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Communications

A New General Method for Preparation of Pentafluorosulfur-Substituted Fluorocarbons: Synthesis of Perfluoroneopentylsulfur Pentafluoride Using Elemental Fluorine as a Reagent

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We wish to report the synthesis of a very sterically crowded and extraordinarily interesting new compound, perfluoroneopentylsulfur pentafluoride. The reaction chemistry is unusual, and one might have predicted that such a compound would be unstable and that it might not be isolable due to steric difficulties. However, we have found that it is a stable organofluorine compound with very unusual properties. The fact that the synthesis of this compound proved possible has led us to develop the direct fluorination of mercaptans and polymermercaptans as a general synthetic method for exotic pentafluorosulfur organofluorine compounds that are of general interest and have been previously impossible to prepare.¹ This general route involves conversion of hydrocarbon mercaptans and polymermercaptans to pentafluorosulfur- and multiply pentafluorosulfur-substituted organofluorine compounds often in yields over 90%. Thus for the mercaptan compounds where R = ethyl, butyl, pentyl, isopentyl, octyl, and 1,4-dimercaptobutane

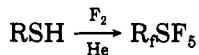
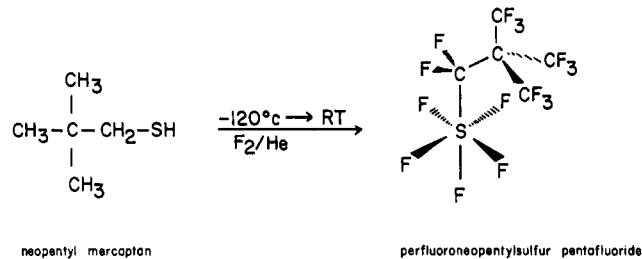


Table I. Fluorination Conditions for Neopentyl Mercaptan

time, days	He, cm ³ /min	F ₂ , cm ³ /min	zone temp, °C			
			1	2	3	4
1	60	1	-120	-120	-120	-120
1	30	1	-120	-120	-120	-120
1	30	2	-120	-120	-120	-120
1	10	1	-120	-120	-120	-120
1	10	2	-110	-110	-110	-110
1	0	1	-110	-110	-110	-110
1	0	1	-95	-95	-95	-95
1	0	1	-85	-85	-85	-85
1	0	1	-78	-78	-78	-78
1	0	1	amb ^a	-78	-78	-78
1	0	1	amb	amb	-78	-78
1	0	1	amb	amb	amb	-78
1	60	0	amb	amb	amb	amb

^a Ambient temperature.

The yields of the new R_fSF₅ compounds (characterized by ¹⁹F and ¹³C{¹⁹F} NMR and by mass spectra) were 71%, 89%, 92%, 91%, 93% and 89%, respectively:



neopentyl mercaptan

perfluoroneopentylsulfur pentafluoride

Neopentyl mercaptan was obtained from API Standard Reference Materials and was used as received. Fluorine gas was technical grade (>98%) and obtained from Air Products and Chemical, Inc. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY. ¹⁹F NMR spectra were obtained on a Varian EM 390 spectrometer operating at 84.67 MHz with external CFCl₃ standard. The ¹³C{¹⁹F} NMR spectrum was run on a Bruker WH-100 instrument with external tetramethylsilane standard. All of the NMR spectra were

(1) Huang, H. N.; Lagow, R. J., manuscript in progress.

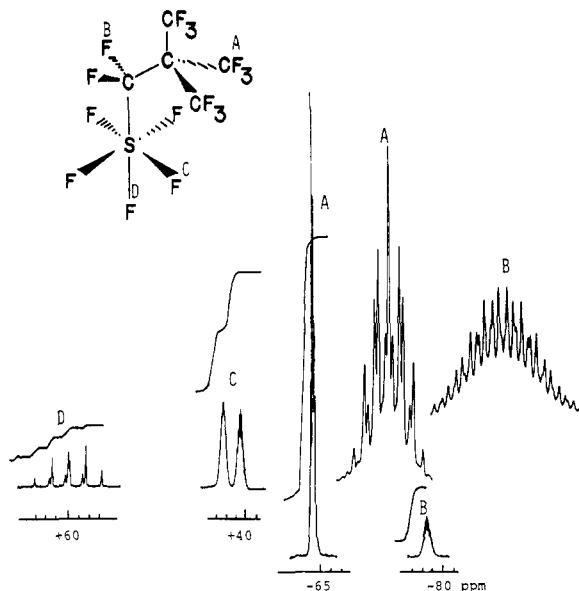


Figure 1. ^{19}F NMR spectrum of perfluoroneopentylsulfur pentafluoride.

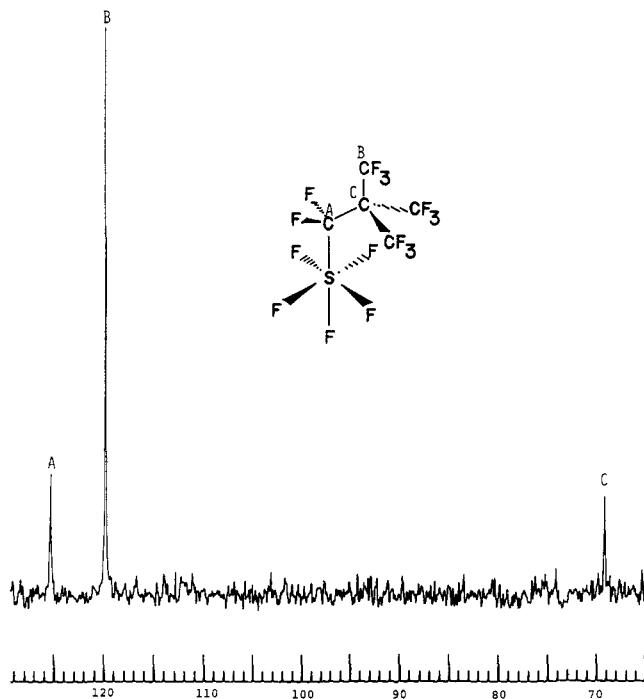


Figure 2. $^{13}\text{C}\{^{19}\text{F}\}$ NMR spectrum of perfluoroneopentylsulfur pentafluoride.

run as neat liquid samples. The mass spectrum was obtained with a Bell and Howell Model 21-490 mass spectrometer at 70 eV. Gas chromatography was done on a Bendix 2300 programmable gas chromatograph equipped with a cryogenic controller and thermal conductivity detector. The gas chromatographic column used for the separation was a $3/8$ in. \times 24 ft column packed with 20% Fomblin (Y-45) on Chromosorb P (60/80 mesh). The helium flow rate was 60 cm^3/min . The melting and boiling points were measured in a 6-mm sealed glass tube as described previously.² The apparatus used for the cryogenic fluorination³ has been described previously and uses a high-surface-area reactor containing packed fluorinated

copper turnings inside a four zone cryogenic reaction system.

A sample (2 mL, 1.690×10^{-2} mol) of neopentyl mercaptan was evaporated into a four-zone cryogenic reactor with zones 3 and 4 cooled to -120°C by a liquid nitrogen cryogenic system. The evaporation coil was held at 90°C by an oil bath, and the helium flow rate was $100 \text{ cm}^3/\text{min}$. Four hours after injection, the first two zones were also cooled to -120°C . The fluorination system was flushed with helium for another 8 h. The helium flow rate was $60 \text{ cm}^3/\text{min}$. Fluorinations were conducted following the reaction conditions listed in Table I. The crude products collected in the glass trap maintained at -78°C with dry ice/isopropyl alcohol slush were vacuum distilled through -45 , -78 , -131 , and -196°C traps and then purified by gas chromatography at 110°C : 1.55 g of perfluoroneopentylsulfur pentafluoride was obtained, corresponding to a 24.5% yield.

Perfluoroneopentylsulfur pentafluoride is a colorless liquid with a melting point of -87°C and a boiling point of 108°C . The ^{19}F and $^{13}\text{C}\{^{19}\text{F}\}$ NMR assignments are shown in Figures 1 and 2, respectively. The highest m/e in the mass spectrum was at 269 and corresponded to the parent minus SF_5 fragment. Other fragments in the mass spectrum were as follows: 200 (C_4F_8) $^+$, 131 (C_3F_5) $^+$, 127 (SF_5) $^+$, 93 (C_3F_3) $^+$, and 69 (CF_3) $^+$ (base peak). Anal. Calcd for $\text{C}_5\text{F}_{16}\text{S}$: C, 15.15; F, 76.77; S, 8.08. Found: C, 15.20; F, 76.74; S, 8.05.

This interesting new molecule is an electron-capture reagent with properties similar to those of sulfur hexafluoride, which is widely used in coaxial cables, communication satellites, and high-voltage equipment.⁴ Perfluoroneopentylsulfur pentafluoride, however, has a lower vapor pressure and may be superior for some applications.⁵ Previously mercaptans have been converted to SF_5 compounds in much lower yield first in the laboratory of Richard Dredner⁶ and in the laboratory of Dr. Abe and co-workers.⁷ Other lower yield techniques have included the silver difluoride conversions which produced the first SF_5 compound, CF_3SF_5 .⁸ Transformations are effected usually in much lower yield using the Simons cell.⁷ It has been found that with electrochemical fluorination only low-to-moderate yields of straight-chain pentafluorosulfur compounds are possible and that highly branched or sterically crowded compounds fragment and give little or no perfluoro products. It is clear that the electrochemical technique would be incapable of the synthesis of such an exotic compound as perfluoroneopentylsulfur pentafluoride.

Acknowledgment. We are grateful for the support of this work by the Air Force Office of Scientific Research (AFOSR-88-0084).

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(3) (a) Marschin, N. J.; Lagow, R. J. *J. Am. Chem. Soc.* 1972, 94, 860. (b) Adcock, J. L.; Beh, R. A.; Lagow, R. J. *J. Org. Chem.* 1975, 40, 3271.

(4) A collaboration is underway with a major industrial firm to explore these interesting electron-capture properties. Dielectric constants and breakdown voltages are comparable to those reported for SF_6 (>85%).

(5) Some SF_5 compounds such as S_2F_{10} and CF_3SF_5 are extremely toxic.

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