

Short Communication

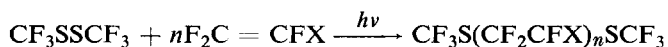
Telomerization of bis(trifluoromethyl)disulfide with polyfluoro-olefins

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Bis(trifluoromethyl)disulfide has been described as an initiator for the free-radical polymerization of perfluoropropylene and of perfluoropropylene-tetrafluoroethylene mixtures^{1,2} but, until a recent report, had not been cited as a telogen for the preparation of low molecular-weight perhalogenated fluids. Haran and Sharp³ showed that it will telomerize with perfluoro-olefins upon irradiation with UV light in Pyrex glass, and were unable to obtain satisfactory results in quartz. The general reaction is:



where n is an integer and $X = \text{F}, \text{Cl}, \text{or } \text{CF}_3$.

We completed a similar study several years ago⁴. Although our findings parallel those of Haran and Sharp in several respects, there are important differences which are undoubtedly due to the different reaction conditions employed in the two studies. These differences are outlined below.

Haran and Sharp used a Pyrex reactor and irradiated an equimolar mixture of disulfide and olefin in a sealed flask whereas we deliberately chose quartz, knowing that Pyrex cuts off most radiation below 3000 Å and that CF_3SSCF_3 has a maximum absorption at 2350 Å⁵. Our reaction procedure involved passing the olefin into irradiated refluxing disulfide. This approach permitted the preparation of substantial quantities of material, with reaction occurring in the presence of a large excess of disulfide. The reaction chain length was therefore short, and formation of the desired low-molecular-weight telomers in all cases predominated, in marked contrast to the procedure using equimolar quantities (*cf.* Table 1). The difference is particularly striking in the case of tetrafluoroethylene, where Haran and Sharp did not obtain the product with $n = 1$ and found only 3% of $n = 2$, in contrast to the 17% and 45% respectively noted by us. By increasing the rate of olefin input, we obtained waxy products as high as $n = 36$.

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TABLE I
PROPERTIES OF TELOMERS

Structure	B.p./°C	Yield ^b /%		n _D ²⁵	Analysis		NMR spectra ^e
		This study	Ref. 3		Calc./%	Found./%	
CF ₃ S(CF ₂ CF ₂) ₂ SCF ₃	80-81	17	0	1.3976	C 15.90 S 21.22	C 15.72 S 20.90	δ(CF ₃) 35.8 δ(CF ₂) 85.0
CF ₃ S(CF ₂ CF ₂) ₃ SCF ₃	123	45	3	1.3206	C 17.92 S 15.94	C 18.19 S 16.05	δ(CF ₃) 35.6 δ(CF ₂) 85.3; δ(CF ₂) 119
CF ₃ SCF ₂ CFC(CF ₂ CFC)SCF ₃	177	52	25	1.3757	C 16.56 S 14.74 Cl 16.30	C 16.87 S 14.75 Cl 16.31	δ(CF ₃) 37.0 δ(CF ₂ S) } 77.8 δ(CF) } δ(CF ₂) 120.8
CF ₃ S(CF ₂ CFCI) ₃ SCF ₃	140/45 mmHg	10	22	1.3862	C 17.42 S 11.63 Cl 19.28	C 17.29 S 11.55 Cl 19.08	e
CF ₃ S(CF ₂ CFCI) ₄ SCF ₃	179/45 mmHg	4	20	1.3918	C 17.98 S 9.60 Cl 21.23	C 17.70 S 9.60 Cl 21.30	e
CF ₃ S(CF ₂ CFCBr) ₂ SCF ₃	114/45 mmHg	e	—	1.4097	C 13.75 Br 30.48 C 14.03	C 13.66 Br 30.24 C 13.89	e
CF ₃ S(CF ₂ CFCBr) ₃ SCF ₃	not determined	e	—	1.4284	Br 35.00 C 21.82	Br 34.44 C 22.13	e
CF ₃ SCH ₂ CF ₂ CF ₂ CH ₂ SCF ₃	85/75 mmHg	d	—	1.3572	H 1.22 S 19.42 C 17.04	H 1.24 S 19.25 C 17.02	δ(CH ₂) 3.49 δ(CF ₃) 45.2; δ(CF ₂) 120
CF ₃ SC(CF ₃)FCF ₂ SCF ₃	96 ^a	69	9	1.3244	S 18.21	S 18.23	δ(CF ₃ SCF) 34.4 δ(CF ₃ SCF ₂) 35.7 δ(CF ₂) 78.8; δ(CF) 157 δ(CF ₃ CF) 74.6

^a Ref. 8 quotes b.p. 100 °C; n_D²⁵ 1.3250. Analyses and NMR data are in agreement.

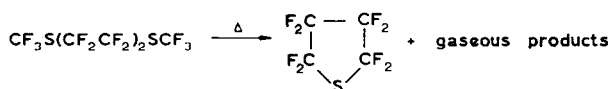
^b Based on CF₃SSCF₃ consumed.

^c Mixtures—no meaningful figures.

^d Yield not measured.

In the case of trifluorochloroethylene, ^{19}F NMR examination showed our material having $n = 2$ to comprise almost entirely of $\text{F}_3\text{CSCF}_2\text{CFCICF}_2\text{CFClSCF}_3$, with only a trace of isomeric material. This may be contrasted with the results obtained with trifluorobromoethylene which gave only mixtures. The previous authors did not study telomerization of this compound. 1,1-Difluoroethylene reacted readily and stereospecifically to give $\text{CF}_3\text{SCH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{SCF}_3$. This reaction was not investigated further since this compound was less thermally stable than the others.

Examination of the thermal stability of some of the compounds led to the observation that 1,4-bis(trifluoromethylthio)perfluorobutane gave rise to almost quantitative amounts of perfluorothiolane, previously prepared by another method⁶.



Experimental

Tetrafluoroethylene and 1,1-difluoroethylene are products of Allied Chemical Corporation. Bis(trifluoromethyl)disulfide* was prepared by methods recently published⁷. Other materials were purchased from Matheson Gas Products. Physical constants, spectral and analytical data are presented in Table 1. NMR spectra were recorded on Varian A60 and DP56 instruments. ^{19}F spectra were calibrated by generating side-bands of Cl_3CF . All elemental analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Telomerization of bis(trifluoromethyl)disulfide

A cylindrical reactor was connected to a round-bottomed flask and contained a 450 W Hanovia lamp in a quartz or Vycor well. A condenser at the reactor exit prevented the escape of volatile reactants and products. All telomerizations were carried out in the same manner and a typical example only is given.

Reaction of CF_3SSCF_3 and $\text{F}_2\text{C}=\text{CF}_2$

Bis(trifluoromethyl)disulfide (24 g; 0.124 mol) was refluxed into the reaction zone from the flask. Tetrafluoroethylene was passed in at a rate of *ca.* 3 l h^{-1} (*ca.* 13.5 g h^{-1}), and the mixture was irradiated. The temperature of the boiling liquid was noted at intervals and over a period of 2 h it rose from 36°C to 71°C . The mixture was distilled through a spinning-band column and gave (a) 4 g of unreacted CF_3SSCF_3 , (b) 5.1 g of $\text{CF}_3\text{S}(\text{CF}_2\text{CF}_2)\text{SCF}_3$, *i.e.* $n = 1$, b.p. $80\text{--}81^\circ\text{C}$,

* Caution : Bis(trifluoromethyl)disulfide is very toxic and must be handled with great care. Due to the volatility of the material, ALL operations involving its use should be carried out under an efficient hood.

yield 17.0%, and (c) 17.8 g of $\text{CF}_3\text{S}(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2)\text{SCF}_3$, *i.e.* $n = 2$, b.p. 121–123 °C, yield 45%. Some intermediate fractions were also produced. The identity of the telomers was confirmed by elemental analysis and ^{19}F NMR spectroscopy.

Perfluorothiolane

1,4-bis(trifluoromethylthio)perfluorobutane (2 g; 0.005 mol) was heated in a sealed glass tube at 350 °C for 7 days. The tube was cooled and opened and *ca.* 1 g perfluorothiolane, b.p. 41 °C, n_D^{25} 1.3048, was obtained. The infrared spectrum agreed with that published previously⁸. The other product(s) of the reaction were gaseous and were not identified.

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