567. *Reaction of Fluoro-olefins with Sulphur.*

By Kenneth V. Martin.

Fluoro-olefins and sulphur vapour react at elevated temperatures in the presence of activated carbons of high surface area to form either thioketones or thioacid fluorides.

Hexafluorothioacetone and certain fluorothioacyl fluorides have been prepared previously in 60% yield by the reaction of fluoroalkylmercurials with boiling sulphur.[1] While this method suffices for the preparation of small quantities, it does not lend itself to a general laboratory synthesis. A general method for the preparation of fluorothioketones

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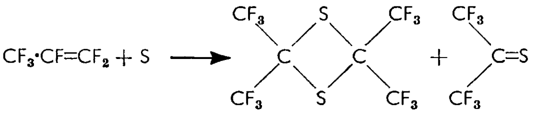
[1] Middleton *et al.*, *J. Amer. Chem. Soc.*, 1961, **83**, 2589.

and fluorothioacyl fluorides, now described, is carried out by passing a mixture of the fluoro-olefin and sulphur vapour through a nickel tube (packed with catalyst) heated in a tube furnace. Alternatively, sulphur vapour could be introduced by passing the fluoro-olefin through the source of sulphur vapour; however, using this method it was not always easy to adjust the fluoro-olefin : sulphur ratio.

Hexafluoropropene reacted with sulphur vapour in the presence of activated carbon at 425° to form hexafluorothioacetone, obtained as a mixture of blue monomer form (b. p. 6°; 74%) and colourless dimer (b. p. 112°; 26%). Above 500° carbon bisulphide was the principal product, while below 380° there was little or no reaction. The dimer was identified as (I) by elemental analysis, molecular weight, and i.r. and n.m.r. spectroscopy; hexafluorothioacetone was identified by i.r. and n.m.r. spectroscopy. Although elemental analyses were not obtained for (II) it was converted quantitatively into the dimer of requesite composition.



(I) (II)

The monomer and dimer had common bands at 700, 747, and 940 cm.$^{-1}$, and absorption in the 1150—1300 cm.$^{-1}$ region. The bands may be C–S stretching frequencies and/or C–F bending or rocking frequencies, while the general absorption in the 1150—1300 cm.$^{-1}$ region is associated with C–F stretching, etc. It seems probable that the 1040 cm.$^{-1}$ band in the spectrum of hexafluorothioacetone is due to the >C=S absorption, being absent from the spectrum of the dimer. The 1515 cm.$^{-1}$ band is similar to the carbon disulphide absorption and may be due to an impurity. The fluorine-19 resonance spectrum revealed only one type of C–F linkage in each material, consistent with the suggested structures.

Activated carbons needed to possess a minimum surface area of 800 m.^{2}/g. in order to effect reaction. No other surface was found to display activity.

Changes that occurred to the carbon are of interest. When the reaction was initiated by heating the catalyst to 430° and then passing through hexafluoropropene and sulphur vapour, there was an induction period of *ca.* 10 minutes before products were observed. During this time, the catalyst temperature rose *ca.* 30°. Examination of the catalyst after use revealed that it had increased in mass by 40% and that the critical physical dimensions of the carbon had changed. This " conditioned " catalyst could be used indefinitely without further change, also in a fresh experiment no induction period was observed. Apparently hexafluoropropene decomposes on the catalyst surface depositing carbon in such a fashion as to catalyse the observed reaction. Use of carbons of lower surface area resulted in lower conversion into sulphur-containing products.

The hexafluorothioacetone could be obtained pure by distillation immediately following preparation, and was relatively stable at —78°; at room temperature it dimerized rapidly. (The dimerization could also be catalysed by bases such as dimethylformamide.) Crude hexafluorothioacetone dimer was pale yellow; probably due to the presence of some perfluorothiopropionyl fluoride. Distillation through a 4-ft. Podbielniak column gave pure colourless dimer, the distillation being made less tedious by washing the dimer several times with carbon disulphide before distillation.

Tetrafluoroethylene reacted with sulphur vapour in the presence of activated carbon to form trifluorothioacetyl fluoride. Best yields (20%) were obtained at 500° with a sulphur–tetrafluoroethylene ratio of 5 : 1. Even under these conditions more than 50% of the tetrafluoroethylene was converted into higher-boiling by-products. Low-temperature distillation gave pure material which slowly polymerized to a colourless elastomer at —78°.

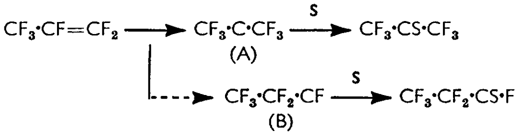
Chlorotrifluoroethylene and sulphur vapour at 460° gave chlorodifluorothioacetyl fluoride in 90% yield; n.m.r. spectroscopy indicated the presence of ~10% of trifluorothioacetyl chloride.

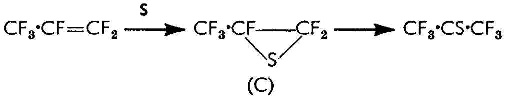
Several other olefins were examined in this reaction; details are collected in the Table. Only low yields of thiocarbonyl compounds were obtained and no reaction was observed with tetrachloroethylene. Structures are tentatively assigned on the basis of n.m.r. spectroscopy.

Fluoro-olefin	Temp.	Product	Conversion (%)	Product
Trifluoroethylene	450°	Yellow liquid, b. p. 10—20°	10	Difluorothioacetyl fluoride
Perfluorocyclobutene	420	Red liquid, b. p. 89—90°	6	Perfluorothiophan-2-thione *
Perfluorobut-1-ene	460	Colourless liquid, b. p. 129—138°	5	Perfluoro-(2,4-diethyl-2,4-dimethyl-1,3-dithietan) †

* Found: C, 22·5. $C_4F_6S_2$ requires C, 21·2%. † Found: C, 21·0; S, 15·0; F, 61·0. $C_8F_{16}S_2$ requires C, 20·7; S, 13·8; F, 65·5%.

Two reaction mechanisms appear evident, and are here discussed in terms of hexafluoropropene: (*a*) The first involves rearrangement of hexafluoropropene to the carbene (A) on the carbon surface, followed by reaction of the carbene with sulphur. Small amounts of an impurity such as perfluorothiopropionyl fluoride is explained by the formation of carbene (B) and subsequent reaction of this with sulphur. (*b*) Alternatively, sulphur might add across the double bond of hexafluoropropene to give the episulphide (C). Ring opening followed by migration of one fluorine atom leads to the observed product.





Toxicity.—Dimeric hexafluorothioacetone has approximately the same effect on rats as phosgene.

EXPERIMENTAL

Reactions were carried out by passing a mixture of the fluoro-olefin and sulphur vapour through a 1 in. nickel tube, packed with granulated carbon catalyst, and heated in a tube furnace. The sulphur vapour was generated by passing a stream of nitrogen through a bath of molten sulphur maintained at 430°. The flow rate of sulphur from the bath was proportional to the flow rate of the nitrogen. It proved easy to obtain a wide variety of sulphur flow rates, and these were calibrated by normal procedures before experiments were commenced. The Figure depicts the apparatus used.

Hexafluorothioacetone.—Hexafluoropropene (250 ml./min.) and sulphur vapour and nitrogen (24 g./hr. of sulphur) were passed over a 120-ml. bed of activated carbon (Cheney, type CH-2; surface area 1,100 m.^{2}/g.), maintained at 425°, and the vapours condensed in a flask at −78°. After 1 hr., a dense blue liquid (170 g.) had collected. Distillation of the product (100 g.) yielded hexafluoropropene (40 g.; b. p. −28°) and then hexafluorothioacetone (42 g.; b. p. 6°; s.g. 1·7), a deep blue liquid which was quite stable at −78° but it was converted slowly at room temperature into a dimer (see below). In the fluorine-19 resonance spectrum one band was observed at 316 c/sec. (low field of external standard of trifluoroacetic acid).* The hexafluorothioacetone exhibited infrared spectral bands at 700, 747, 940, 990, 1040, 1110, 1515, and 1715 cm.$^{-1}$; there was general absorption in the 1150—1300 cm.$^{-1}$ region.

Hexafluorothioacetone Dimer (2,2,4,4-*Tetrakistrifluoromethyl*-1,3-*dithietan*).—(1) Distillation of the residue from the hexafluorothioacetone distillation yielded hexafluorothioacetone *dimer*

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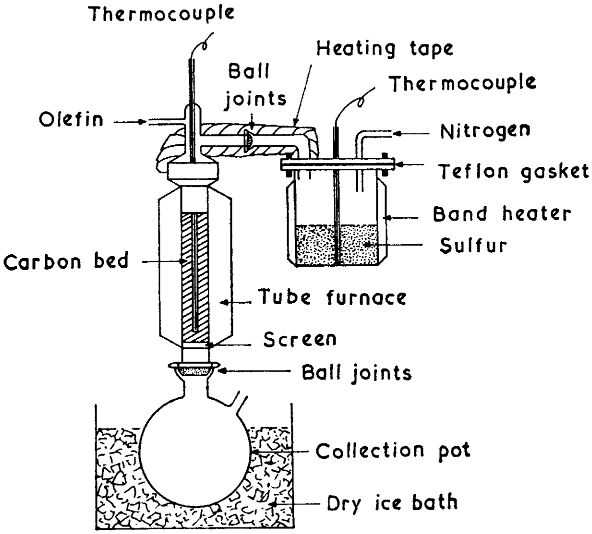
* All n.m.r. spectra were measured by the use of a 40 Mc./sec. R.F. unit.

as a colourless liquid (15·6 g.; b. p. 111°/760 mm.; s.g. 1·71, n_D^{25} = 1·3364) (Found: C, 19·3; F, 62·9; S, 17·5%; *M*, 365. $C_{16}F_{12}S_2$ requires C, 19·6; F, 62·6; S, 17·8%; *M*, 364). One band was observed in the fluorine-19 resonance spectrum at 140·8 c./sec. (low field of external standard of trifluoroacetic acid); $\nu_{max.}$ 940, 747, and 700 cm.$^{-1}$, together with general intense absorption in the 1150—1300 cm.$^{-1}$ region.

(2) Dimethylformamide (1 ml.) was added to hexafluorothioacetone (50 g.) at room temperature. Distillation of the residual colourless liquid yielded the dimer (48 g.), b. p. 111°.



Perfluorothioacetyl Fluoride.—The same apparatus and catalyst were employed as for the preparation of hexafluorothioacetone. A mixture of tetrafluoroethylene (140 ml./min.) and sulphur vapour (60 g./hr. in a nitrogen stream) was passed through the catalyst bed at 500°. The effluent vapours were collected at −78°. After 4 hr., over 100 g. of product had collected. Distillation yielded perfluorothioacetyl fluoride as a dense yellow liquid (30 g.; b. p. 24°). The sample slowly polymerized to an elastomer which was analysed (Found: C, 17·6; S, 32·9. C_2F_4S requires C, 18·0; S, 24·2%); $\nu_{max.}$ 960, 1080, 1160, 1195, 1215, 1240, and 1350 cm.$^{-1}$.

Chloroperfluorothioacetyl Fluoride.—The apparatus and catalyst were as before; chlorotrifluoroethylene (150 ml./min.) and sulphur vapour–nitrogen (15 g./min. of sulphur) were passed over the catalyst at 420°, and the vapours collected at −78°. After 3 hr., 135 g. of liquid were collected. Distillation of the product yielded chlorotrifluoroethylene (60 g.; b. p. −28°) and chloroperfluorothioacetyl fluoride (68 g.; b. p. 18—22°), the latter as a dense yellow liquid which slowly polymerized to a colourless elastomer. Alternatively, this material could be polymerized by addition to acetone chilled to −78°. The polymer was analysed (Found: C, 16·5; S, 21·7. C_2F_3SCl requires C, 16·1; S, 21·3%). Bands at 239, 739, and 4502 c/sec. were observed in the fluorine-19 resonance spectrum of the monomer, and interpreted as caused by presence of $\simeq$15% of perfluorothioacetyl chloride.

Reaction of Other Fluoro-olefins with Sulphur Vapour.—Reactions of several other fluoro-olefins with sulphur vapour in the presence of activated carbons were examined; only low yields of thiocarbonyl compounds were obtained. The results obtained are outlined in the Table. Structural assignments are tentative only, being based on n.m.r. spectroscopy and in some cases, elemental analysis.

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