16.2 [q (7.0 Hz), $(CF_3)_2C(Cl)$] and +6.1 p.p.m. (septet, 7.0 Hz, $CF_3 \cdot CCl_2$) with intensity ratio 2:1, and unchanged olefin (0.65 g, 9%).

Reactions of Perfluoro-2,3-dimethylbut-2-ene (1).—(a) *With methanol.* Methanol (0.16 g, 5.0 mmol) and the olefin (2.0 g, 6.7 mmol) were recovered (100%) after being kept together (110°; 3 days) in a sealed Pyrex ampoule (15 ml). When the olefin (0.77 g, 2.6 mmol) and triethylamine (0.10 g, 1.0 mmol) were condensed together a bright yellow solution resulted at -78° . Addition of methanol (0.08 g, 2.5 mmol) quenched the colour, and the mixture was heated (100°; 4 days) to give unchanged olefin (0.11 g, 14%) and 1,1,1,4,4-hexafluoro-2-methoxy-2,3-bis(trifluoromethyl)butane (0.45 g, 62%) (Found: C, 25.5; H, 1.3. $C_7H_4F_{12}O$ requires C, 25.3; H, 1.2%), ^{19}F n.m.r. δ +17.9 [d (8.4 Hz) of septets (8.4 Hz), $(CF_3)_2CH$] and +7.9 p.p.m. [septet, 8.4 Hz, $(CF_3)_2C(OMe)$] of equal intensities, 1H n.m.r. δ -2.7 [septet, 8.4 Hz, $(CF_3)_2CH$] and -2.85 p.p.m. (s, OCH_3) with intensity ratio 1:3.

(b) *With dimethylamine.* The olefin (1.0 g, 3.3 mmol) and dimethylamine (0.18 g, 4.0 mmol) were allowed to warm slowly from -196° in a sealed Pyrex ampoule. At ca. -50° an exothermic reaction took place, and the only volatile material recovered was the original olefin. This was treated similarly with an excess of dimethylamine; the involatile products were extracted with ether and shown by g.l.c. to contain five major and thirteen minor unidentified components.

(c) *With chlorine.* The olefin (1.26 g, 4.2 mmol) and chlorine (0.60 g, 8.5 mmol) were irradiated in a silica tube (4 days) to give unchanged olefin (0.10 g, 8%) and, after sublimation from an intensely yellow impurity, white solid 2,3-dichlorohexafluoro-2,3-bistrifluoromethylbutane (1.44 g, 100% based on olefin consumed) (Found: C, 19.0; H, 0.2. Calc. for $C_6Cl_2F_{12}$: C, 19.4; H, 0.0%; m.p. 92° (lit.,² 91.5–93°), ^{19}F n.m.r. δ +14.0 p.p.m. (s).

(d) *With hydrogen.* Perfluoro-2,3-dimethylbut-2-ene (4.0 g, 13.3 mmol) was recovered quantitatively after passage ($\times 4$) with an excess of hydrogen over palladium

on alumina at room temperature. When 2,2,2-trifluoro-1-trifluoromethylethylideneimine (1.65 g, 10 mmol) and an excess of hydrogen were passed over the same batch of catalyst at room temperature immediately afterwards, 2,2,2-trifluoro-1-trifluoromethylethylamine (1.34 g, 80%) was obtained.

(e) *Attempted polymerisation.* Sodium pyrophosphate (0.155 g), sodium persulphate (0.155 g), and perfluorooctanoic acid (0.077 g) were dissolved in deionised water (50 ml) and the solution was degassed. Sodium sulphite (0.155 g) was dissolved in deionised water (5 ml) and the solution was degassed, then added to the first solution; the mixture was cooled to -196° *in vacuo*.¹⁰ Perfluoro-2,3-dimethylbut-2-ene (3.0 g, 10.0 mmol) was condensed in, and the sealed tube was allowed to warm very slowly to 20° , then kept at 90° (16 h). The olefin (3.0 g, 10.0 mmol) was recovered.

(f) *Attempted co-polymerisation.* Perfluoro-2,3-dimethylbut-2-ene (2.4 g, 8.0 mmol) and tetrafluoroethylene (1.60 g, 16.0 mmol) were treated with the catalyst solution under the conditions described in (e) (24 h) to give pure perfluoro-2,3-dimethylbut-2-ene (2.35 g, 98%) and polytetrafluoroethylene.

(g) *With hydrogen bromide.* The olefin (4.68 g, 15.6 mmol) and hydrogen bromide (1.26 g, 15.5 mmol) were recovered quantitatively after being kept together *in vacuo* at 20° (2 days) and 80° (4 days). Irradiation (4 days) gave the olefin (4.68 g, 100%), hydrogen, bromine, and unchanged hydrogen bromide.

(h) *With diazomethane.* The olefin (3.0 g, 10 mmol) and diazomethane (*ca.* 0.2 g, 5 mmol) in ether (6.9 ml) were sealed together *in vacuo* at -196° and allowed to warm slowly (16 h) to room temperature to give ether (6.8 ml), unchanged olefin (1.7 g, 57%), and white crystalline 3,3,4,4-tetrakis(trifluoromethyl)- Δ^1 -pyrazoline (1.5 g, 100% based on olefin consumed) (Found: C, 24.6; H, 0.9; N, 8.5%; M^+ 342. $C_7H_2F_{12}N_2$ requires C, 24.6; H, 0.6; N, 8.2%; M , 342), ^{19}F n.m.r. δ +15.1 p.p.m. (complex unresolved m), purified by sublimation *in vacuo*.

Reactions of 2H-Perfluoro-3-methylbut-2-ene (5).—(a) *With water.* The olefin (3.0 g, 12.9 mmol), water (1.0 g, 55.5 mmol), triethylamine (0.3 ml), and acetonitrile (5 ml) were shaken together *in vacuo* at room temperature (10 days). Unchanged olefin (0.70 g, 23%) was removed *in vacuo*, and the residue was washed with dilute hydrochloric acid, then distilled from 20% oleum to give 1,1,1,4,4,4-hexafluoro-3-trifluoromethylbutan-2-ol (2.0 g, 79% based on consumed olefin) (Found: C, 24.2; H, 1.3. $C_5H_3F_9O$ requires C, 24.0; H, 1.2%), b.p. $105-107^\circ$, ^{19}F n.m.r. δ +15.6 [q (*ca.* 9 Hz) of q (*ca.* 9 Hz) of d (*ca.* 9 Hz)], +10.0 [q (*ca.* 9 Hz) of d (*ca.* 9 Hz)], and -1.3 p.p.m. [q (*ca.* 9 Hz) of d (*ca.* 9 Hz)] of equal intensities, 1H n.m.r. δ -2.15 (broadened q, 9 Hz, $CF_3\cdot CH$), -2.97 br (s, OH), and -3.38 p.p.m. [septet (9 Hz) of d (2.5 Hz), $(CF_3)_2CH$] of equal intensities, and $\bar{\nu}$ (OH) 3483br cm^{-1} .

(b) *With methanol.* The olefin (2.32 g, 10.0 mmol) was recovered quantitatively after being shaken *in vacuo* with methanol (0.64 g, 20 mmol) at 100° . After 7 days at room temperature with methanol (0.64 g, 20 mmol) and triethylamine (0.5 g, 5 mmol), the olefin (2.32 g, 10.0 mmol) gave unchanged olefin (1.2 g, 52%) and 1,1,1,4,4,4-hexafluoro-2-methoxy-3-trifluoromethylbutane (1.06 g, 84% based on olefin consumed) (Found: C, 27.4; H, 1.8%; M^+ , 264. $C_6H_5F_9O$ requires C, 27.3; H, 1.9%; M , 264), ^{19}F n.m.r. δ +15.2 (complex), +9.4 [broad d

(*ca.* 9.5 Hz) of q (*ca.* 9.5 Hz)] and +0.4 p.p.m. [broad d (7 Hz) of q (7 Hz), $CF_3\cdot CH(OMe)$], of equal intensities, 1H n.m.r. δ -2.80 [broad q, 7 Hz, $CH(OMe)CF_3$], -3.21 (s, $O\cdot CH_3$), and -3.42 p.p.m. [septet (9.5 Hz) of d (*ca.* 1 Hz), $(CF_3)_2CH$], with intensity ratio 1 : 3 : 1, $\bar{\nu}$ ($O\cdot CH_3$) 2865 cm^{-1} .

(c) *With dimethylamine.* The olefin (2.30 g, 9.9 mmol) and dimethylamine (0.45 g, 10.0 mmol) were sealed together *in vacuo* at -196° . As the mixture warmed to room temperature, a violent reaction took place. Unchanged olefin was the only volatile product, and was treated under similar conditions with an excess of dimethylamine. The involatile material was extracted with ether, the extract was washed (2N-sodium hydroxide, water) and dried, and the ether removed to give a high-boiling yellow residue shown by g.l.c. to contain six major and fourteen minor components. Reaction at -78° with perfluoropentane as diluent gave similar results.

(d) *With methylamine.* The olefin (3.58 g, 15.4 mmol) and methylamine (0.49 g, 15.8 mmol) reacted vigorously on warming slowly to room temperature to give (i) unchanged olefin (0.68 g, 19%); (ii) 1,1,1,4,4,4-hexafluoro-2-methylamino-3-trifluoromethylbutane (9) (2.00 g, 61%) (Found: C, 27.15; H, 2.1; N, 5.5%; M , 263. $C_6H_5NF_9$ requires C, 27.4; H, 2.3; N, 5.3%; M , 263), b.p. 44° , ^{19}F n.m.r. δ +15.8 [q (*ca.* 8.4 Hz) of q (8.4 Hz) of d (8.4 Hz)] and +10.0 and +3.4 p.p.m. [both d (*ca.* 8.6 Hz) of q (8.6 Hz)], of equal intensities, 1H n.m.r. δ -3.20 (broad q, 8.6 Hz, $CF_3\cdot CH$), -3.50 [septet (9 Hz) of d (2.4 Hz), $(CF_3)_2CH$], -4.2 (d, 4.8 Hz, $CH_2\cdot NH$), and -5.42 p.p.m. (broad s, NH), in the intensity ratio 1 : 1 : 3 : 1, $\bar{\nu}$ (NH) 3436 cm^{-1} ; (iii) a high-boiling liquid, and (iv) methylammonium fluoride.

(e) *With hydrogen.* The olefin (5.00 g, 21.5 mmol) and an excess of hydrogen were passed over a palladium-alumina catalyst at room temperature to give 1,1,1,4,4,4-hexafluoro-2-trifluoromethylbutane (4.00 g, 79%) and the same minor product (0.40 g), $\bar{\nu}$ (C:C) 1724 cm^{-1} as was found in the hydrogenation of hexafluoro-2-iodo-3-trifluoromethylbut-2-ene.

(f) *With chlorine.* The olefin (1.14 g, 4.9 mmol) and chlorine (0.71 g, 10.0 mmol) were irradiated *in vacuo* (4 days) to give a compound tentatively identified as 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-trifluoromethylbutane (10) (0.41 g, 28%) (Found: M , 300. Calc. for $C_5HCl_2F_9$: M , 303), ^{19}F n.m.r. δ +12.7 p.p.m. (d, 7.4 Hz) superimposed on a broad singlet, 1H n.m.r. δ -3.2 p.p.m. (complex), and 2,2,3-trichlorohexafluoro-3-trifluoromethylbutane (12) (0.65 g, 39%).

(g) *With hydrogen bromide.* The olefin (0.98 g, 4.2 mmol), hydrogen bromide (0.34 g, 4.2 mmol), and anhydrous zinc chloride (2.5 g) were kept in a sealed tube (100° ; 5 days) to give unchanged olefin (0.95 g, 97%) and hydrogen bromide (0.34 g, 100%). Irradiation of the olefin (0.99 g) and hydrogen bromide (0.34 g) (6 days) gave hydrogen (0.8 mmol), bromine, unchanged olefin (0.90 g, 91%), and hydrogen bromide (0.25 g, 74%).

(h) *Attempted polymerisation and co-polymerisation.* The olefin (1.86 g, 8.0 mmol) did not homopolymerise or co-polymerise with tetrafluoroethylene when treated with the catalyst system already described.

Reactions of Perfluoro-2-methylbut-2-ene (7).—(a) *With methanol.* The olefin (1.30 g, 5.2 mmol) and methanol (0.17 g, 5.3 mmol) were shaken *in vacuo* at room temperature (36 h) without observable reaction. The mixture

was then kept at 100° (16 h) to give unchanged olefin (0.10 g, 8%) and 1,1,1,2,4,4,4-heptafluoro-2-methoxy-3-trifluoromethylbutane (1.25 g, 92% based on olefin consumed) (Found: C, 25.8; H, 1.4%; M^+ , 282. $C_6H_4F_{10}O$ requires C, 25.5; H, 1.4%; M , 282), ^{19}F n.m.r. δ +14.7 (complex), -1.8 (broad q, 8.5 Hz), and -53 (complex, unresolved), with intensity ratio 6 : 3 : 1, 1H n.m.r. δ -3.2 (large band, septet, *ca.* 1 Hz, OCH_3 , overlapping a complex band), $\bar{\nu}(OCH_3)$ 2898 cm^{-1} .

(b) *With dimethylamine.* The olefin (1.30 g, 5.2 mmol) and dimethylamine (0.23 g, 5.1 mmol) reacted vigorously on warming from -196° to give unchanged olefin (0.78 g, 60%) and 2-dimethylaminohexafluoro-3-trifluoromethylbut-2-ene (0.58 g, 94% based on olefin consumed).

(c) *With hydrogen.* The olefin (2.50 g, 10.0 mmol) and an excess of hydrogen were passed over palladium-alumina to give an unidentified minor product (0.10 g), $\bar{\nu}(C=C)$ 1729 cm^{-1} , and 1,1,1,2,4,4,4-heptafluoro-3-trifluoromethyl-

butane (1.50 g, 60%) (Found: C, 24.2; H, 1.0%; M , 252. $C_5H_2F_{10}$ requires C, 23.8; H, 0.8%; M , 252), ^{19}F n.m.r. δ +9.4 [d (9.5 Hz), of d (9.5 Hz) of q (3.5 Hz)], +7.2 [d (7.6 Hz) of q (3.5 Hz)], and -136.8 (complex, CHF).

(d) *With chlorine.* The olefin (0.85 g, 3.4 mmol) and chlorine (0.48 g, 6.8 mmol) were irradiated *in vacuo* (4 days) to give unchanged olefin (0.17 g, 20%) and 2,3-dichloroheptafluoro-2-trifluoromethylbutane (0.65 g, 74%) (Found: C, 18.9; H, 0.1; Cl, 22.3. $C_5Cl_2F_{10}$ requires C, 18.7; H, 0.0; Cl, 22.1%), m.p. 25-27°, ^{19}F n.m.r. δ +11.4, +10.7, +1.8, and -45.1 p.p.m. (complex bands, intensity ratio 3 : 3 : 3 : 1).

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