TABLE I

$MoSe_2$ X-RAY POWDER DIFFRACTION DATA

Hexagonal[a]		Rhombohedral			
d, A	*I*	*h k l*	*d*, A (obsd)[b]	*I*	*d*, A (calcd)[c]
6.44	78				
2.839	63	0 0 3	6.4	100	6.46
2.369	100	1 0 1	2.81	30	2.82
1.914	39	1 0 4	2.46	50	2.46
1.641	49	1 0 5	2.29	70	2.30
1.152	33	1 0 7	1.98	50	1.99
		10 1 0	1.61	70	1.60
		2 0 5	1.34	30	1.34

[a] Reference 12. [b] Cu Kα radiation, λ 1.5418 A; intensities visually estimated. [c] Calculated from lattice constants a = 3.292 A and c = 19.392 A, obtained from ref 11.

products, obtained from the decomposition of WS_3, were always mixed with the hexagonal form. One attempt to prepare the rhombohedral form from the hexagonal form at a pressure of 44 kbars and 2000° for 5 min resulted in an incomplete reaction with a strong X-ray powder diffraction pattern of the starting material still evident.

The strongest lines in the X-ray pattern of uncontaminated rhombohedral WS_2 listed in Table II agree quite well with the *d* spacings calculated from Wildervanek and Jellinek's lattice constants.[13]

TABLE II

RHOMBOHEDRAL WS_2, X-RAY POWDER DIFFRACTION DATA

h k l	*d*, A (obsd)[a]	*I*	*d*, A (calcd)[b]
0 0 3	6.1	100	6.2
0 0 6	3.08	30	3.08
1 0 1	2.71	25	2.71
1 0 4	2.35	20	2.35
0 1 5	2.20	20	2.20
0 0 9	2.06	50	2.06
1 1 0	1.577	30	1.580
0 0 12	1.530	30	1.542

[a] Cu Kα radiation, λ 1.5418 A; intensities visually estimated. [b] Calculated from lattice constants a = 3.162 A and c = 18.50 A taken from ref 13.

Runs with 1:2 atomic ratio tungsten–selenium mixtures covering a very wide pressure–temperature profile up to 70 kbars and 2400° gave only the hexagonal diselenide. Neither was any change apparent when hexagonal WSe_2 was used as starting material. All high-pressure runs with Mo–Te and W–Te 1:2.1 atomic ratio mixtures either did not react or formed the known product hexagonal $MoTe_2$[14] or WTe_2 and the high-temperature form of $MoTe_2$ both reported recently by Brown.[15] The last was obtained in partial yields at 45 kbars, 1800°, and 3 min and in quantitative amounts at 60 kbars, 2200°, and 2 min. Brown[15] reported 900° as the dividing line at atmospheric conditions between hexagonal and high-temperature $MoTe_2$.

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The Chlorofluorination of Acetonitrile. Preparation of N-Chloro-N-fluoro-1,1-difluoroethylamine

BY MAX LUSTIG

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It has been recently reported that the fluorination of cyanogen chloride with elementary fluorine leads to the formation of N-chloro-N-fluorotrifluoromethylamine, CF_3NFCl,[1] the first member of the class of compounds having the general formula RNClF. Chlorine(V) fluoride (ClF_5),[2] whose chemistry has been substantially unexplored, also can be used to prepare a compound of the same type by its reaction with acetonitrile to produce N-chloro-N-fluoro-1,1-difluoroethylamine, CH_3CF_2NFCl, as the major product.

Experimental Section

Reagents.—Acetonitrile (Spectro Grade) was obtained from Eastman Organic Chemicals. Chlorine(V) fluoride was prepared by the literature method.[2]

Apparatus.—A $^5/_8$-in. o.d. copper tubing vacuum apparatus containing Hoke 413K valves and equipped with a Helicoid pressure gauge and a fractionation train consisting of three 65-ml Kel-F or Teflon traps was used for manipulating volatile compounds. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer using a 10-cm path length stainless steel gas cell with AgCl windows. Fluorine-19 and hydrogen-1 nmr spectra were taken with a Varian Model C4310 spectrometer operating at 40 Mc. Samples were measured neat in 5-mm o.d. Pyrex tubes at 25° using trifluoroacetic acid (TFA) and tetramethylsilane (TMS) as external standards for the ^{19}F and ^1H spectra, respectively. Mass spectra were obtained with a Consolidated Engineering Model 21-620 spectrometer operating with an ionization potential of 100 v.

Preparation of CH_3CF_2NFCl.—In a typical reaction both reactants, ClF_5 and CH_3CN (1.5 mmoles each), were charged into a Kel-F trap in the fractionation train at −196°. The mixture was allowed to warm to room temperature over a 1-hr period and then stand for an additional 0.5 hr to ensure completion of the reaction. [*Caution:* This reaction appeared to be smooth when Spectro Grade acetonitrile was used, but violent explosions occurred when distilled but non-Spectro Grade acetonitrile was employed.] The reaction mixture was cooled to −196° and a small amount of noncondensable material was pumped out.

The principal products were CH_3CF_2NFCl (1.2 mmoles or 80% yield), CH_3CF_3, and Cl_2. Smaller quantities of a compound tentatively identified as $CH_3CF_2NNCF_2CH_3$ (*ca.* 0.01 mmole), as well as CF_4 and N_2O, were also present; the latter presumably was formed from the small quantities of chlorine oxides and oxyfluorides present in the chlorine(V) fluoride. The results were substantially the same when a Monel cylinder was used as a reactor. The yields were based upon the quantity of acetonitrile originally used after measurement of the quantities of each purified product component. Purity was established by chromatography as well as by mass, nmr, and infrared spectroscopy. The quantity and per cent composition of gaseous samples were determined by *PVT* measurement and by mass spectrometric analysis. The spectrometer was calibrated with

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(1) J. B. Hynes, B. C. Bishop, and L. A. Bigelow, *Inorg. Chem.*, **6**, 417 (1967).

(2) D. F. Smith, *Science*, **141**, 1039 (1963).

each pure substance. If a liquid phase of a product was present, the liquid was weighed. A 15-ft perfluorotri-*t*-butylamine on Chromosorb P chromatographic column was used for product purification. At a 50-ml/min helium flow rate, CH_3CF_2NFCl evolved in 2.9 min at 25°.

Characterization.—N-Chloro-N-fluoro-1,1-difluoroethylamine is a white solid, mp $-111.6 \pm 1.0°$, and a colorless liquid, bp $36.0 \pm 0.3°$. The compound was prepared for a fluorine analysis by adding a weighed sample into a bulb containing excess 0.1 *N* NaOH. Mass spectral analysis of the vapor phase after allowing the hydrolysis mixture to stand for 24 hr at 60° indicated that substantial quantities of CH_3Cl and N_2 were formed. The fluoride was determined by the thorium nitrate method.[3] Carbon and nitrogen were determined by combustion. *Anal.* Calcd for $C_2H_3ClF_3N$: C, 17.98; F, 42.7; N, 10.49. Found: C, 17.40; F, 42.3; N, 9.94. Its molecular weight by vapor density measurement assuming ideal gas behavior was 133.0 g/GMV (calcd, 133.5).

The ^{19}F nmr spectrum shows a broad absorption at −70.1 ppm, which is assigned to the NFCl group fluorine nuclear resonance,[1] and another at 14.1 ppm due the CF_2 group which is split into a gross quadruplet ($J_{HF} \cong 16$ cps) exhibiting subsplitting. The ^1H spectrum shows a triplet of doublets centered at −1.8 ppm. The triplet splitting is 16 cps presumably due to the interaction between the hydrogen and fluorine nuclei in the H–C–C–F bond and space system while the doublet splitting is 3 cps in the H–C–C–N–F system. The ^{19}F resonance of CF_3CH_3 is located at −14.2 ppm and is divided into a quadruplet, $J_{HF} = 13$ cps, a value consistent with that found in the spectrum of CH_3CF_2NFCl. In addition, the CH_3 group resonance is split into a quadruplet, centered at −1.5 ppm, a location close to that measured in the spectrum of the haloamine.

The following are the infrared spectral bands (cm^{-1}), their relative intensities in parentheses, and tentative assignments: 3049 (w) and 2980 (vw), CH stretch;[4] 1399 (m), C–CH_3 deformation;[4] 1250 (s) and 1217 (vs), C–F stretch; 971 (m) and 909 (m), in the N–F stretch region; 833 (mw) and 702 (mw), unassigned. (See Figure 1.) The mass numbers, ion empirical formulas in parentheses, and relative abundances of the peaks in the mass spectrum of CH_3CF_2NFCl are: 12 (C^+), 5.7; 13 (CH^+), 4.7; 14 (CH_2^+), 11.2; 15 (CH_3^+), 71.9; 24 (C_2^+), 0.8; 25 (C_2H^+, CF_2^{2+}), 1.8; 26 ($C_2H_2^+$, CN^+), 4.8; 27 ($C_2H_3^+$, CHN^+), 3.2; 31 (CF^+), 17.7; 33 (CH_2F^+, NF^+), 54.7; 34 (CH_3F^+), 0.8; 35 (Cl^+), 3.1; 36 (HCl^+), 27; 37 ($^{37}Cl^+$), 0.8; 38 (C_2N^+, $H^{37}Cl^+$), 3.8; 39 (C_2HN^+), 3.3; 40 ($C_2H_2N^+$), 6.7; 41 ($C_2H_3N^+$), 8.2; 44 (C_2HF^+), 4.7; 45 ($C_2H_2F^+$, CFN^+, 32.3); 46 ($C_2H_3F^+$), 31.3; 49 (CH_2Cl^+, NCl^+), 4.5; 50 (CF_2^+), 2.7; 51 (CHF_2^+, $N^{37}Cl^+$), 33; 58 (C_2HFN^+), 1.9; 59 ($C_2H_2FN^+$), 1.0; 60 ($C_2H_3FN^+$), 3.2; 63 ($C_2HF_2^-$), 9.8; 64 ($C_2H_2F_2^+$, CF_2N^+), 6.5; 65 ($C_2H_3F_2^+$), 100.0; 66 ($^{12}C^{13}CH_3F_2^+$ + ?), 2.5; 69 (CF_3^+), 10.5; 78 ($C_2H_2F_2N^+$), 2.2; 79 ($C_2H_3F_2N^+$), 41.3; 83 (CF_3N^+), 1.2; 85 ($CClF_2^+$), 2.0; 87 ($CClF_2^+$), 0.7; 95 ($C_2H_3ClFN^+$), 4.2; 97 ($C_2H_3{}^{37}ClFN^+$), 1.2; 99 (CF_2CN^+), 1.2; 101 ($CF_2{}^{37}ClN^+$), 0.4; 118 (CF_3ClN^+), 1.2; 120 ($CF_3{}^{37}ClN^+$), 0.4.

The compound tentatively identified as $CH_3CF_2N{=}NCF_2CH_3$ has been partially characterized by analysis and by infrared, ^1H nmr, and mass spectra. *Anal.* Calcd for $C_4H_6F_4N_2$: C, 30.4; mol wt, 158. Found: C, 29.7; mol wt, 154 by vapor density measurement and 163 by an effusion method[5,6] from measurement of the peak height decrease with time due to the fragment ion corresponding to mass number 65. Infrared spectrum: bands at 3049 (w) and 2985 (w) cm^{-1}, assigned to CH asymmetric and symmetric stretching vibrations at 1675 (w) and 1610 (mw) cm^{-1} in the N=N stretch domain; 1486 (w), 1447 (w), and 1394 (s) cm^{-1} in the CH_3 asymmetric and symmetric deformation regions; 1253 (vs, b) and 1205 (vs, b) cm^{-1}, C–F stretch; and 1025 (m), 963 (ms), 911 (m), 879 (m), and 724 (w) cm^{-1}. ^1H nmr spectrum: one resonance at −0.8 ppm divided into a triplet showing 13 cps splitting. Mass spectrum: major peaks at mass numbers 28 (N_2^+), 31 $(CF)^+$, 33 (CHF_2^+), 45 (C_2HF^+, CFN^+), 46 ($C_2H_3F^+$), 64 ($C_2H_2F_2^+$, CF_2N^+), 65 ($C_2H_3F_2^+$), 69 (CF_3^+), 79 ($C_2H_3F_2N^+$).

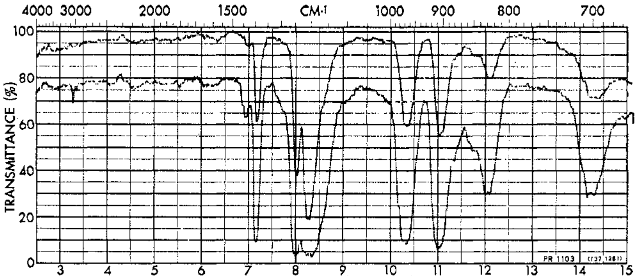

Figure 1.—Infrared spectrum of CH_3CF_2NFCl at 38 and 6 mm of pressure using a 10-cm path length cell.

Vapor pressures were measured at constant volume by use of a Pyrex Bourdon gauge. Some vapor pressures of CH_3CF_2NFCl measured at various temperatures and given as *P* (mm) and *T* (°C) are as follows: 7.8, −52.7; 27.3, −30.6; 46.7, −21.5; 103.3, −8.5; 146.7, −1.4; 252.0, 10.4; and 376.8, 20.4. The equation $\log P = (-1587/T) + 8.012$ is valid above 7.8 mm. The Trouton constant, 23.4 eu, and latent heat of vaporization, 7.23 kcal/mole, were obtained from the Clausius–Clapeyron equation.

Conclusion.—Chlorine(V) fluoride has been used to chlorofluorinate the C–N triple bond in acetonitrile to prepare CH_3CF_2NFCl. The reaction proceeds smoothly below room temperature. Both the physical and the chemical characterizations of the new compound are in accord with the proposed structure.

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Convenient Preparation of B-Trichloroborazine

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Since the original development of a method of synthesis for B-trichloroborazine by Brown and Laubengayer[1] based on the reaction of boron trichloride and ammonium chloride in refluxing chlorobenzene, several methods have been reported[2,3] which require less time to produce useful quantities of product than the original method. However, these newer methods require special apparatus. We wish to report a simple modification of the Brown and Laubengayer method which eliminates the need for a −80° condenser to retain boron trichloride in the reaction system, employs only standard equipment, and leads to good yields of B-

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