hind the very reactive $N^-$ (C) species, which must behave chemically very much like $[N_2^{2-}]$

$$\mathrm{Mo^{V}Cl_5} + [|\underline{\mathrm{N}}{=}\mathrm{N}{=}\underline{\mathrm{N}}|]^- \longrightarrow \underset{\mathrm{A}}{[\mathrm{Cl_5Mo^{V}}{-}\overline{\mathrm{N}}{=}\mathrm{N}{=}\underline{\mathrm{N}}|]^-}$$

$$\underset{\mathrm{B}}{[\mathrm{Cl_5Mo^{V}}{-}\mathrm{N}\cdots\mathrm{N}{\equiv}\mathrm{N}]^-} \longrightarrow \underset{\mathrm{C}}{[\mathrm{Cl_5Mo^{V}N}]^-} + \mathrm{N_2}$$

The $N^-$ species then is reduced by molybdenum and chloride to the $N^{3-}$ species which remains strongly coordinated to the metal

$$[\mathrm{Mo^{V}NCl_5}]^- \longrightarrow \underset{\mathrm{D}}{[\mathrm{Mo^{VI}NCl_4}]^-} + {}^1/_2\mathrm{Cl_2}$$

In the case of the reaction of molybdenum(IV) chloride with azide, a similar initial product must be formed, *i.e.*, $MoCl_4N_3^-$. However, in this case the molybdenum(IV) intermediate $MoNCl_4^-$ can go to the molybdenum(VI) intermediate of the same formula without losing chlorine since two electrons can be transferred from the metal to the nitrogen.

Hydrolysis of the nitrido complex must proceed similarly to that of intermediates proposed by Van Tamelen[11] in the fixation of nitrogen by "titanocene." Nessel's reagent gives a strong positive test for ammonia and yields were around 40%.

No end products were isolated but they must contain $MoO^{4+}$ or $MoO_2^{2+}$ species. It is interesting to note that the ammonia produced by the hydrolysis of the molybdenum nitrido complex does not coordinate to the molybdenum even though there is a coordination position in the nitrido complex.

Further work with other nitrido complexes is presently under way. Similar preliminary results have been found for vanadium(III) and vanadium(IV).

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# Rearrangement of Dimethylchloromethylborane with Nucleophiles

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Previous work from this laboratory reported[1] that treatment of dimethylchloromethylborane (I) with water or lithium azide yields hydroxymethyldimethylborane and azidomethyldimethylborane, respectively. It was also reported that catalytic hydrogenation of the product from the reaction of I with lithium azide yields aminomethyldimethylborane. We have found that these compounds were incorrectly formulated and that the actual structures are ethylated trigonal boranes, $XB(CH_3)C_2H_5$, with the substituent bonded to boron. These arise from an alkyl rearrangement similar to those encountered by other workers.[2,3] Further, isomerization of I in the presence of $SbCl_5$ leads cleanly to methylethylboron chloride (II). In order to clarify the earlier results, the reactions of I and II with several nucleophiles were studied.

## Experimental Section

**Apparatus and Materials.**—All reactions were performed using standard high-vacuum techniques described elsewhere.[4] The $^1H$ nmr spectra were recorded on a Varian Associates A-60 or HR-220 spectrometer. The $^{11}B$ nmr spectra were measured on a Varian Associates HA-100 spectrometer at 32.1 MHz. Mass spectra were measured on a Varian Associates MAT CH-7 mass spectrometer. Dimethylamine, trimethylamine, and methyl mercaptan were purchased from the Matheson Co. in cylinders and used without further purification. Lithium azide (Eastman) was dried under vacuum. Dimethylarsine, dimethylphosphine, trimethylphosphine, and dimethylchloromethylborane were prepared by literature procedures.[5-7]

**Preparations.**—In a typical reaction I or II (1.5–3.0 mmol) and a nucleophile were sealed into a Pyrex tube equipped with a break-seal. Equimolar quantities of reactants were used in all cases except for the reactions of I with dimethylamine or potassium iodide wherein twofold and tenfold excesses of nucleophile were used, respectively. After reaction the tube was opened to a vacuum line and the products were separated by trap to trap distillation or fractional sublimation. Reaction conditions and products are summarized in Table I.

TABLE I

REACTION CONDITIONS AND PRODUCT DATA

| Reactants | Reaction conditions | Product | Yield, % | 0° vapor pressure, mm |
|---|---|---|---|---|
| I + $(CH_3)_2NH$ | *a* | $CH_3(C_2H_5)BN(CH_3)_2$ | 89 | 14 |
| I + $CH_3OH$ | *a* | $CH_3(C_2H_5)BOCH_3$ | 84 | 67 |
| I + $SbF_3$ | *a* | $CH_3(C_2H_5)BF$ | 91 | 21[e] |
| I + $SbCl_5$ | *a* | $CH_3(C_2H_5)BCl$ | 98 | 115 |
| I + KI | *b* | $(CH_3)_2BCH_2I$ | 40 | 11 |
| I + $(CH_3)_2PH$ | *c* | $(CH_3)_2BCH_2P(CH_3)_2$ | 62 | *f* |
| I + $(CH_3)_2AsH$ | *c* | $(CH_3)_2BCH_2As(CH_3)_2$ | 68 | *f* |
| I + $CH_3SH$ | *c* | $(CH_3)_2BCH_2SCH_3$ | 80 | *f* |
| II + $LiN_3$ | *d* | $CH_3(C_2H_5)BN_3$ | 94 | 4 |
| II + $H_2O$ | *a* | $CH_3(C_2H_5)BOH$ | 90 | 16 |

[a] At 80° for 30 min. [b] At 0° for 60 min; acetone solvent. [c] At 100° for 90 min. [d] At 50° for 180 min. [e] At −63°. [f] Solid of low vapor pressure.

## Results and Discussion

Treatment of I with nucleophiles yields B-substituted methylethylboranes by alkyl rearrangement or α-substituted methylboranes without rearrangement. The methylethylboranes were identified by comparison of their proton and boron chemical shift values (Table II) with those of analogous dimethyl- and diethyl-substituted boranes. In all cases agreement was found with literature values.[8] The rearranged compounds were also identified by their mass spectral fragmentation patterns. Intense peaks at masses corresponding to $CH_3BX$ and $C_2H_5BX$ fragments (where X is derived from the nucleophile) occurred as expected in each case. Supporting chemical evidence for the rearranged structures of the azido-[9] and hydroxo-substituted boranes is given by their preparations from either I or II.[10] The proton nmr spectra (Table II) of the α-substituted

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(9) The previously reported aminoo compound was prepared from this azide and is therefore also rearranged.

(10) Hydrogen peroxide causes rearrangement of I prior to oxidation and therefore is not a useful reagent for distinguishing rearranged and unrearranged structures.

TABLE II
$^1$H AND $^{11}$B NMR CHEMICAL SHIFT VALUES

| Compound | B–CH$_3$[a] | B–C$_2$H$_5$[b] | X–CH$_3$ | B–CH$_2$–X | $^{11}$B[c] |
|---|---|---|---|---|---|
| $CH_3(C_2H_5)BNH_2$[d] | −0.23 s | −0.85 s | | | −48.4 s |
| $CH_3(C_2H_5)BN(CH_3)_2$ | −0.27 s | −0.86 s | −2.78 s | | −45.6 s |
| $CH_3(C_2H_5)BN_3$ | −0.6 s | −0.0 s | | | −62.8 s |
| $CH_3(C_2H_5)BOH$[e] | −0.34 s | −0.89 s | | | −55.3 s |
| $CH_3(C_2H_5)BOCH_3$ | −0.32 s | −0.85 s | −3.60 s | | −53.8 s |
| $CH_3(C_2H_5)BF$ | −0.4 d (13 Hz) | −0.95 s | | | −56.4 d (122 Hz) |
| $CH_3(C_2H_5)BCl$ | −0.95 s | [f] | | | −30.1 s |
| $(CH_3)_2BCH_2P(CH_3)_2$[g] | +0.26 d (15 Hz) | | −1.04 d (9.4 Hz) | −0.57[h] | +19.0 d (55.4 Hz) |
| $(CH_3)_2BCH_2As(CH_3)_2$[g] | −0.04 s | | −1.08 s | −1.02 s | −6.1 s |
| $(CH_3)_2BCH_2SCH_3$[g] | +0.08 s | | −1.98 s | −1.84 s | +4.0 s |
| $(CH_3)_2BCH_2Cl$ | −0.9 s | | | −3.4 s | −84.1 s |
| $(CH_3)_2BCH_2I$ | −0.95 s | | | −2.83 s | −70.6 s |

[a] $^1$H nmr chemical shifts are in ppm without solvent relative to internal tetramethylsilane. [b] At 60 MHz the ethyl protons are equivalent. Peak widths at half-height varied from 4 to 6 Hz. [c] The $^{11}$B nmr chemical shifts are in ppm relative to external $BF_3 \cdot O(C_2H_5)_2$. [d] δ(N–H) −3.55 (t, 54 Hz). [e] δ(O–H) −6.56 (s). [f] At 220 MHz the ethyl protons were resolved with the following chemical shifts: δ(CH$_2$–C) −1.34 (q, 7.5 Hz), δ(C–CH$_3$) −1.05 (5, 7.5 Hz). [g] Chloroform solvent. [h] Unresolved coupling.

methylboranes establish the structure of these compounds. The spectra show the expected upfield methyl resonances of area 6 and downfield methylene resonances of area 2. The mass spectra of the $(CH_3)_2BCH_2X$ derivatives show a strong peak at mass 41 corresponding to a $(CH_3)_2B$ fragment which does not occur in the spectra of the methylethylboranes. The high-field boron resonances of $(CH_3)_2BCH_2P(CH_3)_2$, $(CH_3)_2BCH_2As(CH_3)_2$, and $(CH_3)_2BCH_2SCH_3$ suggest that these materials are associated in solution. However, molecular weight determinations (Table III) show that only the phosphorus compound exists as the expected dimer in the vapor phase.

TABLE III
VAPOR DENSITY AND MASS SPECTRAL MOLECULAR WEIGHTS

| Compound | Calcd mol wt | Vapor density mol wt[a] | Mass spectral molecular ion |
|---|---|---|---|
| $CH_3(C_2H_5)BN(CH_3)_2$ | 98.9 | 99.5 | 99 |
| $CH_3(C_2H_5)BOCH_3$ | 85.9 | 85.9 | 86 |
| $CH_3(C_2H_5)BF$ | 73.9 | 74.5 | 74 |
| $CH_3(C_2H_5)BCl$ | 90.4 | 91.0 | 90 |
| $(CH_3)_2BCH_2P(CH_3)_2$ | 232[b] | | 232 |
| $(CH_3)_2BCH_2As(CH_3)_2$ | 160 | 162[c] | 160 |
| $(CH_3)_2BCH_2SCH_3$ | 102 | 112[c] | 102 |
| $(CH_3)_2BCH_2I$ | 182 | 180 | 182 |

[a] Measured at room temperature. [b] Calculated for dimer. [c] Measured at 125°.

The substitution reactions of α-haloalkylboronic esters occur with rate enhancement to give α-substituted alkylboronic esters as shown by Matteson.[3] In view of these results we believe that although extensive alkyl rearrangement might occur in treatment of I with nucleophiles it would be possible to isolate at least some α-substituted methylboranes as by-products from these reactions. Since high electron density on boron would appear to facilitate the rearrangement, weakly basic nucleophiles were used in all cases. Even though the use of high-vacuum techniques in these experiments allowed investigation of trace products from these reactions, α-substituted methylboranes were observed only in the cases of $(CH_3)_2PH$, $(CH_3)_2AsH$, $CH_3SH$, and KI. With these nucleophiles the yields of the α-substituted compounds were good and no rearranged products were observed.

In view of the correct structure of the azido compound, the earlier observation that this material decomposes upon pyrolysis to a mixture of borazines is now much more easily understood. Pyrolysis of other *B*-azidoboranes is known to give borazines.[11]

Trimethylamine and trimethylphosphine form adducts with I which were not completely characterized. When equivalent amounts of trimethylamine and I were condensed directly into an nmr tube with chloroform, the proton nmr spectrum showed the presence of trimethylamine adducts of both I and II. The trimethylamine adduct of I, however, could not be isolated due to its facile rearrangement to form the trimethylamine adduct of II (mp 68–70°). Similar experiments with trimethylphosphine resulted only in the isolation of the trimethylphosphine adduct of I (mp 99–100°) which was sublimed at 80° without significant rearrangement.

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# The Preparation of Bis(sulfinylamino) Sulfide (Trisulfur Dinitrogen Dioxide)

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The structure determination of trisulfur dinitrogen dioxide[1] showed it to be a sulfinylamino derivative of bivalent sulfur, $S(NSO)_2$. A number of methods of preparation have been reported which involve oxides or halides of sulfur with ammonia, ammonium chloride, or tetrasulfur tetranitride.[2-6] Yields are low and separation of the amino sulfide is often difficult.

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