

Short Communication

The preparation of telomers of "pentafluorosulphur iodide" and related reactions*

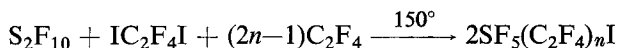
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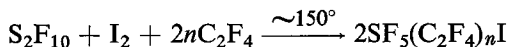
(Received March 21, 1973)

Telomers of pentafluorosulphur chloride and fluoro-olefins were reported some years ago^{1,2} and more recently pentafluorosulphur bromide has been prepared and added to certain fluoro-olefins³. However, the seemingly obvious way of making the potentially useful telomers with the general formula $SF_5(C_2F_4)_nI$, *i.e.* by reaction between SF_5I and C_2F_4 , is not yet available since the preparation of SF_5I has not been reported. Indeed, when one considers the stability and reactivity trends in pentafluorosulphur halides, one can imagine that SF_5I might be very difficult to isolate and characterise. We now wish to report a convenient way of making telomers with the general formula $SF_5(C_2F_4)_nI$.

When disulphur decafluoride was heated with an equimolecular amount of 1,2-di-iodotetrafluoroethane to *ca.* 150° in an autoclave with the simultaneous injection of tetrafluoroethylene, telomers with the general formula $SF_5(C_2F_4)_nI$ were obtained in high yield.

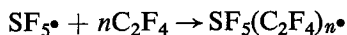
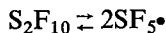


The value of n was a function of the amount of tetrafluoroethylene injected and it was possible to obtain the first member of the series, $SF_5C_2F_4I$, almost exclusively. The isomeric compound SF_5CFICF_3 has been reported recently⁴. It was also possible to obtain these telomers without pre-forming the di-iodide according to the equation:

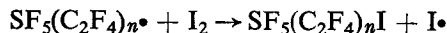
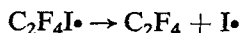
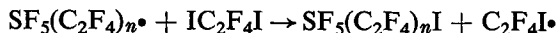


It is noteworthy that no evidence was found for compounds with the formula $SF_5(C_2F_4)_nSF_5$.

One can envisage the most important reactions in the formation of these telomers to be:

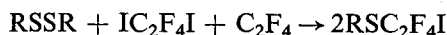


* Presented in part at the 4th European Symposium on Fluorine Chemistry, Ljubljana, 1972.



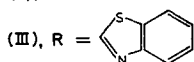
Analogous reactions with C_3F_6 , C_2H_4 and CF_2CFCl did not proceed in a similar manner. Only with CF_2CFCl were any recognisable products obtained and these were $\text{CF}_2\text{ICF}_2\text{Cl}$ and CF_3CFCI .

When dimethyldisulphide, diphenyldisulphide and 2,2'-dithio-bis(benzothiazole) were each heated to *ca.* 150° with equimolecular amounts of 1,2-di-iodotetrafluoroethane and tetrafluoroethylene, 2-iodotetrafluoroethylmethyl sulphide (I), 2-iodotetrafluoroethylphenyl sulphide (II) and 2-iodotetrafluoroethyl-2-benzothiazolyl sulphide (III) were produced in yields of 50, 60 and 70% respectively.



(I), R = CH₃

(II), R = C₆H₅



In none of these reactions were any higher telomers produced but there were compounds which would have been produced exclusively by the simple reactions between the disulphides and tetrafluoroethylene⁵⁻⁷.

Experimental

¹⁹F NMR spectra were recorded with Perkin-Elmer R10 and Varian HA-100 spectrometers with CCl₃F as internal standard. The mass spectra were recorded on an A.E.I. MS9 spectrometer.

Preparation of SF₅C₂F₄I

An Inconel autoclave (300 ml) was charged with dry disulphur decafluoride (32 g, 0.127 mol) and 1,2-di-iodotetrafluoroethane (45 g, 0.127 mol). The vessel was cooled to -78°, evacuated, warmed to room temperature and pressurised with tetrafluoroethylene to 150 psig (*ca.* 14 g, 0.14 mol). The mixture was heated and stirred at 150° for 4 h during which time the pressure fell to a steady value. The vessel was cooled to room temperature and the excess tetrafluoroethylene (*ca.* 10 psig) was vented off. A violet liquid (85 g) was obtained which was washed with aqueous potassium iodide, water and then dried and distilled. The main fraction b.p. 80-86° weighed 70 g and was more than 95% pure by GLC. A pure sample of 2-iodotetrafluoroethyl sulphur pentafluoride (nc) was obtained by preparative GLC; b.p. 86°, (Found: C, 7.0; F, 49.6; I, 36.3%. SF₅C₂F₄I requires C, 6.8; F, 48.4; I, 35.9%) λ_{max.} (cyclohexane) 278 mμ.

The ^{19}F NMR spectrum showed resonances at -64 (a), -46 (b), 60 (d) and 89 (c) ppm [F(a) SF_4 (b) CF_2 (c) CF_2 (d) I]. The mass spectrum showed a parent molecular ion with a one sulphur isotope ratio at m/e , 354.

Preparation of higher telomers

The experiment was carried out as described previously. The autoclave charged with disulphur decafluoride (38 g, 0.149 mol) and 1,2-di-iodotetrafluoroethane (52.8 g, 0.14 mol) was heated at 150° for about 3.5 h and tetrafluoroethylene was injected intermittently at this temperature until a total pressure drop of 235 psig was recorded. Distillation of the liquid product afforded three main fractions; b.p. $86-87^\circ$ (36 g) identified as $\text{SF}_5\text{C}_2\text{F}_4\text{I}$, b.p. $131-132^\circ$ (25 g) and b.p. $178-180^\circ$ (8 g) together with 18 g of intermediate cuts and a residue.

Fraction b.p. $131-132^\circ$: Analysis: Found: C, 10.6; F, 53.7; I, 28.6%. $\text{SF}_5(\text{C}_2\text{F}_4)_2\text{I}$ requires C, 10.6; F, 54.4; I, 28.0%. The ^{19}F NMR spectrum showed resonances at -64 (a), -46 (b), 60 (f), 96 (c), 115 (e) and 124 (d) ppm. [F(a) SF_4 (b) CF_2 (c) CF_2 (d) CF_2 (e) CF_2 (f) I]. The mass spectrum showed a parent molecular ion with a one sulphur isotope ratio at m/e , 454. This was 4-iodo-octafluorobutyl sulphur pentafluoride (nc).

Fraction b.p. $178-180^\circ$: Analysis: Found: C, 13.2; I, 23.3%. $\text{SF}_5(\text{C}_2\text{F}_4)_3\text{I}$ requires C, 13.0; I, 22.9%. The ^{19}F NMR spectrum of a solution of the compound in carbon tetrachloride showed resonances at -64 (a), -44 (b), 59 (h), 94 (c), 113 (g), 121 (e and f) and 122 (d) ppm [F(a) SF_4 (b) CF_2 (c) CF_2 (d) CF_2 (e) CF_2 (f) CF_2 (g) CF_2 (h) I]. The mass spectrum showed a parent molecular ion with a one sulphur isotope ratio at m/e , 554. This was 6-iodododecafluorohexyl sulphur pentafluoride (nc).

The mass spectrum of the residue was examined and parent molecular ions corresponding to $\text{SF}_5(\text{C}_2\text{F}_4)_n\text{I}$, where $n = 4-9$, were observed.

Preparation of the telomers $\text{SF}_5(\text{C}_2\text{F}_4)_n\text{I}$ without pre-forming the di-iodide $\text{C}_2\text{F}_4\text{I}_2$

An Inconel vessel charged with disulphur decafluoride (19 g, 0.072 mol) and iodine (19 g, 0.072 mol) was cooled to -78° , evacuated, warmed to room temperature and pressurised with tetrafluoroethylene to 150 psig. Stirring was started and the temperature was slowly raised to 150° at which the pressure began to fall. Tetrafluoroethylene was injected intermittently until a total pressure drop of 240 psig was recorded. A violet liquid was obtained whose molar composition was estimated by GLC to be $\text{SF}_5\text{C}_2\text{F}_4\text{I}$, 34%; $\text{SF}_5(\text{C}_2\text{F}_4)_2\text{I}$, 35%; $\text{IC}_2\text{F}_4\text{I}$, 10%; $\text{SF}_5(\text{C}_2\text{F}_4)_3\text{I}$, 14%; $\text{SF}_5(\text{C}_2\text{F}_4)_4\text{I}$, 5%; $\text{SF}_5(\text{C}_2\text{F}_4)_5\text{I}$, 2%.

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