alkyl with the starting material, chloromethyl trimethylsilane, while any of the latter remains. When the reaction is complete, generally after approximately 12 hr. of stirring at room temperature, the reaction mixture is filtered to remove the precipitated lithium chloride along with unchanged lithium metal. The solvent then is removed by vacuum distillation from the filtrate to obtain a white solid product. This solid can be sublimed at 100° under a pressure of 10^{-5} mm. and deposits as pure white crystals in the cooler parts of the sublimation apparatus.[3]

The pure crystalline lithiomethyl trimethylsilane thus obtained melts sharply without evident decomposition at 112°. The clear water white liquid is stable below 130° but above this temperature begins to yellow and a slow decomposition into tetramethylsilane and a non-volatile white solid ensues. The apparent stability of the liquid between the temperatures of 112 and 130° is unusual since most of the known solid lithium alkyls melt with appreciable decomposition. The white solid is stable for an indefinitely long period of time at room temperature in the absence of air and moisture. Even in dry air, however, it is extremely pyrophoric.

The compound was characterized by means of its methanolysis wherein a sample weighing 0.0827 g. (0.88 mmole of $LiCH_2Si(CH_3)_3$) reacted rapidly with methanol to produce 0.872 mmole of pure tetramethylsilane.

The apparent molecular weight of resublimed lithiomethyl trimethylsilane in 2-methylpentane solution, obtained by the isopiestic (solvent equilibration) method, was 92, in good agreement with a molecular weight of 94 calculated for the monomer. The behavior of this lithium alkyl in solution thus is in marked contrast to that of the other lithium alkyls so far examined,[4-7] which are extensively associated in solution.

Lithiomethyl trimethylsilane in benzene solution exhibits an n.m.r. spectrum with two proton resonances in a ratio of 4.5 to 1 with an internal shift of -2.16 p.p.m. from the methyl to methylene protons. The methyl proton resonance occurs at -7.07 p.p.m. relative to the benzene proton.

We have been unable to obtain a useful infrared absorption spectrum since the compound reacts readily with fluorolube.

Lithiomethyl trimethylsilane reacts readily with chloromethyl trimethylsilane to form mainly 2,2,5,5-tetramethyl-2,5-disilahexane and tetramethylsilane along with some 2,2,4,4-tetramethyl-2,4-disilahexane and small amounts of less volatile products.

When a heptane solution of the compound is treated with cobaltous chloride, 2,2,5,5-tetramethyl-2,5-disilahexane and tetramethylsilane are the only products.

(3) It occasionally is necessary to repeat this sublimation to obtain samples of lithiomethyl trimethylsilane which are entirely free from coupling side reaction products of low volatility. The presence of these impurities is readily evident since they are liquids at room temperature.

(4) G. Wittig, F. J. Meyer, and G. Lange, *Annalen*, **571**, 167 (1951).

(5) T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957).

(6) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *ibid.*, **84**, 1371 (1962).

(7) M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).

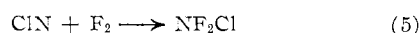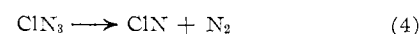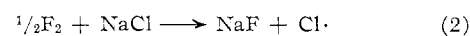## Preparation of Chlorodifluoroamine, NF2Cl[1]

BY T. A. AUSTIN AND R. W. MASON

Recently, Petry[2] reported the preparation of chlorodifluoroamine by the reaction of BCl_3 with HNF_2. We wish to report a new preparation *via* reaction between gaseous F_2 and a mixture of NaN_3 and NaCl.

Two products resulted from this reaction: NF_2Cl and ClN_3. By proper temperature control it was possible to suppress the formation of the latter. When the reactor containing the salt mixture was allowed to remain at ambient temperature, it was found to warm slowly during the passage of fluorine from 20° to about 43°. The product gas contained some NF_2Cl, but also a considerable quantity of ClN_3, which was identified from its infrared spectrum (peaks at 4.4 and 4.8 μ). When the reaction was carried out at 0°, NF_2Cl was the main product and the formation of ClN_3 was completely suppressed. NF_2Cl was also the main product at $-60°$, the lower temperature having the advantage that a higher proportion of NaN_3 could be employed.

The NaN_3:NaCl ratio and the fluorine flow rate affected the vigor of the reaction. If the ratio exceeded 1:4, the reaction was accompanied by frequent explosions within the reactor, and at 1:1 a strong explosion tore the copper reactor apart. If the fluorine rate or concentration exceeded a critical value (dependent on the size of the reactor), the reaction was similarly uncontrollable.

The following reasonable sequence of steps is suggested for the reaction

$$^1/_2F_2 + NaN_3 \longrightarrow NaF + N_3 \cdot \qquad (1)$$

$$^1/_2F_2 + NaCl \longrightarrow NaF + Cl \cdot \qquad (2)$$

$$Cl \cdot + N_3 \cdot \longrightarrow ClN_3 \qquad (3)$$

$$ClN_3 \longrightarrow ClN + N_2 \qquad (4)$$

$$ClN + F_2 \longrightarrow NF_2Cl \qquad (5)$$

Experimental

The apparatus is shown in Fig. 1. A detailed discussion of equipment and the technique for handling fluorine may be found in a recent paper by Gordon and Holloway.[3] An intimate mixture of 2 g. of NaN_3 and 8 g. of NaCl, prepared by grinding the previously dried constituents together in a mortar and pestle, was added to the copper reactor in a drybox. After being connected to the train, the reactor and the Pyrex trap were immersed in a Dry Ice–chloroform bath at $-62°$. Nitrogen, which also was used for preliminary flushing, was passed through the system at a rate of about 5 ml./min. during the reaction. The reaction was initiated with a fluorine flow rate of 10 ml./min. After about 15 min., the inception of reaction was indicated by a

(2) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(3) J. Gordon and F. L. Holloway, *Ind. Eng. Chem.*, **52**, 63A (1960).
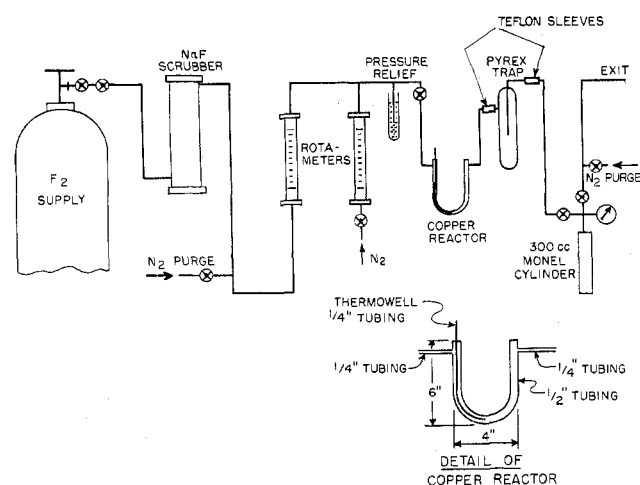
Fig. 1.—Apparatus for preparation of NF$_2$Cl.

temperature rise. The fluorine flow rate then was increased to 25 ml./min. and maintained at that rate until product ceased to be formed (about 2 hr. for the charge given above). The reaction was monitored continuously by running the product gas through an infrared cell before it was condensed in the Monel cylinder. At the completion, the excess fluorine was flushed from the system with nitrogen, the valves on the Monel cylinder closed, and the cylinder permitted to warm to room temperature. The cylinder contained about 8-10 g. of product which consisted of about 50% NF$_2$Cl and 50% Cl$_2$. The Cl$_2$ can be easily removed by bubbling the gas through 5% NaOH solution. After purification, the NF$_2$Cl appears to be unstable to storage in metal cylinders under pressure. On standing for a few hours, the NF$_2$Cl was found to decrease significantly and NF$_3$ to appear (infrared analysis). Therefore, it is recommended that if the product must be stored for a length of time before use, it be kept as a crude material contaminated with Cl$_2$, and then be used directly after purification.

According to reactions 4 and 5, ClN$_3$ should be a useful starting material for NF$_2$Cl. Chlorine azide was generated by dropping dilute phosphoric acid into a solution of NaOCl and NaN$_3$. By means of a slow nitrogen stream the ClN$_3$ was swept into a copper tube reactor cooled to $-20°$. A 1:1 fluorine and nitrogen mixture contacted the ClN$_3$ in the reactor. Then, the gases were passed through an infrared cell. The only gas detected was NF$_2$Cl. The reaction was found to be somewhat erratic, a second run yielding no NF$_2$Cl, but, presumably, only N$_2$, Cl$_2$, and F$_2$.

Acknowledgment.—We wish to thank Professor Robert West and Dr. Abe Maxwell for helpful discussions.

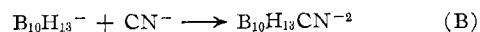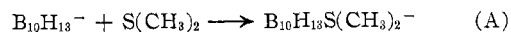## Chemistry of Boranes. VI.[1]
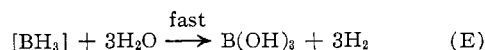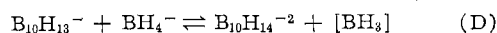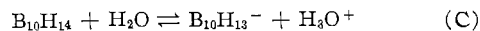## Preparation and Structure of B$_{10}$H$_{14}$$^{-2}$

BY E. L. MUETTERTIES

Received November 24, 1962

We previously[2] have characterized the B$_{10}$H$_{13}$$^-$ anion as an acceptor structure by demonstrating the addition of both neutral and charged donor species to yield B$_{10}$H$_{14}$$^{-2}$ derivatives.

$$B_{10}H_{13}^- + S(CH_3)_2 \longrightarrow B_{10}H_{13}S(CH_3)_2^- \quad (A)$$

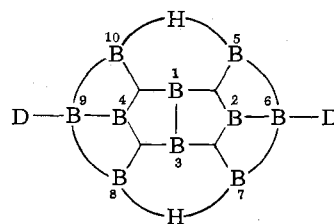$$B_{10}H_{13}^- + CN^- \longrightarrow B_{10}H_{13}CN^{-2} \quad (B)$$

The generality of reaction A to neutral donors, *e.g.*, R$_3$N and R$_3$P, has been reported recently.[3] We now have found that the parent structure B$_{10}$H$_{14}$$^{-2}$ can be prepared in aqueous solution by effective hydride ion transfer from BH$_4$$^-$ to B$_{10}$H$_{13}$$^-$. The reaction simply comprises addition of decaborane to aqueous potassium borohydride, and the reaction sequence may be visualized as

$$B_{10}H_{14} + H_2O \rightleftharpoons B_{10}H_{13}^- + H_3O^+ \quad (C)$$

$$B_{10}H_{13}^- + BH_4^- \rightleftharpoons B_{10}H_{14}^{-2} + [BH_3] \quad (D)$$

$$[BH_3] + 3H_2O \xrightarrow{\text{fast}} B(OH)_3 + 3H_2 \quad (E)$$

A competing reaction that destroys borohydride ion is its acid-catalyzed hydrolysis. However, use of an excess of borohydride ion provides a simple, rapid, and high-yield synthesis of B$_{10}$H$_{14}$$^{-2}$ which is superior from a laboratory standpoint to Na$_2$B$_{10}$H$_{14}$ synthesis from decaborane and sodium in liquid ammonia.[4]

The B$_{10}$H$_{14}$$^{-2}$ anion has moderate stability with respect to hydrolysis in neutral or basic solutions. Saturated aqueous solutions of Rb$_2$B$_{10}$H$_{14}$ degrade slowly to boric acid; the conversion in a period of 4 weeks at $25°$ is about 10–20%. In acid (pH 1–3) solutions of B$_{10}$H$_{14}$$^{-2}$, decomposition as evidenced by hydrogen evolution is quite rapid.

The structure of B$_{10}$H$_{14}$$^{-2}$ has not yet been determined; however, investigations of B$_{10}$H$_{14}$$^{-2}$ derivatives such as B$_{10}$H$_{12}$(NCCH$_3$)$_2$[5] and B$_{10}$H$_{12}$[S(CH$_3$)$_2$]$_2$[6] have established the stereochemistry as depicted topologically below

where D is the donor ligand and each boron atom has a terminal hydrogen atom which is not shown in the structure. Representation of B$_{10}$H$_{14}$$^{-2}$ simply involves replacement of D by H$^-$. We have examined the B^{11} n.m.r. spectra of aqueous solutions of Rb$_2$B$_{10}$H$_{14}$ and find the results consistent with such a structure. In Fig. 1, the B^{11} resonance is reproduced and tentative assignments of peaks are made. On a sweep with a

(1) Paper V: V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

(2) W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

(3) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, **1**, 622 (1962).

(4) R. H. Toeniskoetter, G. W. Schaeffer, E. C. Evers, R. E. Hughes, and G. E. Bagley, Abstracts, 134th National Meeting, American Chemical Society, Chicago, September 7-11, 1958, p. 23-N.

(5) J. M. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 616 (1959).

(6) D. E. Sand and A. Zalkin, *Acta Cryst.*, **15**, 410 (1962).