but has never been isolated from this system, despite considerable effort by investigators.[9] Presumably this is because FC(O)OF is fluorinated much more rapidly than the CO_2, so that reaction leads invariably to $CF_2(OF)_2$ only.

It was therefore of some interest to try to obtain the interesting material FC(O)OF through the stepwise defluorination of $F_2C(OF)_2$. The earlier observation[15] that SF_5OF reacted with COF_2 over a metal fluoride catalyst to produce not the expected SF_5OOCF_3, but rather SOF_4 and CF_3OF, indicated that metal fluoride catalyzed defluorination of fluoroxy compounds was possible.

However, instead of the desired simple defluorination of $F_2C(OF)_2$ to FC(O)OF, the reaction observed in the present study was more complex and can probably be represented by the idealized equation

$$F_2C(OF)_2 + 2F_2CO \longrightarrow CF_3OF + CF_3OOC(O)F \qquad (2)$$

Secondary and/or competing reactions also occur and lead to certain other products, notably CF_3OOOCF_3 and elemental oxygen.

No FC(O)OF was found among the reaction products but the compounds that were obtained are best explained by the defluorination of $F_2C(OF)_2$ followed by immediate reaction of the resultant FC(O)OF with F_2CO. The proposed mechanism is

$$F_2C(OF)_2 + F_2CO \xrightarrow{CsF} CF_3OF + FC(O)OF \qquad (3)$$

$$FC(O)OF + F_2CO \xrightarrow{CsF} CF_3OOC(O)F \qquad (4)$$

In support of this the following facts should be noted: (a) CF_3OF and $CF_3OOC(O)F$ are the principal products of the reaction; (b) fluorination of carbonyl fluoride did occur and consequently defluorination of $F_2C(OF)_2$ must also have occurred; (c) no carbon dioxide was found among the reaction products so that the defluorination of $F_2C(OF)_2$ must have proceeded only to an intermediate stage, namely, FC(O)OF; (d) the reaction of FC(O)OF with F_2CO to produce a peroxidic structure has precedent in the preparation of CF_3OOCF_3[16] and CF_3OOOCF_3;[4] formation of the latter materials effectively involves the insertion of F_2CO into an O–F bond. (In the CF_3OOOCF_3 case, as well as in the present preparation of $CF_3OOC(O)F$, this is probably achieved through displacement of the fluorine of the fluoroxy grouping by trifluoromethoxide ion.)

The reaction time was found to be critical. Yields of $CF_3OOC(O)F$ reached a maximum at about 3 hr and declined thereafter. After a 24-hr period, no $CF_3OOC(O)F$ remained but a small amount of CF_3OOOCF_3 was found. Apparently $CF_3OOC(O)F$ reacts further, but the mechanism and whether or not it is the direct precursor of CF_3OOOCF_3 are uncertain.

The obvious extension of this reaction to the oxidation of $CF_3C(O)F$ and $(CF_3)_2CO$ with $F_2C(OF)_2$ was attempted, but the results were inconclusive. In the particular case of the reaction of $CF_3C(O)F$ with $F_2C(OF)_2$ over cesium fluoride, two products were obtained with the requisite carbonyl stretching frequency in the infrared, but we were unable to separate and identify either material to confirm the existence of the desired $C_2F_5OOC(O)F$. Hexafluoroacetone gave an even more complex mixture of products. It seems likely, however, that if the proposed mechanism is correct, then other reactions of FC(O)OF formed *in situ* may be found.

Caution! Although we have experienced no explosions while working with the peroxides and fluoroxy compounds described here, it should be recognized that these are powerful oxidants and that proper shielding should be used at all times while they are being handled.

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Studies of Boron-Nitrogen Compounds. X. μ-Dimethylaminomethyldiborane

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Although μ-aminodiborane has been known since 1938[1] and a variety of N-substituted derivatives have been prepared,[2-5] there appear to be no known B-substituted derivatives. In relation to the preparation of selectively substituted borazoles and borazanes it seemed desirable to investigate the preparation of B-substituted μ-aminodiboranes since these materials offer one logical starting point in a systematic synthesis of the cyclic compounds. We report here the first example of a B-substituted μ-aminodiborane, μ-dimethylaminomethyldiborane, which has been prepared from μ-dimethylaminodiborane both by a gas-phase exchange using trimethylboron and by reaction with methyl Grignard reagent in ethereal solution.

Experimental Section

The exchange with trimethylboron was carried out for 0.5 hr at 140° in a sealed 1-l. bulb containing approximately 30 mmol of μ-dimethylaminodiborane and 3–4 mmol of trimethylboron. The product was isolated by vacuum distillation of the reaction mixture through a Dry Ice cooled trap, which retained the product as well as some starting material, followed by final purification of the material held in this trap using a low-temperature fractionation column, Figure 1. About 7 mmol of pure product was finally recovered.

Figure 1 is given as a guide to the type of apparatus which has been employed in numerous studies in this laboratory. Several variations upon it have been made and proved useful for specific separation problems.

The mixture to be separated is introduced at the bottom of the column, prechilled to a temperature below which the most volatile component will distil, and the temperature slowly is raised to collect the fractions as they distil in order of volatility from the

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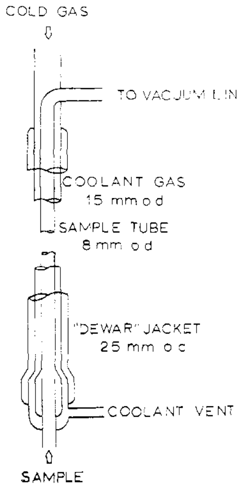

Figure 1.—Low-temperature fractionation column.

column. The pressure in the system is maintained as low as possible by continuous evacuation through a liquid nitrogen cooled trap located as near the head of the column as possible.

The lengths of the columns used have been approximately 1 m and the temperature gradient from top to bottom about 10–30° depending upon the rate of coolant flow (and thus, indirectly, the temperature). Lower temperature gradients can be obtained by applying a silver mirror to the dewar jacket; however, this has been felt unnecessary and less desirable than the ability visually to follow the bands of material on the column walls. Cold gas was supplied from a large dewar of liquid nitrogen in which the rate of heat leakage was regulated by a submerged, Variac-controlled resistance heater. Liquid nitrogen consumption varied from about 3–4 l./hr when operating at temperatures of about $-100°$ to about 1 l./hr in the $-30°$ range. Using well-insulated delivery tubes the lower temperature limit obtainable is nearly that of liquid nitrogen although the consumption becomes quite high.

In the preparation *via* the Grignard method, μ-dimethylaminodiborane was condensed into a bulb containing an equimolar quantity of methylmagnesium iodide in diethyl ether solution. The reaction was carried out at room temperature for about 2 hr; only traces of noncondensable gas were detected upon vacuum removal of the volatile products. The bulk of the diethyl ether was stripped off by fractional condensation using a Dry Ice cooled trap and the residue in the trap was further purified as described above.

The purified material had a vapor pressure of 31.0 mm at 0° and a melting range of -94.5 to $-95.3°$ (Stock plunger method). Analysis for boron content was carried out by fuming nitric acid oxidation and titration of the resulting boric acid by the method of identical pH. *Anal.* Calcd: B, 25.5. Found: B, 25.0. Hydridic hydrogen was determined by hydrolysis at 100° and yielded 4.10 mol of hydrogen per mole of sample, in reasonable agreement with 4.0 expected from the reaction $B_2H_4CH_3N(CH_3)_2 + 5H_2O \rightarrow B(OH)_3 + H_3CB(OH)_2 + HN(CH_3)_2 + 4H_2$. The vapor density molecular weight, 83.2, agreed adequately with the calculated 84.8 and the mass spectrum showed a sharp cutoff at m/e 85, $^{11}B_2H_4CH_3N(CH_3)_2^+$, with only exceedingly weak peaks at higher masses, probably caused by trace impurities.

The 19.3-MHz ^{11}B nmr spectrum of μ-dimethylaminomethyldiborane exhibited an interesting temperature dependence. At temperatures above about $-30°$ the spectrum was composed of, respectively, overlapping doublet and quartet resonances [$\delta(BF_3\cdot O(C_2H_5)_2)$, J(cps)]: 10.0, 126; 14.8, 97. When the sample was cooled below about $-34°$, the quartet structure began to collapse and at $-55°$ resolved to a 1:2:1 triplet of doublets, while the original doublet resonance had remained unaffected. These changes clearly suggest a change in molecular structure from an unbridged, linear system terminated by BH_3 and $BHCH_3$ groups at higher temperatures to a cyclic hydrogen-bridged structure at lower temperatures.

In contrast, it should be noted that μ-dimethylaminodiborane does not undergo a reversible bridge cleavage until brought to relatively elevated temperatures in the presence of weak Lewis bases.[6-8] The lifetime of the unbridged species under these conditions is also very much shorter since, in the limit, a complete equilibration of boron-bound protons was observed in the nmr time scale (about 10^{-3} sec).[8] The substituted case is strikingly different in that the higher temperature spectra indicate that the lifetime of the unbridged species is at least long compared to milliseconds and also that the bridge opening is always in the same direction, *i.e.*, toward the unsubstituted boron.

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Iron Carbonyl Complexes of Azo Compounds[1]

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Prior to 1963 the literature contained very little information on azo groups involved in delocalized bonding with transition metals apart from some azo dye metal chelates. In 1963, Kleiman and Dubeck reported[3] on the reaction of azobenzene and dicyclopentadienylnickel to yield a complex involving nickel bonded to the azo link and to one aromatic ring. In 1965, Cope and Siekman[4] found similar Pt and Pd complexes of azobenzene and substituted azobenzenes. In the same year Porter and Murray[5] examined $PdCl_2$ and $AgNO_3$ complexes of benzo[*c*]cinnoline (**1**), a compound containing a *cis*-azo link, but did not propose any structure for these complexes. Balch and Petridia[6] recently described azo complexes of Pd in which only one nitrogen was thought to be involved in bonding to the metal. Pauson[7] reported on complexes of Schiff bases and of azobenzene with $Fe_2(CO)_9$. The Schiff base complexes are analogous to Cope's complexes involving substitution of iron into the *ortho* position of the aromatic ring. The original communication reported that the azobenzene complex underwent rearrangement to *o*-semidine on lithium aluminum hydride reduction.

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