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}.

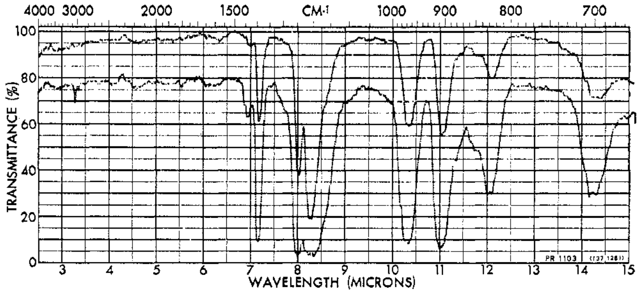

Figure 1.—Infrared spectrum of CH_3CF_2NFCl at 38 and 6 mm of pressure using a 10-cm path length cell.

^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 ($C_2H_3F_2N^+$).

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.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 AMC-11536 (Z).

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[3] T. S. Ma and J. Gwirtsman, *Anal. Chem.*, **29**, 140 (1957).

[4] L. J. Belamy, "Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1959, p 13.

[5] M. Eden, B. E. Burr, and A. W. Pratt, *Anal. Chem.*, **23**, 1735 (1951).

[6] P. D. Zemany, *J. Appl. Phys.*, **23**, 924 (1952).

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Convenient Preparation of B-Trichloroborazine

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Received January 12, 1967

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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[1] C. A. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.*, **77**, 3699 (1955).

[2] G. L. Brennan, G. H. Dahl, and R. Schaeffer, *ibid.*, **82**, 6248 (1960).

[3] R. F. Leifield and L. F. Hohnstedt, Abstracts of Papers, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959 p 35 M.

trichloroborazine after a reaction period of only several hours.

Recent work in this laboratory had shown that the acetonitrile adduct of boron trichloride is a convenient reagent for synthesis of cyclic boron compounds,[4] and our modification is based on the use of this adduct in place of gaseous boron trichloride.

Experimental Section

In a typical run 200 ml of dry chlorobenzene was placed in a 1-l. three-neck flask fitted with an inlet for dry nitrogen as a cover gas and with a water reflux condenser topped with a drying tube. Acetonitrile, 10.2 g (0.25 mole), was added to the chlorobenzene, and boron trichloride was bubbled into the solution from a lecture tank without prior purification; the resulting mixture was thoroughly stirred with a magnetic stirrer. The insoluble acetonitrile–boron trichloride adduct precipitated as formed, and after an addition time of about 20 min, fuming above the flask neck through which the boron trichloride was being added indicated that all of the available acetonitrile had reacted to form the desired complex.

Powdered, dried ammonium chloride, 14.0 g (0.252 mole), was added, and the mixture was heated at reflux temperature for 2.5 hr, by which time practically all solids had reacted to give soluble products. The solvent was removed by vacuum distillation, and the pasty residue was sublimed at 50–60° (0.2 mm). The product obtained by sublimation was identified as B-trichloroborazine by its infrared spectrum and melting point (82–84°). The yield was 8.8 g, 57% of the theoretical maximum.

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[4] H. D. Smith, Jr., M.S. Thesis, St. Louis University, 1966.

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New Syntheses of Nitrosyltetracarbonylmanganese(0) and Trinitrosylcarbonylmanganese(0)

BY HENNING WAWERSIK[1] AND FRED BASOLO

Received December 22, 1966

In order to extend our investigations on the kinetics and mechanisms of substitution reactions of $CoNO(CO)_3$[2] and $Fe(NO)_2(CO)_2$[3] to the compounds $MnNO(CO)_4$ and $Mn(NO)_3CO$, it was necessary to obtain these manganese compounds fairly conveniently and in reasonable quantities. Previous methods of preparation were somewhat tedious or gave the compound in low yield. The syntheses described here are experimentally easier and give higher yields of product.

$MnNO(CO)_4$.—Treichel, *et al.*,[4] prepared this compound by the reaction of $HMn(CO)_5$ with NO generated from N-methyl-N-nitroso-*p*-toluenesulfonamide. Vacuum line techniques were used to fractionate the product from the reaction mixture.

During investigations of substitution reactions of $Mn_2(CO)_{10}$ it was observed[5] that at elevated temperatures $Mn_2(CO)_8[P(C_6H_5)_3]_2$ readily reacts with CO to give $Mn_2(CO)_9P(C_6H_5)_3$. Therefore, it was decided to try the same reaction using NO in place of CO. The striking result was that a *p*-xylene solution of $Mn_2(CO)_8[P(C_6H_5)_3]_2$ reacts with NO, at *ca.* 95° within seconds, almost quantitatively according to eq 1.

$$Mn_2(CO)_8[P(C_6H_5)_3]_2 + NO \longrightarrow MnNO(CO)_4 + MnNO(CO)_3P(C_6H_5)_3 + CO + P(C_6H_5)_3 \quad (1)$$

The mechanism of this reaction is not known, but there is some evidence in support of the reaction scheme represented by

$$Mn_2(CO)_8[P(C_6H_5)_3]_2 + NO \longrightarrow Mn_2NO(CO)_8P(C_6H_5)_3 + P(C_6H_5)_3 \quad (2)$$

$$Mn_2NO(CO)_8P(C_6H_5)_3 \longrightarrow MnNO(CO)_4 + Mn(CO)_4P(C_6H_5)_3 \quad (3)$$

$$Mn(CO)_4P(C_6H_5)_3 + NO \longrightarrow MnNO(CO)_3P(C_6H_5)_3 + CO \quad (4)$$

Reaction 1 was carried out over different reaction times (10–60 sec) and with a fourfold variation in the concentration of $Mn_2(CO)_8[P(C_6H_5)_3]_2$. At all of these conditions, $MnNO(CO)_4$ and $MnNO(CO)_3P(C_6H_5)_3$ were formed in almost equimolar amounts. This was determined by means of infrared measurements of the reaction mixtures. One would not expect such a result for an alternative mechanism that has as its initial step the formation of $Mn(CO)_4P(C_6H_5)_3$ radicals and a subsequent substitution of $P(C_6H_5)_3$ by NO. The substitution reaction of $MnNO(CO)_4$ with $P(C_6H_5)_3$ is first order in both compounds.[6] Consequently, an equimolar formation of $MnNO(CO)_4$ and $MnNO(CO)_3P(C_6H_5)_3$ at all of the experimental conditions appears unlikely for an Mn–Mn bond cleavage radical mechanism. Moreover, under these conditions $MnNO(CO)_3P(C_6H_5)_3$ is the thermodynamically stable product, and one expects a substitution of $Mn(CO)_4P(C_6H_5)_3$ with NO as shown in (4) rather than the formation of $MnNO(CO)_4$. Furthermore, $MnNO(CO)_3P(C_6H_5)_3$ does not react with CO (1 atm of CO in reaction flask) over a period of several days at 80°.

This reaction of $Mn_2(CO)_8[P(C_6H_5)_3]_2$ with NO allows a very convenient preparation of $MnNO(CO)_4$. If tetraline is used as a solvent, $MnNO(CO)_4$ can be distilled almost solvent free from the reaction solution. Further purification can be achieved by several redistillations within minutes. Usually we used *p*-xylene as a solvent. In this case, $MnNO(CO)_4$ was obtained as a *p*-xylene solution, which was satisfactory for our purposes.

The yields obtained were always higher than 75%. A theoretical yield cannot be expected owing to some minor reaction of $MnNO(CO)_4$ with NO or with $P(C_6H_5)_3$ that is formed by the reaction. Also at these temperatures some of the starting material is converted to $Mn_2(CO)_9P(C_6H_5)_3$.[5] Therefore, it is essential that the entire preparation procedure be finished within 5 min. Since the reaction must take place as rapidly as possible, it appears that the best starting material is $Mn_2(CO)_8[P(C_6H_5)_3]_2$. Its substitution reactions are

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[1] Exchange graduate student from the Technischen Hochschule, Munich, Germany.

[2] E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.*, **88**, 3929 (1966); *Inorg. Chem.*, **5**, 1691 (1966).

[3] D. Morris, private communication.

[4] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961).

[5] H. Wawersik and F. Basolo, *Chem. Commun.*, 366 (1966).

[6] H. Wawersik and F. Basolo, unpublished results.