# Polyfluorocarbanion Chemistry. Part IV.[1] Some Reactions of 2H- and 1H-Pentafluoropropene with Nucleophiles

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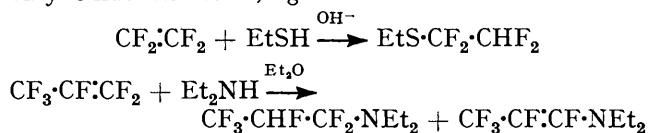
2H-Pentafluoropropene reacts with sodium methanethiolate in ether to give cis-1,3,3,3-tetrafluoroprop-1-enyl methyl sulphide: sodium thiophenolate or sodium 1,1-dimethylethanethiolate similarly give mainly the corresponding cis-tetrafluoropropenyl sulphides. but small amounts of the corresponding trans-isomers and the 1,1,3,3,3-tetrafluoroprop-2-enyl sulphides are also formed. In contrast dimethylamine in ether gives a mixture of NN-dimethyl-1,1,3,3,3-pentafluoropropylamine and trans-NN-dimethyl-1,3,3,3-tetrafluoroprop-1-enylamine. Reaction of the propene with sodium methanethiolate or 1,1-dimethylethanethiolate in the presence of the respective thiols gives mixtures of the three tetrafluoropropenyl alkyl sulphides and the 1,1,3,3,3-pentafluoropropyl alkyl sulphide. 1H-Pentafluoropropene (95% cis-isomer) reacts with sodium methoxide in methanol or m-xylene. sodium methanethiolate in methanethiol or m-xylene, and dimethylamine to give the corresponding trans-2,3,3,3-tetrafluoroprop-1-enyl compounds as the exclusive products.

REPLACEMENT in a fluoro-olefin of vinylic hydrogen by fluorine or, more particularly, by perfluoroalkyl leads to increased susceptibility to nucleophilic attack, e.g.

$$CH_2{:}CF_2 < CHF{:}CF_2 < CF_2{:}CF_2 < R_FCF{:}CF_2 < (R_F)_2C{:}CF_2$$
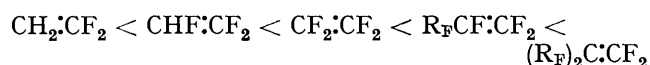
particularly when a terminal difluoromethylene group is present. The products arise by addition across the double bond, by substitution of vinylic fluorine atoms by an addition–elimination mechanism, by substitution of allylic fluorine atoms by the S_N2' mechanism, or by a combination of these various reactions. Halide ion attack has shown how product depends on the structure of the particular olefin.[2]
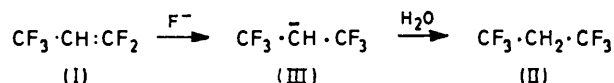
Nucleophilic attack by thiols and secondary amines generally results in mixtures of products arising from addition to the double bond and/or substitution of vinylic fluorine atoms, e.g.[3]

$$CF_2{:}CF_2 + EtSH \xrightarrow{OH^-} EtS{\cdot}CF_2{\cdot}CHF_2$$

$$CF_3{\cdot}CF{:}CF_2 + Et_2NH \xrightarrow{Et_2O}$$
$$CF_3{\cdot}CHF{\cdot}CF_2{\cdot}NEt_2 + CF_3{\cdot}CF{:}CF{\cdot}NEt_2$$

There is a brief report that alkanethiolates in aprotic media yield unsaturated sulphides.[4]

absence and presence of methanethiol, and dimethylamine have now been investigated.

2H-*Pentafluoropropene.*—Reaction with a slight excess of caesium fluoride in moist tetramethylene sulphone at 75 °C gave the expected 1,1,1,3,3,3-hexafluoropropane (II) (81%), presumed to be formed via the carbanion (III).

$$CF_3{\cdot}CH{:}CF_2 \xrightarrow{F^-} CF_3{\cdot}\bar{C}H{\cdot}CF_3 \xrightarrow{H_2O} CF_3{\cdot}CH_2{\cdot}CF_3$$
$$\text{(I)} \qquad\qquad \text{(III)} \qquad\qquad \text{(II)}$$

Reaction of olefin (I) with a ca. 3 molar excess of dimethylamine in ether at −78 °C gave a mixture of dimethyl-1,1,3,3,3-pentafluoropropylamine (IV) (25%) and trans-dimethyl-1,3,3,3-tetrafluoropropenylamine (V) (42%) in the ratio 37 : 63 (n.m.r.) which could not be separated by g.l.c.

$$CF_3{\cdot}CH_2{\cdot}CF_2{\cdot}NMe_2$$
$$\text{(IV)}$$

(V structure drawing)

(V)
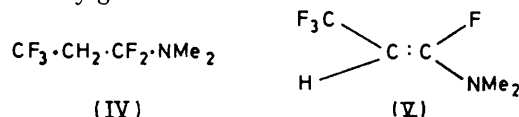
The preferred stereochemistry of olefin (V) is discussed later.

The reactions of olefin (I) with sodium methanethiolate, t-butanethiolate, and thiophenolate in ether or

Reaction of 2H-pentafluoropropene with nucleophiles (RS⁻)

R in RS⁻	Solvent	Ratio RS⁻ : (I)	Temp. (°C)	Time (h)	Recovered (I) (%)	(VI)	(VII)	(VIII)	(IX)
Me	Et₂O	1.66 : 1	22	2.5	Trace	40			
Me	MeSH	0.31 : 1	22	90	10	68	13	2	8
Buᵗ	Et₂O	0.84 : 1	22	3	26	46	17	7	
Buᵗ	BuᵗSH	0.90 : 1	22	6.5	14	51	15	7	4
Ph	Et₂O	0.90 : 1	65	24	17	45	6	ca. 1	*

* Two unidentified products (ca. 5%) also formed.

The reactions of (i) 2H-pentafluoropropene (I) with fluoride ion, alkanethiolates in the absence and presence of the corresponding thiol, sodium thiophenolate, and dimethylamine and (ii) 1H-pentafluoropropene with fluoride ion, sodium methoxide in the absence and presence of methanol, sodium methanethiolate in the

the corresponding thiol as solvent are summarised in the Table.

The structures of the products were determined by n.m.r. spectroscopy since in certain cases it was not possible to separate product mixtures into their components by g.l.c. The relevant n.m.r. chemical shifts and coupling constants are available in the Supplementary

[1] Part III, C. J. Drayton, R. N. Haszeldine, and W. T. Flowers, *J.C.S. Perkin I*, 1975, 1035.

[2] W. T. Miller and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 4164; 4170; J. H. Fried and W. T. Miller, *ibid.*, 1959, **81**, 2078; J. H. Fried, H. Goldwhite, and W. T. Miller, *ibid.*, 1960, **82**, 3091.

[3] I. L. Knunyants and A. V. Fokin, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1952, 261; I. L. Knunyants, L. S. German, and B. L. Dyatkin, *ibid.*, 1956, 1353.

[4] Ger. P. 1,069,143/1959.

Publication (see Experimental section). The *cis*- and *trans*-olefins (VI) and (VII), respectively, were differentiated by (*a*) the magnitude of the vicinal H,F coupling [$J_{2.3}$ *trans* (26.2—31.4 Hz) $> J_{2.3}$ *cis* (11.3—14.7 Hz)] and (*b*) the magnitude of the CF_3,F coupling [$J_{1.2}$ *cis* (16.0—17.1) $> J_{1.2}$ *trans* (12.8—15.2 Hz)]. The olefins (VIII; R = Bu^t or Ph) were identified by the presence
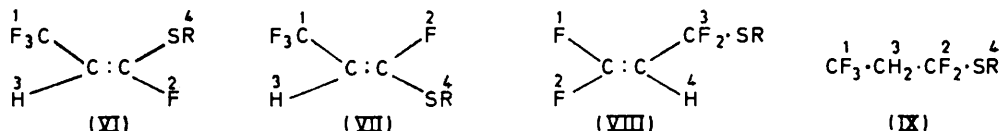

in the ^{19}F n.m.r. spectra of three absorptions (ratio 1 : 1 : 2) with the chemical shifts expected for two vinylic fluorine atoms and an allylic CF_2 group; the observed couplings showed that the group $CF_2 \cdot CH \cdot CF_2$ was present. The saturated products (IX; R = Me or Bu^t) were identified by the presence of two ^{19}F absorptions in the ratio 3 : 2 and the observed coupling constants and chemical shifts which were consistent with the presence of a $CF_3 \cdot CH_2 \cdot CF_2$ grouping.

Reactions with thiol as solvent gave higher yields of products (77—91%) than those carried out in ether (40—70%) when intractable solid coated the reaction tubes. All the reactions, irrespective of solvent, gave the *cis*-olefin (VI) as the major product.

$$RS^- + (I) \longrightarrow RS \cdot CF_2 \cdot \bar{C}H \cdot CF_3 \xrightarrow{-F^-} RS \cdot CF \dot{:} CH \cdot CF_3$$
$$(X)$$
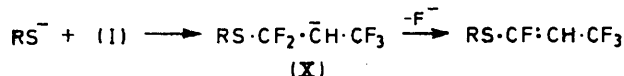
If elimination of fluoride ion from the presumed intermediate carbanion (X) requires the orbital on carbon containing the lone pair of electrons and the fluorine atom to be eliminated as fluoride to have maximum separation, *i.e.* to be *trans*, then (Xa) and (Xb) are possible intermediates, with (Xa) preferred since *cis*-olefin (VI) is produced. On steric grounds
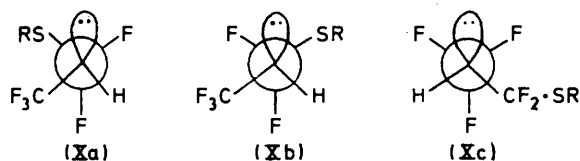
(Xa) would be expected to be less stable than (Xb) because the bulky CF_3 and SR groups are *gauche*. However, conformer (Xb) has two *gauche* CF_3,F arrangements while conformer (Xa) has only one such arrangement and it is possible that electronic *gauche* CF_3,F interactions render conformer (Xb) less favourable than conformer (Xa).

When R in the RS group is small, *i.e.* Me, the *cis*-olefin (VI) is formed exclusively, but with larger R groups, Ph and Bu^t, the *cis* (VI) : *trans* (VII) olefin ratios are 5.7 : 1 and 2.7 : 1, respectively, suggesting that as the R becomes more bulky conformer (Xb) becomes more favoured because of the *gauche* SR and CF_3 steric interaction in conformer (Xa).

The presence of olefins of type (VIII) in the products

may also be attributed to steric effects since the proportion of this product is 0, *ca.* 1, and 7% for R = Me, Ph, and Bu^t, respectively. The probable conformation from which elimination (presumed *trans*) takes place to give olefin (VIII) is (Xc), the steric requirements of which are less than for conformer (Xa), but the presence of two *gauche* F,CF_2 interactions in conformer (Xc) is

possibly the reason why this conformer is less favoured than conformer (Xa).

The reaction of the olefin (I) with sodium 1,1-dimethylethanethiolate in 1,1-dimethylethanethiol gave the saturated sulphide (IX; R = Bu^t) (4%) and a mixture of olefins (VI—VIII; R = Bu^t) in a similar ratio to that observed from reaction in ether. This suggests that the olefinic products arise mainly from the carbanion (X) by loss of fluoride ion, although an *E*2 elimination of hydrogen fluoride from the saturated adduct (IX) cannot be ruled out.

The reaction of olefin (I) with sodium methanethiolate in methanethiol was carried out with a deficiency of thiolate relative to olefin (0.31 : 1.0), *i.e.* conditions conducive to the formation of the saturated adduct (IX; R = Me). However, only a low yield of this product (8%) was observed and the major products were the olefins (VI—VIII; R = Me). Since the reaction of olefin (I) with sodium methanethiolate in ether gave only the *cis*-olefin (VI; R = Me), it is suggested that the *trans*-olefin (VII; R = Me) formed in 13% yield arises by an *E*2 dehydrofluorination of the saturated adduct (IX; R = Me), while the *cis*-olefin (VI; R = Me) is formed by loss of fluoride ion from the carbanion (X; R = Me).
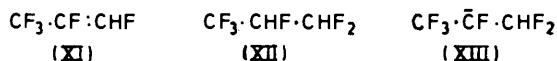
This is supported by the dimethylamine reaction, which gave a mixture of the saturated adduct (IV) and the *trans*-olefin (V); the latter could be formed by dehydrofluorination (*E*2) of the saturated conformer
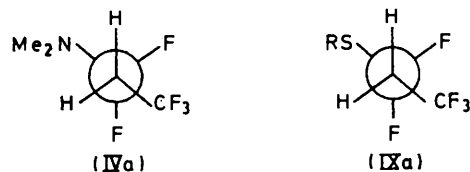
(IVa). It is thus suggested that the preferred conformation of the carbanion (X) is (Xa) and the preferred conformation of the saturated thiol adducts (IX) is (IXa).

1H-*Pentafluoropropene*.—Attempted reaction of (XI), a 95 : 5 mixture of the *cis*- and *trans*-isomers, with caesium fluoride in moist tetramethylene sulphone at room temperature or at 90 °C gave none of the expected hydrogen fluoride adduct (XII) and the olefin was recovered quantitatively. In order to determine if initial fluoride addition to the olefin had taken place the

reaction was repeated at 90 °C using a 40 : 60 mixture of the *cis*- and *trans*-olefin isomers. Again the olefin was recovered quantitatively, but the isomer ratio had changed to 83 : 17 (*cis* : *trans*). This result indicates that initial fluoride ion addition to the olefin does take place, but the intermediate carbanion (XIII) so formed eliminates fluoride ion rather than abstract a proton from the water present to give the adduct (XII); this adduct (XII) is only dehydrofluorinated to the olefin (XI) under relatively severe conditions (conc. NaOH aq. at 150 °C).[5]

$$\text{CF}_3\cdot\text{CF:CHF} \qquad \text{CF}_3\cdot\text{CHF}\cdot\text{CHF}_2 \qquad \text{CF}_3\cdot\bar{\text{C}}\text{F}\cdot\text{CHF}_2$$
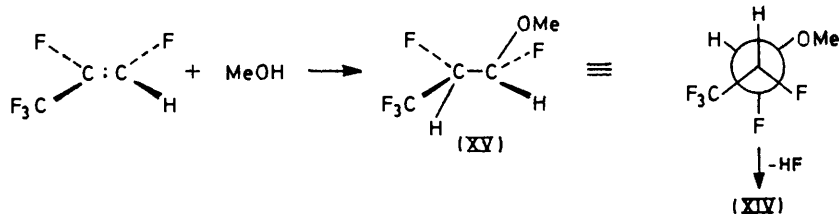$$\text{(XI)} \qquad\qquad\quad \text{(XII)} \qquad\qquad \text{(XIII)}$$

The ready isomerisation of *trans* (XI) to *cis* (XI) suggests that the latter isomer is more thermodynamically stable, a result which is in agreement with the observation that dehydrofluorination of compound (XII) affords the olefin (XI) as a 95 : 5 mixture of the *cis*- and *trans*-isomers.
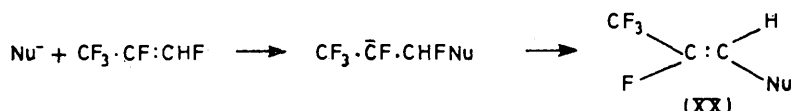
The above results are in sharp contrast to those with 2*H*-pentafluoropropene.

Attempted fluoride-ion-catalysed additions of carbonyl fluoride and perfluoro-1,3,5-triazine to the olefin (XI) were unsuccessful in that the olefin was recovered unchanged; hexafluoropropene, however, readily undergoes such catalysed additions under comparable conditions.[6,7]

It has been reported[8] that the olefin (XI) (95% *cis*-isomer) on reaction with a solution of potassium hydroxide in methanol at 0—5 °C afforded a mixture of the *trans*-ether (XIV) and the 1 : 1 adduct (XV) in the ratio 76 : 24, but the two compounds could not be separated by distillation. In the present work the reaction of the olefin (XI) (95% *cis*-isomer) with potassium hydroxide in methanol at 22 °C gave a mixture of the *trans*-olefin (XIV) (63%), the 1 : 1 adduct (XV)

(XIV) (86%) was the only product detected when (IX) reacted with sodium methoxide in *m*-xylene at 80 °C.

$$\text{CF}_3\cdot\text{CHF}\cdot\text{CHF}\cdot\text{OMe}$$
$$\text{(XV)}$$
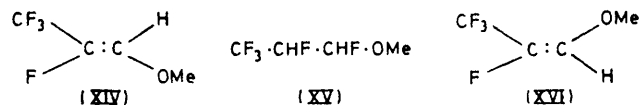
Similarly the reaction of the olefin (XI) with sodium methanethiolate in methanethiol or in *m*-xylene at 80 °C gave only methyl *trans*-2,3,3,3-tetrafluoroprop-1-enyl sulphide (XVII) (83 and 70%, respectively).

The reaction of dimethylamine with the olefin (XI) in ether occurred readily on warming from −78 °C to room temperature to afford the unsaturated *trans*-amine (XVIII) (89%) as the exclusive product.
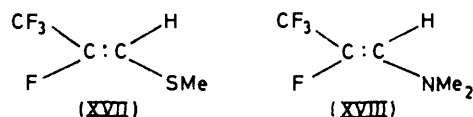
The olefins (XVII) and (XVIII) were identified as the *trans*-isomers on the basis of the observed vinylic H,F coupling constants (*ca.* 30 Hz).

The stereochemistry (*trans*) of the unsaturated ether (XIV) obtained from treatment of olefin (XI) with a solution of potassium hydroxide in methanol was explained[8] on the basis of a *cis*-addition of the alcohol to the olefin (mainly *cis*-isomer) followed by a *trans*-elimination of hydrogen fluoride from the resultant adduct (XV) with its vicinal CHF groups (Scheme). The instability of the CHF·CHF grouping would similarly explain why olefin (XI) with sodium methoxide in methanol and sodium methanethiolate in methanethiol gave only unsaturated products. However, since the reaction of the olefin (XI) with dimethylamine at relatively low temperature also gave only an unsaturated

<div align="center">SCHEME</div>

(18%), and the *cis*-olefin (XVI) (1.5%). Sodium methoxide in methanol required 80 °C for reaction, and the exclusive product was the *trans*-olefin (XIV) (88%);

product (XVIII), an alternative explanation is that in these three reactions the saturated 1 : 1 adducts are never formed, since the intermediate carbanions (XIX) preferentially lose fluoride to give (XX). Methoxide or
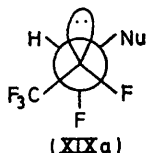
[5] D. Sianesi and R. Fontanelli, *Ann. Chim. (Italy)*, 1965, **55**, 850.
[6] F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Amer. Chem. Soc.*, 1962, **84**, 4275.

[7] R. L. Dresler and J. A. Young, *J. Org. Chem.*, 1967. **32**, 2004.
[8] R. Fontanelli, G. Paschetta, M. Tacchi Venturi, and D. Sianesi, *Ann. Chim. (Italy)*. 1969, **59**. 211.

methanethiolate reaction in *m*-xylene also involves (XIX) ⟶ (XX), possibly *via* (XIXa).

(XIXa)

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a vacuum system to avoid contamination with air or moisture. Reactions were carried out *in vacuo* in sealed Pyrex ampoules (100 or 300 ml), and the results reported are usually the averages of several experiments. Products were separated by fractional condensation *in vacuo* or by g.l.c. [Pye model 104 or Perkin-Elmer F 21 machines; columns packed with Celite impregnated with dinonyl phthalate (DNP) or silicone SE30 oil (10%) and suitably calibrated for quantitative work]; they were identified by molecular weight determination (Regnault's method), elemental analysis, i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer fitted with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60.0 MHz for ^{1}H and 56.46 MHz for ^{19}F or a Varian HA-100 instrument operating at 100.0 MHz for ^{1}H and 94.1 MHz for ^{19}F and using tetramethylsilane as internal reference for ^{1}H and trifluoroacetic acid as external reference for ^{19}F), and mass spectrometry (A.E.I. MS 902 machine). Product analysis by n.m.r. was based on *ca*. 10 integrations. Spectroscopic data are available as Supplementary Publication No. SUP 21417 (11 pp.).*

2*H*-Pentafluoropropene was prepared (90%) by dehydroiodination with potassium hydroxide *in vacuo* of the 1 : 1 adduct, 1,1,1,3,3-pentafluoro-3-iodopropane, from the reaction of trifluoroiodomethane with 1,1-difluoroethylene.[9] 1*H*-Pentafluoropropene[5] was prepared in 76% overall yield by hydrogenation of hexafluoropropene followed by dehydrofluorination of the resultant hexafluoropropane with aqueous potassium hydroxide. The olefin as prepared was a 95 : 5 mixture of *cis*- and *trans*-isomers and was used as such unless stated to the contrary.

Reactions of 2H-Pentafluoropropene.—(a) *With caesium fluoride*. The olefin (1.09 g, 8.3 mmol) and caesium fluoride (0.14 g, 9.0 mmol) in moist tetramethylene sulphone (6 ml), at 75° (20 h), gave a fraction (0.99 g; *M* 145) shown by g.l.c. (3 m DNP at 22 °C) to contain three components (ratio 95 : 3 : 2) and from which the major component was separated and identified as 1,1,1,3,3,3-hexafluoropropane (0.98 g, 6.5 mmol, 81%) (Found: *M*, 154. Calc. for $C_3H_2F_6$: *M*, 152) by a comparison of its n.m.r. spectra with those reported[10] and by mass spectrometry.

(b) *With dimethylamine*. A mixture of the olefin (1.16 g, 8.8 mmol) and dimethylamine (1.15 g, 24.8 mmol) in ether (5 ml), at −78 °C (2 h), gave (i) a mixture (3.41 g) of ether and unchanged dimethylamine and (ii) a higher boiling fraction (0.97 g) which gave only one peak on g.l.c. (2 m DNP at 56—90 °C) but which was shown by ^{19}F n.m.r. spectroscopy to be a 37 : 63 mixture of *NN*-dimethyl-1,1,3,3,3-pentafluoropropylamine (0.39 g, 2.2 mmol, 25%) and *trans-NN*-dimethyl-1,3,3,3-tetrafluoroprop-1-enylamine (0.58 g, 3.7 mmol, 42%). Attempted isolation of pure

components of the mixture by g.l.c. (6 m DNP at 55 °C) was unsuccessful.

(c) *With sodium methanethiolate in ether*. A mixture of the olefin (1.29 g, 9.2 mmol) and sodium methanethiolate (1.07 g, 15.3 mmol) in ether (5 ml), at 22 °C (2.5 h), gave unchanged olefin (trace) and *methyl* cis-1,3,3,3-*tetrafluoroprop*-1-*enyl sulphide* (0.59 g, 3.7 mmol, 40%) (Found: C, 30.2; H, 2.8; F, 47.4%; *M*, 160. $C_4H_4F_4S$ requires C, 30.0; H, 2.5; F, 47.5%; *M*, 160), b.p. (Siwoloboff) 96.0 °C. An attempted reaction at −78 °C gave only unchanged reactants.

(d) *With sodium methanethiolate in methanethiol*. A mixture of the olefin (2.37 g, 17.9 mmol) and sodium methanethiolate (0.39 g, 5.7 mmol) in methanethiol (6.4 g), at 22 °C (90 h), gave unchanged olefin (0.23 g, 1.7 mmol, 10% recovered), unchanged methanethiol (5.16 g), and a higher-boiling fraction (2.37 g) which was separated by g.l.c. (10 m SE30 at 90 °C) into its four components identified as (i) methyl 1,1,3,3-tetrafluoroprop-2-enyl sulphide (0.04 g, 0.3 mmol, 2%), M^+ 160 ($C_4H_4F_4S$); (ii) methyl 1,1,3,3,3-pentafluoropropyl sulphide (0.24 g, 1.3 mmol, 8%), M^+ 180 ($C_4H_5F_5S$); (iii) *methyl* trans-1,3,3,3-*tetrafluoroprop*-1-*enyl sulphide* (0.33 g, 2.1 mmol, 13%) (Found: C, 29.4; H, 2.8%; M^+, 160); and (iv) methyl *cis*-1,3,3,3-tetrafluoroprop-1-enyl sulphide (1.76 g, 11.0 mmol, 68%).

(e) *With sodium 1,1-dimethylethanethiolate in ether*. A mixture of the olefin (1.73 g, 13.0 mmol) and sodium 1,1-dimethylethanethiolate (1.22 g, 10.9 mmol) in ether (10 ml), at 22 °C (3 h), gave unchanged olefin (0.45 g, 3.4 mmol, 26% recovered) and a higher-boiling fraction (1.35 g, 6.7 mmol, 70%) (Found: C, 41.7; H, 5.1. Calc. for $C_7H_{10}F_4S$: C, 41.5; H, 4.95%) which was resolved into two peaks by g.l.c. (2 m DNP at 90 °C) but was shown to contain three components (by n.m.r. spectroscopy), identified as t-butyl *cis*-1,3,3,3-tetrafluoroprop-1-enyl sulphide (0.88 g, 4.4 mmol, 46%), t-butyl *trans*-1,3,3,3-tetrafluoroprop-1-enyl sulphide (0.32 g, 1.6 mmol, 17%), and t-butyl 1,1,3,3-tetrafluoroprop-2-enyl sulphide (0.15 g, 0.7 mmol, 7%).

(f) *With sodium 1,1-dimethylethanethiolate in 1,1-dimethylethanethiol*. A mixture of the olefin (1.50 g, 12.1 mmol), sodium 1,1-dimethylethanethiolate (1.22 g, 10.9 mmol), and 1,1-dimethylethanethiol (5.0 g), at 22 °C (5 h), gave unchanged olefin (0.22 g, 1.7 mmol, 14% recovered), and a product fraction (1.62 g) which was shown by n.m.r. spectroscopy to contain t-butyl *cis*-1,3,3,3-tetrafluoroprop-1-enyl sulphide (1.07 g, 5.3 mmol, 51%), t-butyl *trans*-1,3,3,3-tetrafluoroprop-1-enyl sulphide (0.32 g, 1.6 mmol, 15%), t-butyl 1,1,3,3-tetrafluoroprop-2-enyl sulphide (0.15 g, 0.7 mmol, 7%), t-butyl 1,1,3,3,3-pentafluoropropyl sulphide (0.09 g, 0.4 mmol, 4%).

(g) *With sodium thiophenolate in ether*. A mixture of the olefin (1.72 g, 13.0 mmol) and sodium thiophenolate (1.54 g, 11.7 mmol) in ether (10 ml), at 65 °C (24 h), gave unchanged olefin (0.29 g, 2.2 mmol, 17% recovered) and a product fraction (1.44 g) which was shown by n.m.r. spectroscopy to contain (i) phenyl *cis*-1,3,3,3-tetrafluoroprop-1-enyl sulphide (1.09 g, 4.9 mmol, 45%), (ii) phenyl *trans*-1,3,3,3-tetrafluoroprop-1-enyl sulphide (0.20 g, 0.9 mmol, 6%), (iii) phenyl 1,1,3,3-tetrafluoroprop-2-enyl sulphide (0.1 g, 0.05 mmol, 1%), and (iv) two unidentified components (*ca*. 5% of the fraction).

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

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[10] D. D. Elleman, L. C. Brown, and D. Williams. *J. Mol. Spectroscopy*, 1961, **7**, 393.

Reactions of 1H-*Pentafluoropropene.*—(a) *With caesium fluoride.* A mixture of the cis- (0.064 g, 0.48 mmol) and trans- (0.096 g, 0.72 mmol) isomers of the olefin was sealed *in vacuo* in a Pyrex ampoule (*ca.* 20 ml) together with caesium fluoride (0.20 g, 1.3 mmol) and moist tetramethylene sulphone (2 ml) and shaken at 90 °C (24 h). The product (0.16 g, 1.20 mmol, 100%), M^+ 132 (C_3HF_5), was shown by n.m.r. spectroscopy to be a mixture of the cis- (0.133 g, 0.99 mmol, 83%) and trans- (0.028 g, 0.21 mmol, 17%) isomers of the reactant olefin.

(b) *With sodium methoxide.* A mixture of the olefin (3.07 g, 23.2 mmol), sodium methoxide (0.45 g, 8.2 mmol), and methanol (5.5 ml) was sealed *in vacuo* in a Pyrex ampoule (*ca.* 300 ml) and shaken at 80 °C (45 h). The volatile product was condensed *in vacuo* onto phosphoric oxide (to remove methanol) and left in contact with the oxide at room temperature (1 h) to afford unchanged 1H-pentafluoropropene (2.22 g, 16.8 mmol, 72% recovered) and *methyl* trans-2,3,3,3-*tetrafluoroprop*-1-*enyl ether* (0.81 g, 5.6 mmol, 88%) (Found: C, 33.6; H, 2.9%; M, 144. $C_4H_4F_4O$ requires C, 33.3; H, 2.8%; M, 144), b.p. (Siwoloboff) 72 °C.

When the reaction was repeated at 80 °C (96 h) with a mixture of the olefin (2.97 g, 22.5 mmol) and sodium methoxide (1.08 g, 20.0 mmol) in *m*-xylene (5 ml) the exclusive product was again methyl trans-2,3,3,3-tetrafluoroprop-1-enyl ether (0.52 g, 3.6 mmol, 86%); unchanged olefin (2.42 g, 18.3 mmol) was recovered (81%).

(c) *With a solution of potassium hydroxide in methanol.* A mixture of the olefin (1.44 g, 10.9 mmol), potassium hydroxide (1.0 g), and methanol (10 ml), was sealed *in vacuo* in a Pyrex ampoule (*ca.* 150 ml) and shaken at room temperature (19 h). The resultant material was treated with water (10 ml) and the lower layer was separated, dried over molecular sieves (B.D.H. Type 4A), and shown by g.l.c. (2 m DNP at 55 °C) to contain three components (ratio 20 : 2 : 78) which were identified by n.m.r. spectro-scopy as (i) methyl 1,2,3,3,3-pentafluoropropyl ether (0.29 g, 1.75 mmol, 16%); (ii) methyl cis-2,3,3,3-tetrafluoroprop-1-enyl ether (0.03 g, 0.15 mmol, 1.5%); and (iii) methyl trans-2,3,3,3-tetrafluoroprop-1-enyl ether (0.98 g, 6.8 mmol, 63%).

(d) *With sodium methanethiolate.* A mixture of the olefin (2.92 g, 22.1 mmol), methanethiol (6.0 g), and the thiolate (0.35 g, 5.0 mmol), sealed in a stainless steel autoclave (*ca.* 50 ml) at 80 °C (72 h), gave (i) unchanged olefin (2.63 g, 19.9 mmol, 90% recovered), (ii) unchanged methanethiol (5.78 g, 83% recovered), and (iii) *methyl* trans-2,3,3,3-*tetrafluoroprop*-1-*enyl sulphide* (0.28 g, 1.8 mmol, 83%) (Found: C, 30.3; H, 2.8%; M, 160 $C_4H_4F_4S$ requires C, 30.0; H, 2.5%; M, 160), b.p. (Siwoloboff) 99 °C.

In a second reaction a mixture of the olefin (2.98 g, 22.6 mmol) and the thiolate (1.05 g, 15.0 mmol) in *m*-xylene (5 ml), sealed *in vacuo* in a Pyrex tube (*ca.* 300 ml) which was shaken at 83 °C (90 h), gave unchanged olefin (0.95 g, 7.2 mmol, 32% recovered), and a mixture of *m*-xylene and product, which on distillation afforded methyl trans-2,3,3,3-tetrafluoroprop-1-enyl sulphide (1.72 g, 10.8 mmol, 70%), and a residue of *m*-xylene containing a small amount of the methyl propenyl sulphide.

(e) *With dimethylamine.* A mixture of the olefin (1.12 g, 8.4 mmol), dimethylamine (1.13 g, 25.1 mmol), and diethyl ether (5 ml), condensed *in vacuo* into a Pyrex tube (*ca.* 300 ml) and allowed to warm from -196 °C to room temperature (18 h), gave a mixture (3.42 g) of unchanged dimethylamine and ether and trans-NN-*dimethyl*-2,3,3,3-*tetrafluoroprop*-1-*enylamine* (1.17 g, 7.5 mmol, 89%) (Found: C, 38.5; H, 4.5; N, 8.8%; M^+, 157. $C_5H_7F_4N$ requires C, 38.2; H, 4.5; N, 8.9%; M, 157), b.p. (Siwoloboff) 112—113 °C.