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PREPARATION OF 2-CHLORO-3-PENTAFLUROSULFUR TETRAFLUOROPROPYLENE, AND ITS USE IN TELOMERIZATION REACTIONS

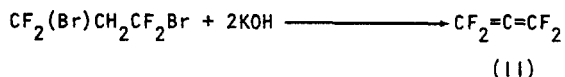
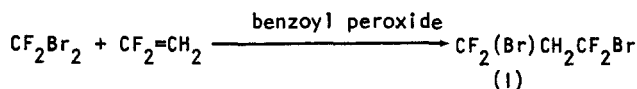
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## SUMMARY

The synthesis of a new SF monomer, 2-chloro-3-pentafluorosulfur tetrafluoropropylene,  $\text{SF}_5\text{CF}_2\text{C}(\text{Cl})=\text{CF}_2$ , is reported.

We wish to report the synthesis of a new SF monomer, 2-chloro-3-pentafluorosulfur tetrafluoropropylene,  $\text{SF}_5\text{CF}_2\text{C}(\text{Cl})=\text{CF}_2$ . The synthesis involves the following sequence of reactions:



The preparation of (I), 1,2-dibromo-1,1,3,3-tetrafluoropropane, was carried out according to the method of Tarrant et al [1]. The preparation of (II), tetrafluoroallene (TFA), was essentially that of Muehlner [2] with slight modification. We were able to obtain consistent yields of about 70% using a larger excess of KOH with an efficient ice condenser. The reactor was heated slowly and held at about 90°C with a nitrogen sweep to remove TFA as it was formed. The preparation of (III), 2-chloro-3-pentafluorosulfur tetrafluoropropylene was carried out in a metal bomb at 90-100°C for 1 to 16 hours with a yield of 20 percent.

Compound (II) is a clear colorless liquid. It was characterized by elemental analysis, vapor density, infrared and mass spectroscopy. Qualitative  $^{19}\text{F}$  NMR spectra were in agreement with the presence of a double bonded  $\text{CF}_2$  group (two nonequivalent fluorines at  $\delta$  - 55.0 and -63.8) and an internal  $\text{CF}_2$  group ( $\delta$  - 45.1) and an  $\text{SF}_5$  group (second order multiplet).

The monomer (II) should be very useful in the preparation of high density fluids by telomerization with high density telogens such as  $(\text{SF}_5\text{O})_2$  or  $\text{SF}_5\text{Cl}$ . We have telomerized (II) with  $\text{CF}_3\text{I}$  resulting in telomers which are viscous oils with densities of about two.

## EXPERIMENTAL

### Materials

Dibromodifluoromethane, 1,1-difluoroethylene, and trifluoromethyl iodide were obtained commercially from Peninsular Chem Research, Inc. Sulfur chloride pentafluoride was prepared according to the method of Tullock et al [3].

### 2-Chloro-3-Pentafluorosulfur Tetrafluoropropylene

Tetrafluoroallene (6.4 g; 57 mmol) and sulfur chloride pentafluoride (9.3 g; 57 mmol) were charged from the vacuum line into a 30 cc stainless steel bomb. The bomb was heated to and held at  $100^\circ\text{C}$  for 3 hours. After cooling to ambient temperature, the reaction products were separated by fractional condensation at  $-46$ ,  $-80$ , and  $-196^\circ\text{C}$  yielding 5 g of high molecular weight oil, 3.1 g (20% yield) of 2-chloro-3-pentafluorosulfur tetrafluoropropylene and 5 g of unreacted sulfur chloride pentafluoride. Analyses: Found: C, 12.70; F, 63.4. Calculated for  $\text{C}_3\text{F}_9\text{ClS}$ : C, 13.11; F, 62.3%. Molecular Weight: Found: 278. Calculated for  $\text{C}_3\text{F}_9\text{ClS}$ : 274.5.

The infrared spectrum had major absorptions at 1700 (s), 1350 (s), 1250, 1175, 1060 (s), 905 (s), 815 (s), 680 and  $605\text{ cm}^{-1}$ . Mass spectrum (m/e, ion, relative intensity): 12, C, 0.57; 19, F, 0.36; 31, CF, 12.58; 35, Cl, 1.76; 50,  $\text{CF}_2$ , 1.26; 55, CF-C=C, 0.55; 70,  $\text{SF}_2$ , 9.64; 74,  $\text{CF}_2\text{-C=C}$ , 5.24; 89,  $\text{SF}_3$ , 100; 93,  $\text{CF}_2\text{-C=CF}$  25.16; 112,  $\text{CF}_2\text{-C=CF}_2$ , 11.53; 127,  $\text{SF}_5$ , 10.48; 147,  $\text{CF}_2\text{-C(Cl)=CF}_2$ , 2.09; 220,  $\text{SF}_5\text{CF}_2\text{C=CF}$ , 0.69; 239,  $\text{SF}_5\text{CF}_2\text{C=CF}_2$ , 31.45.

Reaction of 2-Chloro-3-Pentafluorosulfur Tetrafluoropropylene with  
Trifluoromethyl Iodide

2-Chloro-3-pentafluorosulfur tetrafluoropropylene (12.2 mmol) and trifluoromethyl iodide (3 mmol) were combined in a 500 ml glass reaction vessel with a quartz center tube containing a standard Nester Faust NF UV-300 source (power supply UV-400). The reactants were irradiated for 5 days at ambient temperature after which time the volatiles were removed under high vacuum. Fractionation at  $-80$  and  $-196^{\circ}\text{C}$  yielded unreacted starting materials (92.5%) and a trace of  $\text{I}_2$ . There remained 0.3 g (7.5% conversion, 100% yield) of a non-volatile oil. Its viscosity was about 400 centistokes; its density was  $2.0 \text{ g cm}^{-3}$ . Its infrared spectrum exhibited major absorptions at 1350, 1175 (broadband), 1025, 960, 888, 833, and  $740 \text{ cm}^{-1}$ .

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