Perfluoroalkyl Derivatives of Sulphur. Part XVII.[1] Some Reactions of Perfluorovinylsulphur Pentafluoride,[2] and a Re-examination of the Thermal Reaction between Perfluoropropene and Buta-1,3-diene

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Perfluorovinylsulphur pentafluoride is attacked by sodium methoxide in methanol to give 1,2,2-trifluoro-2-methoxyethylsulphur pentafluoride, and by bromine (⟶ $SF_5\cdot CFBr\cdot CF_2Br$), hydrogen bromide (⟶ $SF_5\cdot CHF\cdot CF_2Br$), and trifluoroiodomethane (⟶ $SF_5\cdot CFI\cdot C_2F_5$) under photochemical conditions and bromine monochloride (⟶ $SF_5\cdot CFCl\cdot CF_2Br$, $SF_5\cdot CFBr\cdot CF_2Cl$) under thermal conditions to yield the corresponding 1 : 1 adducts and by-products derived from C–S bond fission. Hexafluoro-1,1-di-iodopropane, a by-product of the reaction between the olefin and trifluoroiodomethane, yields perfluorohex-3-ene when irradiated in the presence of mercury, and cleavage of the dibromide $SF_5\cdot CFBr\cdot CF_2Br$ with aluminium bromide gives 1,2-dibromotetrafluoroethane. Reaction of perfluorovinylsulphur pentafluoride with butadiene at 140—195 °C yields essentially a 1 : 1 mixture of *cis*- and *trans*-1,1,2-trifluoro-2-pentafluorothio-3-vinylcyclobutane: re-examination of the corresponding reaction involving perfluoropropene has shown that the major product is a mixture of *cis*- and *trans*-1,1,2-trifluoro-2-trifluoromethyl-3-vinylcyclobutane, 4,4,5-trifluoro-5-(trifluoromethyl)cyclohexene being formed in only small amounts. Details of the preparation of copoly(perfluorovinylsulphur pentafluoride–vinylidene fluoride) and n.m.r. data for the cycloadducts named above are presented.

ATTENTION was drawn recently[3] to the scarcity of information in the literature concerning the chemistry of perfluorovinylsulphur pentafluoride, a colourless volatile liquid (b.p. 19 °C) known for more than a decade to be obtainable *via* reaction of sulphur chloride pentafluoride with trifluoroethylene.[4,5] Thus the reactions summarised in Scheme 1 are now described; details of the copolymerization of perfluorovinylsulphur pentafluoride with vinylidene fluoride or with vinylidene fluoride and perfluoropropene have already been disclosed,[6] and studies on thermal vulcanization of the Viton-like elastomers thus obtained will be described shortly.[7] Previous publications concerning this olefin dealt with photochlorination (⟶ $SF_5\cdot CFCl\cdot CF_2Cl$),[4] thermal reaction with iodine monofluoride (⟶ $SF_5\cdot CFI\cdot CF_3$),[3] u.v.-initiated oxetan formation with hexafluoroacetone [⟶ $SF_5\cdot\overline{CF\cdot CF_2\cdot O\cdot C}(CF_3)_2$ (mainly) and $SF_5\cdot\underline{CF\cdot CF_2\cdot C(CF_3)_2\cdot O}$],[8] and copolymerization with tetrafluoroethylene.[9]

Perfluorovinylsulphur pentafluoride shows considerable thermal and radiation stability: it is unaffected when heated at 300 °C in Pyrex for 6 h, and is destroyed only slowly when subjected to u.v. or γ-radiation in silica or Pyrex, respectively, decomposition apparently occurring *via* homolysis of the $C–SF_5$ linkage since sulphur hexafluoride, disulphur decafluoride, thionyl fluoride, sulphuryl fluoride, and silicon tetrafluoride are produced.

Methanol does not attack perfluorovinylsulphur pentafluoride at room temperature, but sodium methoxide in methanol at 60 °C converts the olefin cleanly into the ether $SF_5\cdot CHF\cdot CF_2\cdot OMe$, indicating[10] that an α-SF_5 group stabilises a carbanionic site more than an α-fluorine atom does.†

The π-system of perfluorovinylsulphur pentafluoride shows the expected[10] resistance to attack by bromine or hydrogen bromide under 'electrophilic' conditions. Thus, no reaction was detected when a mixture of the olefin and hydrogen bromide was kept in the dark at room temperature for about 2 weeks, and similar storage of a bromine–olefin mixture gave only traces of the dibromide $SF_5\cdot CFBr\cdot CF_2Br$. This product could have arisen from the onset of photobromination when the reaction mixture was exposed to artificial daylight during work-up, since photoaddition occurred smoothly under the influence of light from domestic lamps to give the dibromide in 92·5% yield after 2 h. The yield of the by-product $CFBr_2\cdot CF_2Br$ increased from 2 to 7% at the expense of the olefin dibromide when u.v. light was employed, and the gaseous product was found to comprise SF_6, S_2F_{10}, SOF_2, SO_2F_2, SO_2, and SiF_4—clear evidence for the generation of SF_5 radicals. These by-products, formation of which parallels that of $CHBr_2\cdot CHBrCl$ and S_2F_{10} during photobromination of $SF_5\cdot CH\colon CHCl$,[11] have been shown by separate experi-

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† Kinetic acidity studies (M. G. Barlow, R. N. Haszeldine, and H. I. Jones, unpublished results) on the compound $CF_3\cdot CHF\cdot SF_5$, in MeONa–MeOD, where the relative rate of H exchange at 0 °C is 2·1 × 10^2 times that for the compound $(CF_3)_2CHF$, indicate that the SF_5 group is more effective even than an α-CF_3 group in this respect.

[1] Part XVI, R. N. Haszeldine, B. Hewitson, and A. E. Tipping, *J.C.S. Perkin I*, in the press.

[2] A preliminary account of this work was presented (by R. N. H.) at a Ministry of Aviation Conference on Polymer Synthesis and Properties, London, March 1965.

[3] G. L. Gard and C. Woolf, *J. Fluorine Chem.*, 1971/72, **1**, 487.

[4] J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 1961, 2070; see also R. E. Banks, R. N. Haszeldine, and W. D. Morton, *J. Chem. Soc.* (*C*), 1969, 1947; H. W. Sidebottom, J. M. Tedder, and J. C. Walton, *Chem. Comm.*, 1970, 253.

[5] The corresponding route involving sulphur bromide pentafluoride has been described more recently: J. Steward, L. Kegley, H. F. White, and G. L. Gard, *J. Org. Chem.*, 1969, **34**, 760.

[6] R. E. Banks and R. N. Haszeldine, B.P. 1,145,263/1969.

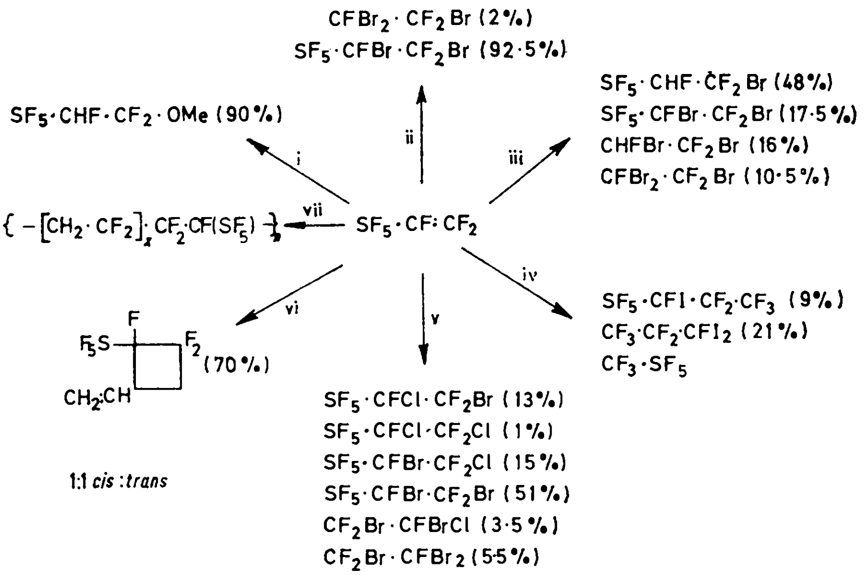
[7] R. E. Banks, F. Fitton, R. N. Haszeldine, P. Mitra, W. D. Morton, and S. Smith, in preparation.

[8] C. Woolf and G. L. Gard, U.S.P. 3,448,121/1969 (*Chem. Abs.*, 1970, **72**, 12,547h); see also G. L. Gard, C. Woolf, and R. M. Shaw, U.S.P. 3,519,725/1970 (*Chem. Abs.*, 1970, **73**, 114,434g).

[9] S. Sherratt, B.P. 929,990/1963.

[10] R. E. Banks, 'Fluorocarbons and Their Derivatives,' Macdonald, London, 1970, 2nd edn., ch. 2.

[11] J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 1961, 2066.



SCHEME 1 Reagents: i, MeOH, MeONa, 60 °C; ii, Br_2, light; iii, HBr, u.v. light; iv, CF_3I, u.v. light; v, Br_2, Cl_2, 80 °C; vi, $CH_2{:}CH{\cdot}CH{:}CH_2$, 190 °C; vii, $CH_2{:}CF_2$, $K_2S_2O_8$–Na_2SO_3 aq., 85 °C

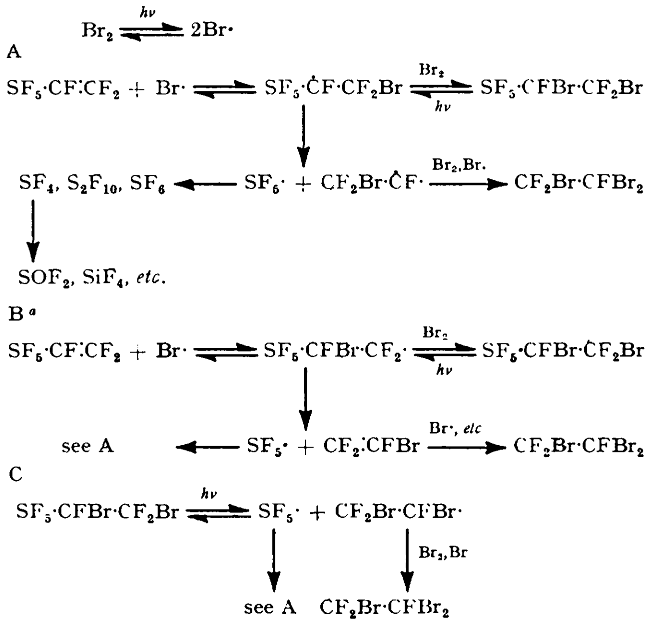
ments to arise when $SF_5{\cdot}CFBr{\cdot}CF_2Br$ is irradiated alone or in the presence of bromine.

Similar but more extensive complications arose in reactions between perfluorovinylsulphur pentafluoride and hydrogen bromide, trifluoroiodomethane, or bromine monochloride (see Scheme 1), and, in the cases of the first two addends, precluded definitive determination of attack by bromine atom or trifluoromethyl radical on the olefin. Separate experiments revealed that photolysis of the sole HBr adduct isolated ($SF_5{\cdot}CHF{\cdot}CF_2Br$) in the presence of bromine or hydrogen bromide yields the ethanes $CHFBr{\cdot}CF_2Br$ (*ca.* 80%), $CFBr_2{\cdot}CF_2Br$ (4%), and products derived from SF_5 radicals (SF_6, S_2F_{10}, and compounds derived from attack by SF_4 on silica and adventitious moisture). The low yield and isolation problems precluded such studies on the CF_3I adduct $SF_5{\cdot}CFI{\cdot}CF_2{\cdot}CF_3$.

The results relating to photobromination of perfluorovinylsulphur pentafluoride can be accommodated by the operation of one or more of Schemes 2A—C, which can also be adapted[12] to explain the other reactions described above.

The bromine and hydrogen bromide adducts $SF_5{\cdot}CFBr{\cdot}CF_2Br$ and $SF_5{\cdot}CHF{\cdot}CF_2Br$ revert to perfluorovinylsulphur pentafluoride when treated with copper at 188 °C or potassium hydroxide at 20 °C, respectively. The dibromide is cleaved by aluminium bromide at room temperature, giving 1,2-dibromotetrafluoroethane in 59% yield, possibly as shown in Scheme 3 (*cf.* the formation of $CF_3{\cdot}CF_2I$ in the reaction of perfluorovinylsulphur pentafluoride with a mixture of iodine, iodine pentafluoride, and aluminium tri-iodide[3]).

*Thermal Cycloadditions between Perfluorovinylsulphur Pentafluoride or Perfluoropropene and Buta-*1,3-*diene*.—Reaction of perfluorovinylsulphur pentafluoride with an excess of butadiene at 190 °C for 22 h under autogenous pressure in the presence of a free-radical scavenger gave 4-vinylcyclohexene, a 1 : 1 mixture of the *cis*- and *trans*-vinylcyclobutanes (1) and (2) ($X = SF_5$) in 70% yield based on 33% consumption of the fluoro-olefin, and traces of unidentified material that could have contained the [2 + 4] cycloadduct (3) ($X = SF_5$). At 195 °C for 90 h the conversion of fluoro-olefin was greater (86%), and (1) and (2) were formed in yields of 47 and 48%, respectively. The contrast between



SCHEME 2

[a] Note that attack by bromine atom or trifluoromethyl radical on perfluoropropene, the carbon analogue of perfluorovinylsulphur pentafluoride, is clearly bi-directional, with attack at C-1 preferred.[10]

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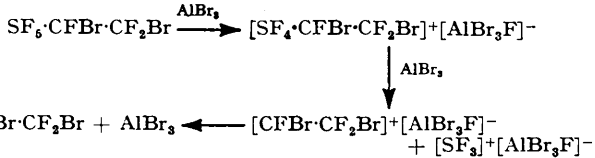
[12] W. D. Morton, Ph.D. Thesis, University of Manchester, 1967.

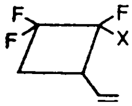
this result and the claim[13] that perfluoropropene combines with butadiene at 175 °C to give a 3 : 1 mixture of a 1,1,2-trifluoro-2-trifluoromethyl-3-vinylcyclobutane



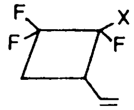
$$\begin{tikzcd} \mathrm{SF_5\cdot CFBr\cdot CF_2Br} \arrow[r, "\mathrm{AlBr_3}"] & {\mathrm{[SF_4\cdot CFBr\cdot CF_2Br]^+[AlBr_3F]^-}} \arrow[d, "\mathrm{AlBr_3}"] \\ \mathrm{CF_2Br\cdot CF_2Br + AlBr_3} & {\mathrm{[CFBr\cdot CF_2Br]^+[AlBr_3F]^- + [SF_3]^+[AlBr_3F]^-}} \arrow[l] \end{tikzcd}$$

SCHEME 3

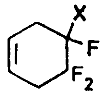
[*either* (1) *or* (2) ($X = CF_3$), the absolute geometry being unknown] and the cyclohexene (3) ($X = CF_3$), prompted a re-examination of the propene case. The product was shown to contain (1), (2), and (3) ($X = CF_3$) in the ratio of *ca.* 9 : 11·5 : 1, in accord with expectation.[10,14]



(1)



(2)



(3)

*N.m.r. Spectra of the Buta-*1,3-*diene Adducts.*—The [2 + 2] adducts (1) and (2) are readily distinguished from the [4 + 2] adduct (3) on the basis of the number and pattern of olefinic protons shown in their ^{1}H n.m.r. spectra (the cyclobutanes show a typical $CH_2{:}CH$ pattern at τ *ca.* 4—5 and the corresponding cyclohexenes a band due to CH:CH at τ *ca.* 4·6). The ^{19}F n.m.r. spectra provide additional support where the geminal F,F coupling constant of the CF_2 group, if apparent, is some 50 Hz smaller in magnitude for cyclobutanes. Assignment to individual cyclobutanes remains more difficult. ^{19}F N.m.r. spectral data are summarised as follows:

(1; $X = SF_5$) chemical shifts: * −153·8 (SF), −133·9 (SF_4), 23·6 (F of CF_2 *trans* to SF_5), 32·8 (F of CF_2, ^2J 206 Hz), and 55·9 p.p.m. (CF·S); (2; $X = SF_5$): −153·0 (SF), −128·4 (SF_4, ^2J 146·3 Hz), 26·1 (F of CF_2 *trans* to SF_5), 36·4 (F of CF_2, ^2J 208 Hz), and 79·6 p.p.m. (CF·S).

(1; $X = CF_3$): −2·3 (CF_3), 23·7 (F of CF_2 *cis* to CF_3), 40·1 (F of CF_2, ^2J 216 Hz), and 94·4 p.p.m. (CF); (2; $X = CF_3$): 1·3 (CF_3), 29·9 (CF_2, ^2J not apparent), and 114·1 p.p.m. (CF); (3; $X = CF_3$): 0·2 (CF_3), 26·8 and 33·3 (CF_2, ^2J 258 Hz), and 103·4 p.p.m. (CF).

We have studied the ^{19}F n.m.r. spectra of a number of tri- and tetra-fluorocyclobutanes; these indicate that replacement of hydrogen by a vinyl group causes substantial shielding (by *ca.* 15 p.p.m.) of adjacent *cis*-fluorines, and small deshielding (by *ca.* 4 p.p.m.) of *trans*-fluorines. On this basis, the above assignments of individual cyclobutanes may be made. Assignment of individual CF_2 group fluorines remains more difficult. Replacement of hydrogen by a β-vinyl group usually causes a small deshielding (*ca.* 3 p.p.m.) of *cis*-fluorines and shielding (*ca.* 3 p.p.m.) of *trans*-fluorines. Thus the assignments for the hexafluoropropene adducts follow. The $CF_2{:}CF\cdot SF_5$ adducts appear anomalous in this respect. However, the CF_2 absorption to higher field showed coupling [*J* 18 Hz for (1), 19 Hz for (2), analysed by the methods of ref. 15] to the basal fluorines of the SF_4 group, and we suggest that this is due to the fluorine nucleus *cis* to SF_5. Alternative structures with SF_5 not adjacent to $CH{:}CH_2$ give a much poorer fit to the observed chemical shifts.

EXPERIMENTAL

Distillation of the volatile product from dehydrochlorination[4] of a 95 : 5 mixture[16] of 2-chloro-1,2,2-trifluoroethylsulphur pentafluoride and 2-chloro-1,1,2-trifluoroethylsulphur pentafluoride gave perfluorovinylsulphur pentafluoride (Found: C, 11·5%; *M* 205·5. Calc. for C_2F_8S: C, 11·5%; *M* 208), b.p. 19 °C, in 77% yield; this material possessed an i.r. spectrum identical with that recorded,[17] and g.l.c. analysis (4 m Kel-F No. 3 oil–Celite; 20 °C) indicated that it was 100% pure.

Molecular weights were determined by Regnault's method. G.l.c. and spectroscopic instrumentation were as stated previously.[16] Volatile products were subjected to trap-to-trap fractional condensation at 1—2 mmHg (simply referred to as ' fractionation ' in the text) prior to examination.

Detailed i.r. data for compounds marked with an asterisk are available in Supplementary Publication No. SUP 20962 (4 pp.).†

Reactions of Perfluorovinylsulphur Pentafluoride.—(a) *Pyrolysis.* Perfluorovinylsulphur pentafluoride (0·129 g) was heated at 300 °C for 6 h in a Pyrex ampoule (35 ml) in the absence of air. The volatile product (0·129 g) was shown by i.r. spectroscopy to be unchanged starting material. When similarly heated at 380 °C for 16 h in a platinum-lined autoclave (15 ml), a sample (0·085 g, 0·41 mmol) of the vinyl compound gave sulphur tetrafluoride and a mixture (0·38 mmol) of perfluorovinylsulphur pentafluoride and unidentified fluorocarbons [analysed by i.r. spectroscopy, which revealed the presence of unsaturated material (C=C str. at 5·63 μm)].

(b) *Photolysis.* Perfluorovinylsulphur pentafluoride (3·15 g, 15·1 mmol), contained in a silica ampoule (250 ml), was irradiated for 500 h with u.v. light from a Hanovia S500 lamp placed 30 cm distant. Fractionation of the volatile product gave a mixture (−196 °C trap; 1·66 g, 17·6 mmol) that was shown by i.r. spectroscopy and hydrolysis with aqueous 40% sodium hydroxide to contain silicon tetrafluoride, thionyl fluoride, sulphuryl fluoride, and sulphur hexafluoride; disulphur decafluoride (−120 °C trap; 0·20 g, 0·78 mmol); and unidentified fluorocarbon material contaminated with disulphur decafluoride (0·13 g). A non-volatile liquid (0·77 g) [Found: C, 21·6; S, 11·9.

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* Relative to external $CF_3\cdot CO_2H$, positive values to high field.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Index Issue.

[13] R. Johnson, Ph.D. Dissertation, University of Florida, Gainsville, U.S.A., 1959. The identification was based upon ^{19}F n.m.r. spectroscopy, but no spectral details were given. This reaction was thought initially to yield only the [2 + 4] product (3; $X = CF_3$) (E. T. McBee, C. G. Hsu, O. R. Pierce, and C. W. Roberts, *J. Amer. Chem. Soc.*, 1955, **77**, 915).

[14] P. D. Bartlett, *Quart. Rev.*, 1970, **24**, 473.

[15] M. G. Barlow, R. R. Dean, and J. Lee, *Trans. Faraday Soc.*, 1969, **65**, 321.

[16] R. E. Banks, R. N. Haszeldine, and W. D. Morton, *J. Chem. Soc.* (*C*), 1969, 1947.

[17] L. H. Cross, G. Cushing, and H. L. Roberts, *Spectrochim. Acta*, 1961, **17**, 344.

Calc. for $(C_2F_8S)_x$: C, 11·5; S, 15·4%], λ_{max} *ca.* 5·6w (C=C str.), 8·2vs (C–F str.), and 11·2vs ($-SF_5$) μm, was recovered from the reaction vessel.

(c) *Radiolysis.* Perfluorovinylsulphur pentafluoride (1·54 g, 7·4 mmol), contained in a Pyrex ampoule (6 ml), was subjected to γ-radiation ($5{\cdot}7 \times 10^5$ rad h^{-1}) for 408 h. Fractionation of the volatile product gave a mixture (−196 °C trap; 0·23 g, 2·53 mmol) of silicon tetrafluoride, thionyl fluoride, and sulphur hexafluoride; pure perfluorovinylsulphur pentafluoride (−120 °C trap; 0·34 g, 1·65 mmol); a mixture (−95 °C trap; 0·12 g, 0·55 mmol) (Found: *M*, 218) of perfluorovinylsulphur pentafluoride (0·43 mmol; total recovery 28%) and disulphur decafluoride (0·12 mmol); and a multi-component [8 g.l.c. peaks (2 m silicone MS550–Celite; 80 °C)] mixture (−76 °C trap; 0·31 g) [Found: C, 13·1; S, 10·9. Calc. for $(C_2F_8S)_x$: C, 11·5; S, 15·4%], showing i.r. absorptions indicative of the presence of C=C, C–F, and SF_5 groups (at *ca.* 5·6w, 8·2vs, and 11·3vs μm, respectively). The oily non-volatile product (0·5 g) (Found: C, 15·5; S, 14·2%) possessed an i.r. spectrum similar to, but more diffuse than, that of the −76 °C fraction.

(d) *With methanol.* Perfluorovinylsulphur pentafluoride (0·94 g) was recovered unchanged after treatment with methanol (0·15 g) at 20 °C for 20 h in a Pyrex ampoule (20 ml). Treatment of the vinyl compound (1·0 g, 4·8 mmol) with sodium methoxide (1·3 mmol) in methanol (4·0 mmol) at 60 °C for 20 h gave a volatile product that was fractionated to yield perfluorovinylsulphur pentafluoride (−196 °C trap; 1·3 mmol, 28% recovery) and a mixture (−45 °C trap; 0·80 g) of 1,2,2-*trifluoro*-2-*methoxyethylsulphur pentafluoride* * and methanol. The −45 °C fraction was stored over sodium for 20 h and then the volatile material was pumped off and shown by elemental analysis (Found: C, 15·3; H, 1·8. $C_3H_4F_8OS$ requires C, 15·0; H, 1·7%) and n.m.r. spectroscopy [15] to be the above methoxy-derivative (0·76 g, 3·17 mmol; 90%), b.p. 73·4 °C (isoteniscope).

(e) *With bromine.* A mixture of perfluorovinylsulphur pentafluoride (1·00 g, 4·80 mmol) and bromine (0·95 g, 5·94 mmol) was stored in a Pyrex ampoule (300 ml) at 20 °C in the dark for 20 days. The product was shaken with mercury to destroy free bromine and then fractionated to give perfluorovinylsulphur pentafluoride (4·68 mmol; 97% recovery) and a trace of 1,2-dibromotrifluoroethylsulphur pentafluoride (identified by i.r. spectroscopy).

U.v. irradiation (Hanovia S500 lamp; distance 30 cm) of a silica ampoule (300 ml) containing perfluorovinylsulphur pentafluoride (7·00 g, 33·6 mmol) and bromine (9·50 g, 59·3 mmol), for 20 h, followed by fractionation, gave a mixture (0·36 g, 3·66 mmol) of silicon tetrafluoride, thionyl fluoride, sulphuryl fluoride, and sulphur hexafluoride; a mixture (0·05 g) (Found: *M*, 91) of sulphur dioxide (0·47 mmol) and disulphur decafluoride (0·08 mmol); and a mixture (−45 °C trap; 12·0 g) which was separated by g.l.c. (2 m DDP–Celite; 100 °C) into 1,2-*dibromo*-1,2,2-*trifluoroethylsulphur pentafluoride* * (calc. yield 11·2 g, 30·4 mmol, 90·5%) (Found: C, 6·7%; *M* 370·5. $C_2Br_2F_8S$ requires C, 6·5%; *M*, 368), b.p. 114 °C at 768 mmHg, $n_D^{20\cdot5}$ 1·3872, d_4^{20} 2·40 (for ^{19}F n.m.r. analysis see ref. 15), and 1,1,2-tribromotrifluoroethane (0·8 g, 2·49 mmol, 7%) (Found: C, 7·7. Calc. for $C_2Br_3F_3$: C, 7·5%) [identified spectroscopically (i.r. and mass) and by debromination to bromotrifluoroethylene (93% yield) with activated zinc dust], b.p. (isoteniscope) 90·0 °C.

Irradiation of a Pyrex ampoule (300 ml) containing perfluorovinylsulphur pentafluoride (0·90 g, 4·32 mmol) and bromine (0·78 g, 4·87 mmol) with light from two tungsten-filament lamps (each 250 W; distance 30 cm) for 2 h gave 4·00 mmol (92·5%) of 1,2-dibromo-1,2,2-trifluoroethylsulphur pentafluoride, 0·09 mmol (2%) of 1,1,2-tribromotrifluoroethane, and traces of silicon tetrafluoride, disulphur decafluoride, and perfluorovinylsulphur pentafluoride.

(f) *With hydrogen bromide.* In a 5 l photochemical reactor of the type described previously,[18] a mixture of perfluorovinylsulphur pentafluoride (3·95 g, 19·0 mmol) and hydrogen bromide (7·8 g, 96·3 mmol) was irradiated with u.v. light for 50 min. Hydrogen (2·19 mmol) was vented from the reactor and the condensible volatile product (10·85 g) was shaken with mercury (to remove free bromine) then fractionated to give a mixture (−196 °C trap; 5·4 g) of silicon tetrafluoride (5·96 mmol), hydrogen bromide (60·5 mmol), sulphuryl fluoride (0·10 mmol), and sulphur hexafluoride (0·18 mmol) (analysed by a combination of i.r. spectroscopy and hydrolysis followed by gravimetric determination of Br^-); a mixture (−120 °C trap; 0·34 g) of perfluorovinylsulphur pentafluoride (0·91 mmol; 5% recovery), disulphur decafluoride (0·40 mmol), and an unknown component (trace) (analysed by g.l.c. and i.r. techniques and *M* determination); and a mixture (−65 °C trap; 5·1 g) of 2-bromo-1,2,2-trifluoroethylsulphur pentafluoride (2·52 g, 8·73 mmol, 48%), 1,2-dibromo-1,1,2-trifluoroethane (0·71 g, 2·93 mmol, 16%), 1,2-dibromotrifluoroethylsulphur pentafluoride (1·16 g, 3·15 mmol, 17·5%), 1,1,2-tribromotrifluoroethane (0·61 g, 1·90 mmol; 10·5%), and an unidentified component (0·14 g) [analysed by g.l.c. (2 m silicone MS550 oil–Celite; 78 °C)]. Samples of 2-*bromo*-1,2,2-*trifluoroethylsulphur pentafluoride* * (Found: C, 8·3; H, 0·3%; *M*, 287. C_2HBrF_8S requires C, 8·5; H, 0·5%; *M*, 289), b.p. (isoteniscope) 75·9 °C, $n_D^{20\cdot5}$ 1·340 (see ref. 15 for n.m.r. data), and 1,2-dibromo-1,1,2-trifluoroethane (Found: C, 9·9; H, 0·5%; *M*, 240. Calc. for $C_2HBr_2F_3$: C, 9·8; H, 0·4%; *M*, 242) were isolated by g.l.c. (21 ft × 3/8 in DDP–Celite; 145 °C); a sample of the latter (0·066 g) was shaken with powdered potassium hydroxide at 20 °C for 30 h to give bromotrifluoroethylene (0·030 g, 68%), characterised by i.r. spectroscopy. A non-volatile liquid (0·5 g) recovered from the reactor showed i.r. absorptions indicative of the presence of water and organic material containing C=C, C–F, and SF_5 groups; aqueous washings from the reactor gave positive tests for F^- and SO_4^{2-}.

No reaction occurred when an equimolar mixture of hydrogen bromide and perfluorovinylsulphur pentafluoride (1·2 mmol of each) was sealed in a Dreadnought glass ampoule (100 ml) and kept in the dark at room temperature for 13 days; the mixture was returned to the vessel and irradiated with light from two tungsten-filament lamps (each 250 W; distance 30 cm) for 10 h, but again no reaction was detected.

(g) *With trifluoroiodomethane.* A mixture of perfluorovinylsulphur pentafluoride (5·13 g, 24·65 mmol) and trifluoroiodomethane (23·6 g, 120·4 mmol), sealed in a vertical silica ampoule (250 ml) with black tape wrapped around the lower end to prevent photolysis of liquid product, was irradiated with u.v. light (Hanovia S500 lamp; distance 30 cm) for 285 h. A black film formed

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[18] A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 1675.

on the inner walls of the vessel and carbon monoxide (2·73 mmol) was formed; the condensible volatile product was shaken with mercury to destroy free iodine then shown by fractionation and analysis of each fraction by g.l.c. and i.r. techniques to comprise trifluoroiodomethane (92·9 mmol, 77% recovery), hexafluoro-1-iodopropylsulphur pentafluoride * (0·91 g, 2·25 mmol; 9%), hexafluoro-1,1-di-iodopropane * (2·10 g, 5·20 mmol; 21%), silicon tetrafluoride (16·6 mmol), thionyl fluoride (8·45 mmol), sulphuryl fluoride (1·27 mmol), and (total 15·7 mmol) sulphur hexafluoride, disulphur decafluoride, hexafluoroethane, trifluoromethylsulphur pentafluoride, and unidentified material. Samples of hexafluoro-1-iodopropylsulphur pentafluoride [98% pure by g.l.c.; extrapolated b.p. (isoteniscope) 98·7 °C] (Found: C, 9·2. Calc. for $C_3F_{11}IS$: C, 8·9%), $\lambda_{max.}$ (hexane) 284 nm (ε 230) (see ref. 15 for n.m.r. data), and hexafluoro-1,1-di-iodopropane (96% pure by g.l.c.), extrapolated b.p. (isoteniscope) 131·9 °C, δ_F (56·46 MHz; ext. $CF_3\cdot CO_2H$, high field shifts designated positive) −4·3 (CF_3, d), +7·1 (CF, t of q), and +31·0 (CF_2, d), $\lambda_{max.}$ (hexane) 305—307 nm (ε 1020), were isolated by g.l.c. (2 m DDP–Celite; 120 °C). Fractionation of the product obtained by irradiation of a vigorously shaken silica ampoule (*ca.* 5 ml) containing mercury (5·4 g) and 96% pure hexafluoro-1,1-di-iodopropane (0·099 g) with u.v. light from a Hanovia S500 lamp (distance 30 cm) gave perfluorohex-3-ene (0·025 g, 68%), identified spectroscopically (i.r. and mass).

(h) *With bromine monochloride.* A Dreadnought glass ampoule (175 ml) containing a mixture of perfluorovinylsulphur pentafluoride (5·2 g, 25 mmol), bromine (4·0 g, 25 mmol), chlorine (1·77 g, 25 mmol), and dichloromethane (11·3 g) was stored in the dark at 0 °C for 2 days then at 20 °C for 14 days. The product was shaken with mercury to destroy free halogens then fractionated; analysis of the fractions by standard g.l.c. and i.r. techniques revealed that the composition of the product was: $CF_2{:}CF\cdot SF_5$ (21·8 mmol, 87% recovery), $CF_2Br\cdot CFCl\cdot SF_5$ (0·31 mmol, 9·5% based on perfluorovinylsulphur pentafluoride consumed), $CF_2Cl\cdot CFCl\cdot SF_5$ (0·04 mmol, 1%), $CF_2Cl\cdot CFBr\cdot SF_5$ (0·21 mmol, 6·5%), $CF_2Br\cdot CFBr\cdot SF_5$ (1·99 mmol, 62%).

A reaction between perfluorovinylsulphur pentafluoride (2·01 g, 9·67 mmol), bromine (1·45 g, 9·07 mmol), and chlorine (0·606 g, 8·54 mmol) at 80 °C for 22 h in a Dreadnought ampoule (100 ml) gave the following products: $CF_2{:}CF\cdot SF_5$ (4·60 mmol, 48% recovery), $CF_2Br\cdot CFCl\cdot SF_5$ (0·67 mmol, 13%), $CF_2Cl\cdot CFCl\cdot SF_5$ (0·07 mmol 1%), $CF_2Cl\cdot CFBr\cdot SF_5$ (0·78 mmol, 15%), $CF_2Br\cdot CFBr\cdot SF_5$ (2·60 mmol, 51%), $CF_2Br\cdot CFBrCl$ (0·18 mmol, 3·5%), $CF_2Br\cdot CFBr_2$ (0·28 mmol, 5·5%), SOF_2 (0·20 mmol), and SiF_4 (0·56 mmol). The material which condensed in a −45 °C trap when the product was fractionated was subjected to preparative g.l.c. (21 ft × 3/8 in DDP–Celite; 140 °C) to yield a 46 : 54 molar mixture (Found: C, 7·6%; *M*, 317. Calc. for C_2BrClF_8S: C, 7·4%; *M*, 323·5) of 2-bromo-1-chloro-1,2,2-trifluoroethylsulphur pentafluoride and 1-bromo-2-chloro-1,2,2-trifluoroethylsulphur pentafluoride (see ref. 15 for n.m.r. data).

(i) *With butadiene.* A mixture of perfluorovinylsulphur pentafluoride (1·90 g, 9·13 mmol), butadiene (0·51 g, 9·44 mmol), and terpene B (0·05 g) was heated at 190 °C for 22 h in a Pyrex ampoule (250 ml). The volatile product was fractionated to give a mixture (−196 °C trap) of perfluorovinylsulphur pentafluoride (1·46 g, 7·02 mmol, 77% recovery) and butadiene (0·36 g, 6·67 mmol, 71% recovery), and a mixture (−65 °C trap; 0·57 g) shown by g.l.c. (2 m silicone oil–Celite; 100 °C) to contain 1,1,2-trifluoro-*r*-2-pentafluorothio-*t*-3-vinylcyclobutane (2; $X = SF_5$) (0·25 g, 0·95 mmol, 35% based on $CF_2{:}CF\cdot SF_5$ consumed), 1,1,2-trifluoro-*r*-2-pentafluorothio-*c*-3-vinylcyclobutane (1; $X = SF_5$) (0·25 g, 0·95 mmol, 35%), 4-vinylcyclohex-1-ene (0·05 g, 0·48 mmol, 35% based on C_4H_6 consumed), and two unidentified components (0·02 g). A 99% pure sample of the trans-*adduct* (2) * (Found: C, 27·7; H, 2·3. $C_6H_6F_8S$ requires C, 27·5; H, 2·3%), b.p. 120 °C, and a 9 : 1 mixture of the *cis*- and *trans*-adducts * were isolated by g.l.c. (21 ft × 3/8 in DDP–Celite; 130 °C) for spectroscopic (i.r. and n.m.r.) analysis.

The reaction was repeated at 140 °C for 50 h, at 160 °C for 95 h, and at 195 °C for 90 h; the respective yields of *cis*- and *trans*-adducts (% conversion of $CF_2{:}CF\cdot SF_5$ in parentheses) were: 46, 50 (4); 43, 46 (58); and 47, 48 (86).

(j) *Copolymerization.* A thick-walled Dreadnought tube (*ca.* 100 ml) was charged with a solution of sodium persulphate (0·5 g), tetrasodium pyrophosphate (0·5 g), and perfluoro-octanoic acid (0·25 g) in deoxygenated water (50 ml). The tube was cooled to −72 °C (intermittent agitation prevented the solution from freezing into a solid block and so causing the tube to crack) and the contents were freed from oxygen by three thaw–pump–freeze cycles, in which the frozen solution was allowed to thaw and then the tube was pressurised to 1 atm with oxygen-free nitrogen, evacuated, and recooled to −72 °C. During the second cycle and when the tube contained a nitrogen atmosphere, a solution of sodium sulphite heptahydrate (0·5 g) in the minimum quantity of deoxygenated water was added to the initiation system. Finally, the tube was cooled to −196 °C to allow the introduction of perfluorovinylsulphur pentafluoride (2·31 g, 11·1 mmol) and vinylidene fluoride (2·13 g, 33·3 mmol), sealed, and placed in a stout steel guard tube that was subsequently pressurised to *ca.* 8 atm with nitrogen, sealed, and agitated by end-over-end rotation for 20 h on a wheel rotating in a hot (85 °C) water tank. Fractionation of the gaseous product gave vinylidene fluoride (0·08 g, 1·27 mmol, 4% recovery) and perfluorovinylsulphur pentafluoride (0·39 g, 1·92 mmol, 17% recovery). Filtration of the aqueous product gave white elastomeric crumbs of copoly(perfluorovinylsulphur pentafluoride–vinylidene fluoride) * (3·0 g, 68%) (Found: C, 26·0; H, 1·9%), $\lambda_{max.}$ (film cast from Me_2CO soln.) 11·53vs,br (diagnostic for SF_5 [17]) µm.

Reactions of 1,2-*Dibromo*-1,2,2-*trifluoroethylsulphur Pentafluoride*.—(a) *With copper.* The dibromide (0·11 g, 0·30 mmol) was passed at *ca.* 3 mmHg during 30 min through a silica tube (100 × 1 cm), the central portion (50 cm) of which contained a layer of copper powder (25 g) and was heated to 188 °C. Fractionation of the product gave 1,2-dibromo-1,2,2-trifluoroethylsulphur pentafluoride (−65 °C trap; 0·05 g, 44% recovery), perfluorovinylsulphur pentafluoride (−120 °C trap; 0·03 g, 0·14 mmol, 88% based on $CF_2Br\cdot CFBr\cdot SF_5$ consumed), and a mixture (−196 °C trap; 0·03 mmol) of bromotrifluoroethylene and thionyl fluoride.

(b) *With aluminium bromide.* 1,2-Dibromotrifluoroethylsulphur pentafluoride (0·183 g, 0·497 mmol) and aluminium tribromide (4·0 g) were left in an evacuated Pyrex ampoule (25 ml) at 20 °C for 21 h in the dark. The volatile product was shaken with mercury, to destroy free bromine, then fractionated to give pure [analysed by g.l.c. and spectroscopic methods (i.r. and mass)] 1,2-dibromotetrafluoroethane (−120 °C trap; 0·076 g, 0·292 mmol, 59%) (Found: C, 9·8%; *M*, 259·5. Calc. for $C_2Br_2F_4$: C, 9·7%; *M*, 258).

(c) *Photolysis.* The dibromide (0·53 g, 1·44 mmol), contained in a silica ampoule (300 ml), was irradiated with u.v. light (Hanovia S500 lamp; distance 60 cm) for 20 h. An unidentified noncondensible product (*ca.* 0·1 mmol) was removed, and the condensible volatile product was shaken with mercury (to destroy traces of free bromine) then fractionated, to give a mixture (−72 °C trap; 0·245 g; analysed by g.l.c. and i.r. spectroscopy) of 1,2-dibromotrifluoroethylsulphur pentafluoride (0·01 g, 0·03 mmol, 2% recovery), 1,1,2-tribromotrifluoroethane (0·22 g, 0·69 mmol, 49% based on $CF_2Br\cdot CFBr\cdot SF_5$ consumed), and four unidentified components (total 0·015 g); disulphur decafluoride (−95 °C trap; 0·054 g, 0·22 mmol) (Found: *M*, 247. Calc. for $F_{10}S_2$: *M*, 254), with a correct i.r. spectrum; and a mixture (−196 °C trap; 0·173 g, 1·76 mmol) shown by a combination of g.l.c., i.r. spectroscopy, and hydrolysis to comprise silicon tetrafluoride (0·76 mmol), thionyl fluoride (0·74 mmol), sulphuryl fluoride, disulphur decafluoride, sulphur hexafluoride, and bromotrifluoromethane.

The reaction was repeated (0·44 g $CF_2Br\cdot CFBr\cdot SF_5$; 300 ml silica tube; Hanovia S500 lamp 30 cm distant; time 45 min) in the presence of mercury (5 g), with agitation of the vessel; the product comprised $CF_2Br\cdot CFBr\cdot SF_5$ (0·84 mmol, 70% recovery), $CF_2{:}CF\cdot SF_5$ (0·24 mmol, 67% based on dibromide consumed), S_2F_{10} (0·03 mmol), SiF_4, SOF_2, and SF_6.

Irradiation (Hanovia u.v. S500 lamp; distance 60 cm) for 24 h of a mixture of 1,2-dibromotrifluoroethylsulphur pentafluoride (0·30 g, 0·81 mmol) and bromine (0·3 g, 1·9 mmol) sealed in a silica tube (300 ml) gave $CF_2Br\cdot CFBr_2$ (0·78 mmol, 96%), SO_2 (0·22 mmol, 27%), S_2F_{10} (0·01 mmol), SiF_4, SOF_2, SO_2F_2, and SF_6 (total 1·05 mmol.)

*Reactions of 2-Bromo-*1,2,2-*trifluoroethylsulphur Pentafluoride.*—(a) *Dehydrobromination.* Treatment of 2-bromo-1,2,2-trifluoroethylsulphur pentafluoride (0·059 g, 0·204 mmole) with powdered potassium hydroxide (3 g) at 20 °C for 90 h in a Pyrex ampoule (5 ml) gave, as the sole gaseous product, perfluorovinylsulphur pentafluoride (0·029 mmol, 14%), identified by i.r. spectroscopy and g.l.c.

(b) *With hydrogen bromide.* A mixture of 2-bromo-1,2,2-trifluoroethylsulphur pentafluoride (0·234 g, 0·810 mmol) and hydrogen bromide (0·18 g, 2·22 mmol), sealed in a silica ampoule (300 ml), was irradiated for 18 h with u.v. light from a Hanovia S500 lamp placed 30 cm distant. Hydrogen (0·29 mmol) was removed from the product and the condensible volatile material was shaken with mercury (to destroy free bromine) then fractionated to give a mixture (−72 °C trap; 0·72 mmol) shown by i.r. spectroscopy and g.l.c. to comprise 1,2-dibromo-1,1,2-trifluoroethane (0·16 g, 0·66 mmol, 81·5%), 1,1,2-tribromotrifluoroethane (0·01 g, 0·03 mmol, 4%) and a trace of an unidentified component; and a mixture (−196 °C trap; 0·10 g) shown by i.r. spectroscopy and hydrolysis with water and aqueous 40% sodium hydroxide to contain silicon tetrafluoride (0·91 mmol), hydrogen bromide (trace), thionyl fluoride, sulphuryl fluoride, and unidentified material.

Reaction of Perfluoropropene with Butadiene.—A mixture of perfluoropropene (3·14 g, 20·9 mmol), butadiene (1·13 g, 20·9 mmol), and terpene B (0·05 g) was heated at 180 °C for 70 h in a Pyrex ampoule (250 ml). Fractionation of the product gave a mixture (−196 °C trap; 11·69 mmol) (Found: *M*, 132) shown by i.r. spectroscopy to comprise perfluoropropene (1·42 g, 9·47 mmol, 45% recovery) and butadiene (0·12 g, 2·22 mmol); and a volatile liquid (−45 °C trap; 2·64 g) that was shown by a combination of analytical g.l.c. (2 m DNP–Celite; 100 °C), preparative g.l.c. (21 ft × 3/8 in DDP–Celite; 120 °C), and i.r. and n.m.r. spectroscopy to comprise 1,1,2-*trifluoro*-r-2-*trifluoromethyl*-t-3-*vinylcyclobutane* * (1·12 g, 5·64 mmol, 49% based on C_3F_6 consumed) (Found: C, 41·4; H, 2·8. $C_7H_6F_6$ requires C, 41·2; H, 3·0%), b.p. 94·4 °C (isoteniscope), 1,1,2-*trifluoro*-r-2-*trifluoromethyl*-c-3-*vinylcyclobutane* * (0·89 g, 4·36 mmol, 38% based on C_3F_6 consumed) (Found: C, 41·0; H, 2·8%), b.p. 80·4 °C (isoteniscope), 4-vinylcyclohex-1-ene (0·53 g, 4·91 mmol, 52·5% based on C_4H_6 consumed), and 4,4,5-trifluoro-5-(trifluoromethyl)-cyclohexene * (0·10 g, 0·49 mmol, 4% based on C_3F_6 consumed) with an unsatisfactory carbon analysis (Found: C, 42·2; H, 3·2; F, 56·1%; M^+, 204. $C_7H_6F_6$ requires C, 41·2; H, 3·0; F, 55·9%; *M*, 204).

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