Notes

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Synthetic Methods and Reactions. 38.[1a] The Convenient Preparation of Sulfuryl Chloride Fluoride and Sulfur Tetrafluoride from Sulfuryl Chloride and Sulfur Dichloride with Pyridinium Poly(hydrogen fluoride)

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The use of fluorosulfur compounds in chemistry is of increasing significance. The preparation of these compounds is however frequently tedious, requiring rigorous conditions or equipment not found in the average laboratory. We would like now to report the simple preparation of two of the most used fluorosulfur compounds, sulfuryl chloride fluoride and sulfur tetrafluoride, from sulfuryl chloride and sulfur dichloride, respectively, via convenient fluorination with pyridinium poly(hydrogen fluoride).

Experimental Section

Pyridinium Poly(hydrogen fluoride). Into 42 g (0.53 mol) of reagent grade pyridine (dried over molecular sieves) at −78 °C in a polyethylene bottle was condensed 100 g (5 mol) of anhydrous hydrogen fluoride (Harshaw). The mixture was allowed to warm gradually to room temperature, the resulting solution being 30% by weight pyridine. The concentration of pyridine may be readily increased by decreasing the amount of HF added. When pyridinium poly(hydrogen fluoride) is already available it can be used as a convenient solvent medium to carry out the reaction of additional pyridine and anhydrous HF at low temperature.

Sulfuryl Chloride Fluoride. To 40 mL of pyridinium poly(hydrogen fluoride) (53% by weight pyridine) magnetically stirred at 30 °C in a polyethylene reaction vessel was added dropwise 38 g (0.28 mol) of SO_2Cl_2 (purified by reflux and subsequent distillation under reduced pressure). The product as formed was distilled out of the reaction vessel, was passed over a bed of anhydrous potassium fluoride to remove entrained HF, and was condensed into a cold trap at −78 °C. The SO_2ClF formed was purified by first refluxing for 2 h to remove low-boiling impurities and then by distillation from 1 g (0.004 mol) of antimony pentafluoride, to complex any sulfur dioxide present, to yield 27 g (80% yield) of SO_2ClF, bp 7 °C (^{19}F NMR and physical properties were identical with those of authentic sample).

Sulfur Tetrafluoride. To 200 mL of pyridinium poly(hydrogen fluoride) (30% pyridine by weight) was added 50 g (0.5 mol) of sulfur dichloride (technical) in a polyethylene reaction vessel. The reaction mixture was heated to 45 °C and the SF_4 formed was distilled into a cold trap at −78 °C. The product was purified by trap-to-trap distillation to yield 12.4 g (68% yield) of SF_4. (^{19}F NMR and physical properties are identical with those of the authentic compound.)

Results and Discussion

Because of its low nucleophilicity[2] and wide liquid range (−120 to +7 °C) sulfuryl chloride fluoride, SO_2ClF, has been extensively used as a solvent for the generation of stable carbocations[3] and is also useful as a synthetic reagent. Existing syntheses of SO_2ClF require the reaction of fluoride salts with sulfuryl chloride,[4] the treatment of potassium fluorosulfite with chlorine,[5] the reaction of hydrogen fluoride, chlorine, and sulfur dioxide with potassium bifluoride impregnated charcoal,[6] or the reaction of nitrogen trifluoride with sulfuryl chloride.[7] Schack and Wilson have also reported the preparation of SO_2ClF by the reaction of ClF and SO_2 at low temperature.[8] None of these methods is convenient. We have found that sulfuryl chloride reacts smoothly with pyridinium poly(hydrogen fluoride) ($C_5H_5N^+H(HF)_xF^-$)[9] to form SO_2ClF in good yield under mild conditions.

$$SO_2Cl_2 \xrightarrow[(HF)_x]{\text{pyridine}} SO_2ClF$$

Sulfur tetrafluoride has been shown to be an extremely useful reagent in the preparation of fluorine compounds.[10] Although a variety of procedures for the preparation of SF_4 are known[10c,11] the most convenient laboratory procedure to date is that of Tullock, Fawcett, Smith, and Coffman,[12] where SCl_2 is heated in a solvent of high dielectric constant, such as acetonitrile, with a metal fluoride, such as sodium fluoride. SF_4 was now found to be conveniently prepared from SCl_2 and pyridinium poly(hydrogen fluoride).

$$3SCl_2 \xrightarrow[(HF)_x]{\text{pyridine}} SF_4 + S_2Cl_2\ (S_2ClF)$$

Pyridinium poly(hydrogen fluoride), being extremely polar as well as containing a large reservoir of fluoride ion, is a good medium for the reaction, which proceeds smoothly at 45 °C and atmospheric pressure.

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Registry No. SO_2ClF, 13637-84-8; SF_4, 7783-60-0; SO_2Cl_2, 7791-25-5; SCl_2, 10545-99-0; pyridinium poly(hydrogen fluoride), 62778-11-4.

References and Notes

(1) (a) Part 37: G. A. Olah and J. Welch, submitted for publication in *Synthesis*. (b) Address correspondence to the Department of Chemistry, University of Southern California, Los Angeles, Calif. 90007.
(2) P. A. W. Dean and R. J. Gillespie, *J. Am. Chem. Soc.*, **91**, 7260 (1969).
(3) G. A. Olah, "Carbocations and Electrophilic Reactions", Wiley, New York, N.Y., 1974.
(4) M. Woyski, *J. Am. Chem. Soc.*, **72**, 919 (1950); (b) G. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).
(5) F. Seel, *Inorg. Synth.*, **9**, 111 (1967).
(6) *Chem. Abstr.*, **64**, 12248a (1966); Allied Chemical, British Patent 1017323 (1966).
(7) O. Glemser and U. Biermann, *Chem. Ber.*, **100**, 2484 (1967).
(8) C. J. Schack and R. D. Wilson, *Inorg. Chem.*, **9**, 311 (1970).
(9) G. A. Olah, M. Nojima, and I. Kerekes, *Synthesis*, 779 (1973).
(10) (a) W. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1961; (b) R. D. Chambers, "Fluorine in Organic Chemistry", Wiley, New York, N.Y., 1973; (c) W. C. Smith, *Angew. Chem., Int. Ed. Engl.*, **1**, 467 (1962).
(11) (a) D. Naumann and D. K. Padma, *Z. Anorg. Allg. Chem.*, **401**, 53 (1973); (b) W. Becher and J. Massone, *Chem. Ztg.*, **98**, 117 (1974).
(12) C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).

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Thermal Decomposition of Nitrosyl Cyanide

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Since the recent first synthesis of nitrosyl cyanide,[1,2] several physical chemical studies have been carried out on the compound,[2-4] but relatively little is known about its chemical