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

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SUMMARY

The synthesis of a new SF monomer, 2-chloro-3-pentafluorosulfur tetrafluoropropylene, $SF_5CF_2C(Cl)=CF_2$, is reported.

We wish to report the synthesis of a new SF monomer, 2-chloro-3-pentafluorosulfur tetrafluoropropylene, $SF_5CF_2C(Cl)=CF_2$. The synthesis involves the following sequence of reactions:

$$CF_2Br_2 + CF_2=CH_2 \xrightarrow{\text{benzoyl peroxide}} CF_2(Br)CH_2CF_2Br \quad (I)$$

$$CF_2(Br)CH_2CF_2Br + 2KOH \longrightarrow CF_2=C=CF_2 \quad (II)$$

$$CF_2=C=CF_2 + SF_5Cl \longrightarrow SF_5CF_2C(Cl)=CF_2 \quad (III)$$

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.

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Compound (III) is a clear colorless liquid. It was characterized by elemental analysis, vapor density, infrared and mass spectroscopy. Qualitative ^{19}F NMR spectra were in agreement with the presence of a double bonded CF_2 group (two nonequivalent fluorines at Ø - 55.0 and-63.8) and an internal CF_2 group (Ø - 45.1) and an SF_5 group (second order multiplet).

The monomer (III) should be very useful in the preparation of high density fluids by telomerization with high density telogens such as $(SF_5O)_2$ or SF_5Cl. We have telomerized (III) with CF_3I 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°C for 3 hours. After cooling to ambient temperature, the reaction products were separated by fractional condensation at -46, -80, and -196°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 C_3F_9ClS: C, 13.11; F, 62.3%. Molecular Weight: Found: 278. Calulated for C_3F_9ClS: 274.5.

The infrared spectrum had major absorptions at 1700 (s), 1350 (s), 1250, 1175, 1060 (s), 905 (s), 815 (s), 680 and 605 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, CF_2, 1.26; 55, CF-C=C, 0.55; 70, SF_2, 9.64; 74, CF_2-C=C, 5.24; 89, SF_3, 100; 93, CF_2-C=CF 25.16; 112, CF_2-C=CF_2, 11.53; 127, SF_5, 10.48; 147, CF_2-C(Cl)=CF_2, 2.09; 220, SF_5CF_2C=CF, 0.69; 239, SF_5CF_2C=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°C yielded unreacted starting materials (92.5%) and a trace of 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 g cm^{-3}. Its infrared spectrum exhibited major absorptions at 1350, 1175 (broad band), 1025, 960, 888, 833, and 740 cm^{-1}.

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