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Nitrogen Ylides. V.[1] Coordination Chemistry of Trimethylammonium Methylide[2]

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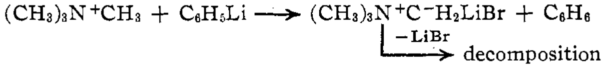
The coordination chemistry of trimethylammonium methylide, $(CH_3)_3N^+C^-H_2$, with various Lewis acids is examined. The crystalline BF_3 complex $(CH_3)_3N^+CH_2B^-F_3$ appears to ionize in nitromethane giving $[(CH_3)_3N^+CH_2BF_2]F^-$ and decomposes thermally giving $(CH_3)_3NBF_3$ and ethylene. The BCl_3 complex was prepared and characterized by nmr but it could not be purified. No BH_3 complex could be detected chemically or spectroscopically. Trialkylborane adducts can be prepared, but they undergo a rearrangement to give products resulting from methylene insertion into the B–C bond. The $Al(CH_3)_3$ complex was isolated and was also found to rearrange when heated to 120° to give products which can be considered to result from a methylene insertion into the Al–C bond. The latter rearrangement is rather unusual in aluminum chemistry. Compounds of the following type were also isolated: $[(CH_3)_3N^+CH_2M(CH_3)_3]Br^-$, where M = Si, Ge, Sn. The silicon and germanium compounds decompose thermally by N-demethylation whereas the tin complex decomposes giving trimethylamine, trimethylbromostannane, and, presumably, polymethylene. Complexes with dipentylzinc were not observed, and two mercury-containing complexes could not be purified. The behavior of nitrogen ylide adducts is compared with phosphorus and arsenic ylide adducts.

In 1947, Wittig[3] observed that the treatment of tetramethylammonium bromide with phenyllithium in ether results in proton abstraction giving a nitrogen ylide, trimethylammonium methylide, $(CH_3)_3N^+C^-H_2$. The ylide is stabilized by 1 mol of lithium bromide and, if the lithium bromide is removed by adding 1,2-dimethoxyethane[4] or if phenylsodium is used in the preparation, the ylide decomposes.[5] The lithium bromide complex can be considered as an organolithium reagent because it reacts with carbonyl compounds to give aminoalcohols, exchanges with organomercurials, and undergoes typical reactions of organolithium reagents.[6] On the basis of this behavior, Daniel and Paetsch[7] formulated the reagent as $[(CH_3)_3N^+CH_2Li]Br^-$; however, since anion solvation in ethers is not extensive and a change of the anion from bromide to iodide[3] markedly changes the properties of the ylide, perhaps the formulation $(CH_3)_3N^+C^-H_2$-LiBr more accurately describes the reagent. In this representation the reagent can be considered as a lithium bromide adduct of a dipolar nitrogen ylide.



$$(CH_3)_3N^+CH_3 + C_6H_5Li \longrightarrow (CH_3)_3N^+C^-H_2LiBr + C_6H_6 \xrightarrow{-LiBr} \text{decomposition}$$

Although the chemical characteristics of trimethylammonium methylide and its lithium halide adducts have been studied in some detail,[8] the chemistry of the phosphorus ylide, methylenetriphenylphosphorane, has undergone a much more detailed investigation since its discovery in 1949 by Wittig and Reiber.[9] This more thorough study of the phosphorus ylide is due primarily to its greater stability in solution, its greater ease of preparation, and its greater synthetic utility (Wittig reagent) compared to the same characteristics of trimethylammonium methylide.[8]

Investigations concerning the reactivity of methylenetriphenylphosphorane[10,11] and methylenetriphenylarsenane[12] toward such Lewis acids as borane, boron halides, and a few organoboranes have demonstrated that betaine-like salts are formed in which the ylide is coordinated to and stabilized by the Lewis acid with which it reacts as shown in

$$(C_6H_5)_3P^+C^-H_2 + BX_3 \xrightarrow{\text{ether}} (C_6H_5)_3P^+CH_2B^-X_3$$

where X = H, F, Cl, C_6H_5. In addition, these phosphorus and arsenic ylides were found to react with organometallic halides of group IV metals[13,14] to form organometallic-substituted phosphonium salts by a displacement mechanism which may have involved initial coordination of the ylide to the metal

$$(C_6H_5)_3P^+C^-H_2 + (CH_3)_3MBr \longrightarrow [(C_6H_5)_3P^+CH_2M(CH_3)_3]Br^-$$

where M = Si, Ge, Sn.

It was therefore of interest to investigate the reactions of trimethylammonium methylide with similar Lewis acids and organometallic halides of group IV metals in an effort to characterize and compare nitrogen ylide adducts with similar phosphorus and arsenic ylide adducts.

Experimental Section

The **vacuum line** was of a standard design, equipped with a three-trap manifold, two mercury manometers, and a cyclic system which included a Toepler pump with automatic control and a calibrated gas buret. **Melting points** are uncorrected and were measured in capillary tubes using a Thomas-Hoover capillary melting point apparatus. **Infrared spectra** were recorded

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[1] Part IV: W. K. Musker and R. R. Stevens, *J. Am. Chem. Soc.*, **90**, 3515 (1968).

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[3] G. Wittig and M. Wetterling, *Ann.*, **557**, 193 (1947).

[4] G. Wittig, *Naturwissenschaften*, **30**, 696 (1942).

[5] G. Wittig and R. Polster, *Ann.*, **599**, 1 (1956).

[6] F. Weygand, H. Daniel, and A. Schroll, *Ber.*, **97**, 1217 (1964).

[7] H. Daniel and J. Paetsch, *ibid.*, **98**, 1915 (1965).

[8] W. K. Musker, *J. Chem. Educ.*, **45**, 200 (1968).

[9] G. Wittig and M. Reiber, *Ann.*, **562**, 177 (1949).

[10] D. Seyferth and S. O. Grim, *J. Am. Chem. Soc.*, **83**, 1613 (1961).

[11] M. F. Hawthorne, *ibid.*, **83**, 367 (1961).

[12] D. Seyferth and H. M. Cohen, *J. Inorg. Nucl. Chem.*, **20**, 73 (1961).

[13] W. Schlenk and J. Holtz, *Ber.*, **49**, 603 (1916).

[14] D. Seyferth and S. O. Grim, *J. Am. Chem. Soc.*, **83**, 1610 (1961).

with Beckman IR-4 and Perkin-Elmer 237B spectrophotometers. **Nuclear magnetic resonance spectra** were recorded using a Varian Associates A-60A nmr spectrometer. **Vapor phase chromatography** was performed using an Aerograph A-90-P chromatograph and a Honeywell nonintegrating recorder. **Elemental analyses** were performed by the Microanalytical Laboratory, University of California, Berkeley, Calif.

Preparation of the Trimethylammonium Methylide Lithium Bromide Complex (General Procedure).—Phenyllithium was prepared according to the method of Gilman and Morton.[15] The freshly prepared solution of phenyllithium was filtered in the drybox into a 500-ml, round-bottom flask, containing 50 g (325 mmol) of powdered tetramethylammonium bromide which had previously been dried for 24 hr at 150° under high vacuum. The flask, which had a tight constriction in the neck, was evacuated, cooled to −78° in a Dry Ice–acetone bath, and sealed at the constriction using a gas–oxygen torch. After warming to room temperature, the flask was placed on an automatic shaker and shaken vigorously for 5 days.

The flask was opened in the drybox, and the solid material was filtered by suction into a large Büchner funnel and washed with 300 ml of anhydrous diethyl ether to remove unreacted phenyllithium, lithium nitride, and any dimetalation product which had formed. Owing to its ready reaction with oxygen or water vapor, the white solid was stored and used in the drybox after drying under high vacuum at room temperature.

To ascertain the purity of the trimethylammonium methylide, weighed samples were placed in distilled water and titrated with 0.57 *N* HCl to a phenolphthalein end point. In all titrations of random samples of the white solid, the equivalent weight was approximately half that calculated for the lithium bromide complex of trimethylammonium methylide. The product obtained was, therefore, assumed to be between 49 and 51% pure ylide complex when samples were weighed out for various reactions. In subsequent pages describing experimental details, this impure material will be referred to as "solid ylide."

Preparation of Tetrahydrofuran Solutions of the Trimethylammonium Methylide Lithium Bromide Complex (General Procedure).—In the drybox, 5.0-g samples of "solid ylide" were weighed into each of two dry, 50-ml centrifuge tubes. Large rubber septums were wired over the tops of each of the tubes, and the tubes were cooled in an ice bath after being connected to a dry nitrogen line by the use of long syringe needles. Using a large syringe, 30 ml of anhydrous tetrahydrofuran was injected into each of the tubes while they remained in the ice bath. Cooling is required to prevent premature decomposition of the ylide because its dissolution in tetrahydrofuran is quite exothermic. After addition of the tetrahydrofuran solvent, the tubes were placed on a shaker and shaken vigorously for 10 min. All insoluble material was removed by centrifuging for 5 min. A light yellow solution was left which decomposed quite rapidly at room temperature with the evolution of trimethylamine and the formation of an amorphous precipitate. The yellow solution was removed with a syringe and a portion was titrated with 0.57 *N* HCl to a bromothymol blue end point to determine its normality. The required amount of remaining solution was then used in the particular reaction being carried out. The solutions prepared in this manner usually had normalities ranging between 0.5 and 0.6 *N* and hereafter will be referred to as "ylide solution."

Reaction with Boron Trifluoride.—A solution of 10 g (147 mmol) of boron trifluoride in 40 ml of anhydrous 1,2-dimethoxyethane was prepared by allowing gaseous boron trifluoride to expand slowly into a flask containing the solvent which had been cooled to −78° on the vacuum line. The 1,2-dimethoxyethane was stirred vigorously and the gas was added very slowly in order to prevent formation of decomposition products which cause the solution to become dark brown.

A suspension of ylide in 1,2-dimethoxyethane was prepared by first placing 8.0 g (25 mmol) of "solid ylide" in a dry, 150-ml round-bottom flask equipped with a magnetic stirrer and a side arm sealed with a rubber septum. The flask was connected to a dry nitrogen inlet and cooled to −78°. With vigorous stirring, 40 ml of anhydrous 1,2-dimethoxyethane was slowly injected into the flask using a large syringe. The previously prepared 1,2-dimethoxyethane solution of boron trifluoride (147 mmol) was injected into the ylide suspension. The mixture was warmed slowly to room temperature and stirred for 24 hr.

The reaction mixture was cooled to 0°, and all of the solid material was removed by filtration and washed with 20 ml of cold 1,2-dimethoxyethane in the drybox. After drying under vacuum, the solid product was placed in a Soxhlet extractor, kept under a positive pressure of dry nitrogen, and extracted with 100 ml of anhydrous methylene chloride for 5 hr. The volume of methylene chloride was reduced to about 40 ml on a rotary evaporator. Cooling the remaining solution to 0° resulted in the formation of a white, crystalline solid. The solid was filtered in the drybox and dried under vacuum to give 1.6 g of white, crystalline product, mp 207–211°. Recrystallization of the impure material from anhydrous methanol gave 1.4 g (10 mmol) of material having properties consistent with the boron trifluoride adduct of trimethylammonium methylide: mp 215–216°; ir spectrum (KBr pellet): 3000, 2950 (C–H), 1475 ($C-N^+$), 1350 (B–C), 1060, 945, and 865 cm^{-1} (B–F); nmr spectrum (nitromethane): δ 2.51 (s, 9, $N(CH_3)_3$), δ 1.77 (t, 2, $J = 10$ Hz, NCH_2B); the ^{11}B nmr spectrum (nitromethane) showed the singlet $\delta + 1.5$ with respect to $BF_3O(C_2H_5)_2$. *Anal.* Calcd for $C_4H_{11}BF_3N$: C, 34.10; H, 7.82; N, 9.94. Found: C, 34.16; H, 7.64; N, 9.91.

Pyrolysis of the Boron Trifluoride Adduct of Trimethylammonium Methylide.—A small sample of the adduct, 0.2 g (1.4 mmol), was sealed in an evacuated glass tube equipped with a breakable, sealed, standard-tapered side arm. The lower half of the tube was immersed in an oil bath at 275° for 15 hr. The solid immediately melted when the tube was placed in the heating bath and the melt slowly decomposed as evidenced by slow bubbling and the formation of long needlelike crystals in the cool part of the pyrolysis tube.

The tube was connected to the vacuum line *via* a tube-breaking apparatus[16] and opened to allow the gaseous decomposition products to pass through a trap cooled to −78° and into a Toepler pump. A total of 0.53 mmol of gas was collected. The infrared spectrum of the gas was identical with an infrared spectrum of pure ethylene. Since nothing was collected in the trap at −78° through which all of the ethylene had passed, no higher boiling or easily sublimable products appeared to be present. The needlelike crystals remaining in the pyrolysis tube were dissolved and recrystallized from anhydrous methanol to give 0.09 g (0.7 mmol) of trimethylamine–trifluoroborane, mp 144–146° (lit.[17] mp 146°). The infrared spectrum of the amine–borane was identical with that of an authentic sample.

Reaction with Boron Trichloride.—This reaction was carried out in exactly the same manner as that described for the reaction of boron trifluoride with the ylide. After extraction with methylene chloride, 1.3 g of an impure, white solid was obtained. The material softened at 180° and melted with decomposition at 200°. Attempts to recrystallize the product from methanol, ethanol, nitromethane, or water were unsuccessful. In each case only a gray, gummy resin was recovered after dissolution of the product in the hot solvent. No other solvents were found which would dissolve the impure product.

The infrared spectrum (KBr pellet) of the impure product showed strong absorption bands, centered at 2930 (C–H), 1475 ($C-N^+$), 1375, 1325 (B–C or B–N), and 880 cm^{-1} (B–Cl); nmr spectrum (deuterium oxide): δ 3.15 (s, 9, $N(CH_3)_3$), δ 2.45 (s, 1.8H, NCH_2B). *Anal.* Calcd for $C_4H_{11}BCl_3N$: C, 25.2; H, 5.78; N, 7.35. Found: C, 27.1; H, 6.51; N, 8.04.

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(15) H. Gilman and J. W. Morton, *Org. Reactions*, **8**, 286 (1954).

(16) R. E. Dodd and P. L. Robinson, "Experimental Inorganic Chemistry," 1st ed, Elsevier Publishing Co., New York, N. Y., 1954, p 110.

(17) G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 146 (1945).

Reaction of the Trimethylammonium Methylide Boron Trifluoride Adduct with Butyllithium.—Into a 50-ml, round-bottom flask, equipped with a magnetic stirrer and a side arm sealed with a rubber septum, was placed 0.28 g (2 mmol) of the ylide adduct of boron trifluoride, 10 ml of anhydrous tetrahydrofuran, and 10 ml of anhydrous 1,2-dimethoxyethane. The flask was maintained under a nitrogen atmosphere, and 4 ml of 1.5 *N* butyllithium in diethyl ether was slowly injected into the suspension of adduct with vigorous stirring. As the butyllithium was added, the ylide adduct seemed to dissolve, but this was masked by formation of another white, insoluble solid, probably lithium fluoride. After addition of all of the butyllithium, the reaction mixture was stirred at room temperature for 6 hr. The solution was then basified with 2 ml of 3 *N* sodium hydroxide, oxidized with 2 ml of 30% hydrogen peroxide, saturated with sodium carbonate, and extracted with diethyl ether. After drying over magnesium sulfate, the ether extract was analyzed by gas chromatography using a 5-ft aluminum column, packed with 20% Carbowax 20 M, supported on 60–80 mesh Chromosorb W at 110°. The chromatogram indicated that neither 1-butanol nor 1-pentanol was present.

Reaction with Trihexylborane.—Trihexylborane was prepared as described by Zweifel and Brown.[18] A suspension of 3.0 g (8.8 mmol) of solid ylide in 25 ml of anhydrous 1,2-dimethoxyethane at −78° was prepared in a 150-ml, round-bottom flask, equipped with a condenser, a dry-nitrogen inlet, and a side arm sealed with a rubber septum. The previously prepared solution of trihexylborane in tetrahydrofuran was slowly injected into the suspension of ylide which was maintained at −78° in a Dry Ice–acetone bath. As the reaction mixture was allowed to warm slowly to room temperature, trimethylamine began to evolve rapidly. The reaction mixture was stirred and heated to reflux (65°) until evolution of trimethylamine ceased.

After cooling to room temperature, the reaction mixture was basified with 4 ml of 3 *N* sodium hydroxide, and 4 ml of 30% hydrogen peroxide was slowly added with vigorous stirring to keep the temperature below 50°. After stirring for 30 min the oxidized solution was saturated with sodium carbonate and extracted with three 20-ml portions of diethyl ether in a 50-ml separatory funnel. The ether extract was dried over anhydrous magnesium sulfate and analyzed by gas chromatography using a 10-ft aluminum column, packed with 20% Carbowax 1500, supported on 60–80 mesh Chromosorb W at 145°. Using cyclohexanol as an internal standard, the yields of 1-hexanol and 1-heptanol were 15.9 and 5.2 mmol, respectively.

Reaction with Bis(3-methyl-2-butyl)borane.—Bis(3-methyl-2-butyl)borane (disiamylborane) was prepared in the same manner as described for preparation of trihexylborane,[18] using 3.5 g (50 mmol) of 2-methyl-2-butene and 25 mmol of borane in 20 ml of tetrahydrofuran. The reaction of disiamylborane with "solid ylide" was carried out in the same manner as that described for the reaction of trihexylborane with ylide. The dried ether solution was analyzed by gas chromatography using a 5-ft aluminum column, packed with 20% 1,2,3-tris(2-cyanoethoxy)-propane, supported on 60–80 mesh firebrick at 130°. Using cyclohexanol as an internal standard, the yields of 2,3-dimethyl-1-butanol and 3-methyl-2-butanol were found to be 5.5 and 33.5 mmol, respectively. No methanol could be detected when the temperature of the chromatography column and the rate of carrier gas flow were decreased. A measurement of the amount of hydrogen evolved on adding sodium hydroxide was obtained in a subsequent experiment. This showed that 490 ml of a possible 560 ml of hydrogen was given off. This closely approaches the amount of hydrogen evolved in a control run in which no ylide was added (210 ml of a possible 225 ml of hydrogen).

Reaction with Bis(3-methyl-2-butyl)hexylborane.—Bis(3-methyl-2-butyl)hexylborane was prepared according to the method of Zweifel and Brown[18] and was injected into a freshly prepared suspension of 8.0 g (25 mmol) of "solid ylide" in 30 ml of 1,2-dimethoxyethane at −78°. Oxidation and workup of the reaction mixture was carried out in exactly the same manner as described under reaction of trihexylborane with the "solid ylide." The dried ether extract was analyzed by gas chromatography using a 10-ft aluminum column, packed with 20% Carbowax 1500, supported on 60–80 mesh Chromosorb W at 140°. Using cyclohexanol as an internal standard, the following yields of products were measured: 1-hexanol, 20 mmol; 1-heptanol, 1.5 mmol; 3-methyl-2-butanol, 31 mmol; 2,3-dimethyl-1-butanol, 15 mmol.

Reaction with Triphenylborane.—In a dry, 150-ml, round-bottom flask equipped with a magnetic stirrer and a side arm sealed with a rubber septum was placed 3.0 g (12.5 mmol) of powdered triphenylborane and 4.0 g (12.5 mmol) of "solid ylide." The flask was fitted with a condenser, attached to a dry nitrogen inlet, and cooled to −78° in a Dry Ice–acetone bath. Using a syringe, 25 ml of tetrahydrofuran and 25 ml of 1,2-dimethoxyethane were slowly injected into the flask with vigorous stirring to form a suspension of "solid ylide" and triphenylborane. The reaction mixture was heated, basified, and oxidized in exactly the same manner as described under the reactions of other organoboranes with "solid ylide" in a 1,2-dimethoxyethane suspension. Gas chromatographic analysis of the dried ether extract using a 5-ft aluminum column packed with 20% 1,2,3-tris-(2-cyanoethoxy)propane, supported on 60–80 mesh firebrick at 150°, showed the yields of phenol and benzyl alcohol to be 5.7 and 26 mmol, respectively.

Reaction with Borane (BH_3).—A 1.86 *M* solution of borane in tetrahydrofuran was prepared according to the method described by Zweifel and Brown.[18] A measured portion of this solution containing an amount of borane equivalent to the amount of "solid ylide" used was injected into the previously prepared ylide suspension, allowed to react, and worked up in the same manner as described for reaction of trihexylborane with the "solid ylide." This procedure was repeated numerous times using different reaction times, different reaction temperatures, and different amounts of 1,2-dimethoxyethane in the reaction mixture. Under no conditions, however, could any methanol be detected in the dried ether extract of the reaction mixture by gas chromatography. Measurement of the hydrogen evolved when the reaction mixtures were basified with 3 *N* sodium hydroxide gave an average of 85% recovery of hydrogen available from the added borane. Evolution of trimethylamine was much lower in the reactions with borane than in the reactions with alkylboranes.

Reaction with Borane (Attempted Isolation of Adduct).—Into a dry, 150-ml, round-bottom flask, equipped with a magnetic stirrer, a dry-nitrogen inlet, and a side arm sealed with a rubber septum, was injected 15 ml of 2.0 *M* borane in tetrahydrofuran and 60 ml of 0.5 *N* "ylide solution" at 0°. The original yellow color of the "ylide solution" was partially discharged and a small amount of a gelatinous precipitate formed as the reaction mixture was stirred at 0° for 1 hr and at room temperature for 12 hr. The flask was attached to the vacuum line and the volatile contents were distilled through three traps cooled to −78° into a flask cooled to −196° in liquid nitrogen. Hydrolysis of the distillate obtained in the final flask yielded only a trace of hydrogen, indicating that most of the borane had been used. The material collected in the −78° traps was separated into a small portion of higher boiling liquid (not identified) and 1.1 g (15 mmol) of trimethylamine–borane, identified by its melting point (94°; lit.[19] mp 94°) and its mass spectrum (mol wt 73).

The dry, nonvolatile salts remaining in the original reaction flask were dissolved in 10 ml of anhydrous 1,2-dimethoxyethane. To this solution was added 15 ml of anhydrous methylene chloride, causing precipitation of a white solid which was removed by filtration and identified by qualitative tests as lithium bromide.

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[18] G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

[19] W. Gerrard, "The Organic Chemistry of Boron," 1st ed, Academic Press, New York, N. Y., 1961, p 163.

Infrared spectra of the solid (KBr pellet) showed no absorption bands. The filtrate was distilled to dryness on the vacuum line leaving a white solid. This solid was dissolved in 5 ml of 1,2-dimethoxyethane, and 20 ml of methylene chloride was added to the solution, again causing precipitation of lithium bromide which was removed by filtration. The filtrate was distilled to dryness on the vacuum line leaving a white solid which was soluble in water. However, the water solution slowly gave off hydrogen and acidification caused more rapid gas evolution. The addition of silver nitrate to a water solution of hydride-containing material, after hydrolysis with perchloric acid, caused immediate precipitation of silver bromide and indicated that the hydride was contaminated with lithium bromide. Infrared spectra (KBr pellet and tetrahydrofuran solution) showed only one absorption band centered at 2250 cm^{-1} characteristic of the B–H bond in the borohydride ion BH_4^-. The product is apparently a mixture of lithium bromide and lithium borohydride. Pyrolysis of a sample of the mixture at 450–500° produced only hydrogen gas, indicating that no organic material was present. Hydrolysis of a 0.21-g sample of the salt mixture with 3 *N* HCl gave 8.7 mmol of hydrogen gas (theoretically for pure lithium borohydride: 38 mmol of hydrogen).

Reaction with Trihexylaluminum.—A suspension of 6.0 g (19 mmol) of "solid ylide" in 15 ml of tetrahydrofuran and 15 ml of 1,2-dimethoxyethane was prepared at −78° in a dry, 150-ml, round-bottom flask, equipped with a magnetic stirrer, a nitrogen inlet, and a side arm sealed with a rubber septum. Using a syringe, 5 ml of 3.1 *M* trihexylaluminum was injected into the suspension and the mixture was warmed to room temperature and stirred vigorously for 20 hr.

The solid material in the reaction mixture was removed by centrifuging, washed with anhydrous *n*-pentane to remove unreacted trihexylaluminum, centrifuged again, and dried under vacuum. The dry solid was hydrolyzed with 10% sulfuric acid. The aqueous solution was saturated with sodium nitrate and extracted with diethyl ether. An analysis of the dried ether extract by gas chromatography failed to detect any *n*-hexane. This indicated that no trihexylaluminum adduct of trimethylammonium methylide was present in the solid recovered from the reaction.

The solvent mixture from the reaction was distilled on the vacuum line until no more volatile material could be removed at 50°. This left a viscous liquid (unreacted trihexylaluminum) along with some white solid. Anhydrous *n*-pentane was added to the flask causing precipitation of more solid material which was removed by filtration and washed in the drybox with *n*-pentane. The solid was dissolved in 10% sulfuric acid. The solution formed was saturated with sodium nitrate, extracted with ether, and dried over anhydrous magnesium sulfate. Analysis of the ether extract by gas chromatography failed to detect any *n*-hexane.

The filtrate of *n*-pentane and unreacted trialkylaluminum was combined with the reaction solvents removed by distillation. The mixed solution was hydrolyzed with 10% sulfuric acid, saturated with sodium nitrate, and extracted with diethyl ether. After drying over anhydrous magnesium sulfate, gas chromatographic analysis of the extract using a 5-ft aluminum column, packed with 10% adiponitrile, supported on 30–60 mesh firebrick at 30°, showed that no *n*-heptane had formed in the reaction. Using *n*-heptane as an internal standard, the measured yield of *n*-hexane was 44 mmol. This represents an 85% recovery of unreacted trihexylaluminum.

Reaction with Trimethylaluminum.—Into a dry, 150-ml, round-bottom flask equipped with a dry-nitrogen inlet, a side arm sealed with a rubber septum, and a magnetic stirrer, was placed 4.13 g (57 mmol) of trimethylaluminum in 25 ml of anhydrous tetrahydrofuran. The flask was cooled to 0° in an ice bath and 69 ml of 0.6 *N* "ylide solution" (41 mmol) was slowly injected into the solution of trimethylaluminum using a large syringe. As the dark yellow solution of ylide was added, its color was partially discharged and a small amount of gelatinous, white precipitate formed giving a slightly cloudy, yellow solution. After addition of the "ylide solution" the reaction mixture was warmed to room temperature and stirred for 4 hr.

The solution was decolorized with 1.0 g of Norit and filtered into a 100-ml flask inside the drybox. The solvent was removed on a rotary evaporator at reduced pressure, leaving a yellow solid which was triturated with 60 ml of anhydrous methylene chloride. All insoluble material was removed by filtration giving a clear yellow filtrate which was reduced in volume to 30 ml on a rotary evaporator. To this solution was added 60 ml of anhydrous *n*-hexane causing precipitation of a light yellow solid which was removed by filtration and dried under vacuum. The product was recrystallized from a mixture of methylene chloride and *n*-hexane to give 3.9 g (28 mmol) of material having properties consistent with the trimethylaluminum adduct of trimethylammonium methylide: mp 155° (sealed tube); nmr spectrum (methylene chloride): δ 3.05 (s, 9, $N(CH_3)_3$), δ 2.44 (s, 2, NCH_2Al), δ −0.92 (s, 9, $Al(CH_3)_3$). *Anal.* Calcd for $C_7H_{20}AlN$: Al, 18.6. Found: Al, 18.3.

A 0.075-g (0.51-mmol) sample of the trimethylaluminum adduct was weighed into a 20-ml glass tube equipped with a standard-tapered joint. The tube was attached to the vacuum line, evacuated, and cooled to −196° in liquid nitrogen. Three milliliters of 1 *N* HCl was allowed to condense into the tube, which was then warmed to room temperature causing evolution of methane. The methane was pumped by a Toepler pump through two traps cooled to 196° into a calibrated gas buret. A total of 1.48 mmol of pure methane, identified by a mass spectrum, was collected (theoret, 1.55 mmol). A 0.094-g (0.65-mmol) sample of adduct yielded 1.91 mmol of methane (theoret, 1.95 mmol).

Pyrolysis of the Trimethylaluminum Adduct of Trimethylammonium Methylide.—A 0.12-g (0.71-mmol) sample of the adduct was weighed into a dry, 20-ml glass tube equipped with a standard-tapered joint. The tube was attached to the vacuum line, evacuated, and heated in an oil bath to 160°. The adduct melted and slowly decomposed as evidenced by the slow evolution of gas and the formation of long, clear crystals in the unheated portion of the tube. After 12 hr a total of 0.19 mmol of gas was collected. The infrared spectrum of the gas indicated a mixture of methane and ethylene. The volatile material collected in the −130° traps was identified by its infrared spectrum as trimethylamine.

The solid material remaining in the pyrolysis tube was hydrolyzed with 3 ml of water which was condensed on the solid at −196°. The gaseous products of hydrolysis were pumped by a Toepler pump through three traps cooled to −78° into a calibrated gas buret. A total of 1.69 mmol of gas was collected. A mass spectrum of this gas indicated a mixture of 77.1% methane, 19.2% ethane, and 2.9% propane.

Reaction with Trimethylbromosilane.—A suspension of 6.0 g (19 mmol) of "solid ylide" in 25 ml of anhydrous tetrahydrofuran was prepared at −78° in a dry, 100-ml, round-bottom flask, equipped with a dry-nitrogen inlet, a magnetic stirrer, and a side arm sealed with a rubber septum. A mixture of 5.7 g (37 mmol) of trimethylbromosilane in 5 ml of tetrahydrofuran was injected into the suspension with a syringe. The reaction mixture was allowed to warm slowly to room temperature, heated to reflux (65°), and stirred for 12 hr.

The reaction mixture was distilled to dryness at reduced pressure giving a light tan solid which was dried completely by heating to 75° under vacuum for 3 hr. The dry solid was placed in a Soxhlet extractor maintained under a positive pressure of nitrogen and extracted with 100 ml of anhydrous 1,2-dichloroethane for 10 hr. Cooling the extraction solvent to 0° induced crystallization of 1.9 g (8.5 mmol, 45% yield based on ylide) of flat lustrous crystals which were removed by filtration and dried under vacuum, mp 255–259°. Recrystallization of the product from a mixture of methylene chloride and 1,2-dimethoxyethane gave pure trimethyl[(trimethylsilyl)methyl]ammonium bromide: mp 260–261° dec, lit.[20] mp 260–262°; ir spectrum (chloroform): 2925 (C–H), 1470 (C–N$^+$) 1252, and 850 cm^{-1} (Si–(CH$_3$)$_3$); nmr spectrum (chloroform): δ 3.63 (s, 9, $N(CH_3)_3$), δ 3.49 (s, 2, NCH_2Si), δ 0.33 (s, 9, $Si(CH_3)_3$). *Anal.* Calcd for $C_7H_{20}BrNSi$: C, 37.2; H, 8.85; N, 6.20. Found: C, 37.6; H, 8.68; N, 6.05.

The reaction of excess trimethylbromosilane with "ylide solution" in tetrahydrofuran gave a 60% yield of trimethyl[(trimethylsilyl)methyl]ammonium bromide. Product isolation from this system was much easier owing to the immediate precipitation of the ammonium salt when the "ylide solution" was added to the silane.

Preparation of Trimethyl[(trimethylsilyl)methyl]ammonium Bromide.—A 50-ml reaction tube with a tight constriction in the neck was attached to the vacuum line, evacuated, and cooled to −196° in liquid nitrogen. Into the tube was condensed 5.9 g (30 mmol) of bromomethyltrimethylsilane and 2.1 g (35 mmol) of trimethylamine. The tube was sealed at the constriction with a gas–oxygen torch and placed in a small oven for 12 hr at 100°.

The tube, which now contained a white solid, was cooled to room temperature and opened in the drybox. The solid was recrystallized from a mixture of methylene chloride and 1,2-dimethoxyethane giving 3.0 g (13.9 mmol) of trimethyl[trimethylsilyl)methyl]ammonium bromide: mp 260–261° dec; ir spectrum (chloroform): 2925 (C–H), 1470 (C–N$^+$), 1250, and 850 cm^{-1} ($Si(CH_3)_3$); nmr spectrum (chloroform): δ 3.63 (s, 9, $N(CH_3)_3$), δ 3.49 (s, 2, NCH_2Si), δ 0.33 (s, 9, $Si(CH_3)_3$).

Pyrolysis of Trimethyl[(trimethylsilyl)methyl]ammonium Bromide.—In the drybox, a 0.5-g (2.2-mmol) sample of trimethyl[(trimethylsilyl)methyl]ammonium bromide was weighed into a 20-ml pyrolysis tube equipped with a standard-tapered joint. The tube was attached to the vacuum line, evacuated, and heated in an oil bath to 280°. The ammonium salt melted at about 270° and rapidly decomposed until only a slight film of material remained in the tube. The volatile products were collected continuously during decomposition in a Dry Ice–acetone trap (−78°). After the decomposition was complete, the higher boiling and lower boiling components of the product mixture were separated by fractionation on the vacuum line. The lower boiling material which collected in a −196° trap was measured (1.95 mmol) and identified as methyl bromide by comparison of its infrared spectrum with that of an authentic sample. The high boiling component was removed from the vacuum line and purified from traces of impurities by gas chromatography using a 5-ft aluminum column, packed with 20% Carbowax 20 M, supported on Chromosorb W at 75°. The purified product was identified as dimethyl[(trimethylsilyl)methyl]amine; $n^{20}{}_D$ 1.4124, lit.[21] $n^{25}{}_D$ 1.4102; ir spectrum (neat): 2950, 2750 (C–H), 1450 (C–N$^+$), 1250, and 850 cm^{-1} ($Si(CH_3)_3$); nmr spectrum (neat): δ 2.46 (s, 9, $N(CH_3)_3$), δ 2.08 (s, 2, NCH_2Si), δ 0.05 (s, 9, $Si(CH_3)_3$.

Reaction with Trimethylbromogermane.—Tetramethylgermane was prepared according to the method of Dennis and Hance[22] and trimethylbromogermane was prepared according to the method of Dennis and Patnode[23] and purified by fractionation on a vacuum line; $n^{23}{}_D$ 1.4691, lit.[24] $n^{24}{}_D$ 1.4713; nmr spectrum (neat): δ 0.80 (s, $Ge(CH_3)_3$.

A solution of 2.0 g (10 mmol) of trimethylbromogermane in 10 ml of anhydrous 1,2-dimethoxyethane was placed in a dry, 100-ml, round-bottom flask equipped with a dry-nitrogen inlet, a magnetic stirrer, and a side arm sealed with a rubber septum. Using a syringe, 30 ml of 0.5 *N* "ylide solution" was injected into the flask at room temperature. As the "ylide solution" was added, its color was partially discharged and a white solid slowly formed. More precipitate formed as the reaction mixture was stirred vigorously for 6 hr at room temperature. The bulk of the solvent was removed from the reaction mixture at reduced pressure, but attempts to remove all of the solvent by warming the flask to 50° under high vacuum appeared to cause some decomposition. Further drying was stopped, and 30 ml of anhydrous chloroform was added to the syrup-like mass remaining in the flask. Much of the material dissolved giving a brown solution which was filtered to remove insoluble material (lithium bromide). The clear, brown filtrate was decolorized with 0.5 g of Norit giving a light yellow solution to which was added 50 ml of anhydrous diethyl ether causing precipitation of a white solid. The solid was filtered in the drybox and reprecipitated three more times from chloroform–ether mixtures giving 0.18 g (0.7 mmol) of white, crystalline trimethyl[(trimethylgermyl)methyl]ammonium bromide; mp 190–195° dec; nmr spectrum (deuterium oxide): δ 3.12 (s, 2, $GeCH_2N$), δ 3.04 (s, 9, $N(CH_3)_3$), δ 0.35 (s, 9, $Ge(CH_3)_3$). *Anal.* Calcd for $C_7H_{20}BrGeN$: C, 31.4; H, 7.47; N, 5.23. Found: C, 29.6; H, 7.12; N, 5.64.

Pyrolysis of Trimethyl[(trimethylgermyl)methyl]ammonium Bromide.—In the drybox, 0.1 g (0.4 mmol) of trimethyl[(trimethylgermyl)methyl]ammonium bromide was pyrolyzed in the same manner as described for the pyrolysis of the silicon analog. The infrared spectrum of the gaseous fraction indicated it was methyl bromide containing a small amount of trimethylamine. The higher boiling liquid was identified as dimethyl(trimethylgermyl)methyl]amine as evidenced by its nmr spectrum (neat): δ 2.22 (s, 6, $N(CH_3)_2$), δ 2.08 (s, 2, $N\text{-}CH_2\text{-}Ge$), δ 0.30 (s, 9, $Ge(CH_3)_3$.

Reaction with Trimethylbromostannane.—Trimethylbromostannane was prepared according to the method of Krauss and Sessions.[25] A 3.5-g (14.3-mmol) sample of trimethylbromostannane in 5 ml of anhydrous tetrahydrofuran was placed in a dry, 50-ml flask, equipped with a dry-nitrogen inlet, a magnetic stirrer, and a side arm sealed with a rubber septum. Into the flask was injected 25 ml of 0.6 *N* "ylide solution" which caused an immediate precipitation of a white solid with the evolution of heat. The reaction mixture was stirred at room temperature for 6 hr, filtered in the drybox, and dried under high vacuum to give 2.5 g of the impure tan product, mp 198–209° dec. Recrystallization of the product from a mixture of chloroform and 1,2-dimethoxyethane gave 2.1 g (6.6 mmol) of trimethyl[(trimethylstannyl)methyl]ammonium bromide; mp 204–205° dec; ir spectrum (KBr pellet): 3000, 2910 (C–H), 1480, 1430 (C–N$^+$), 960, 930, and 755 cm^{-1} ($Sn(CH_3)_3$); nmr spectrum (chloroform): δ 3.77 (s, 2, $SnCH_2N$), δ 3.63 (s, 9, $N(CH_3)_3$), δ 0.47 (s, 9, $Sn(CH_3)_3$. In addition, splitting of the peak at δ 0.47 (J = 28 Hz) by the ^{119}Sn nucleus was observed. *Anal.* Calcd for $C_7H_{20}BrNSn$: C, 27.1; H, 6.31; N, 4.42. Found: C, 27.0; H, 6.12; N, 4.45.

Pyrolysis of Trimethyl[(trimethylstannyl)methyl]ammonium Bromide.—In the drybox, 0.5 g (1.6 mmol) of trimethyl[(trimethylstannyl)methyl]ammonium bromide was pyrolyzed in the same manner as that described for the pyrolysis of the silicon analog. The material collected in the −78° traps was identified as trimethylbromostannane by its infrared spectrum which was identical with a spectrum of an authentic sample. The lower boiling fraction (1.25 mmol), collected in the −196° trap, was identified by its infrared spectrum as trimethylamine, containing a trace of ethylene. The amorphous brown material remaining in the pyrolysis tube was thought to be polymethylene, since it was insoluble in organic solvents, strong base (KOH(aq)), and strong acid (HCl) but burned completely in a flame.

Reaction with Dipentylzinc.—Dipentylzinc was prepared according to the method of Noller.[26] A suspension of 6.0 g

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(20) J. E. Noll, J. L. Speier, and B. F. Daubert, *J. Am. Chem. Soc.*, **73**, 3867 (1951).

(21) T. A. Manuel, *Advan. Organometal. Chem.*, **3**, 181 (1965).

(22) L. M. Dennis and F. E. Hance, *J. Phys. Chem.*, **30**, 1055 (1926).

(23) L. M. Dennis and W. D. Patnode, *J. Am. Chem. Soc.*, **52**, 2779 (1930).

(24) D. Quane and R. S. Bottei, *Chem. Rev.*, **63**, 403 (1963).

(25) C. A. Krauss and W. V. Sessions, *J. Am. Chem. Soc.*, **47**, 2362 (1925).

(26) C. R. Noller, "Organic Synthesis," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 184.

(19 mmol) of "solid ylide" in 15 ml of anhydrous tetrahydrofuran and 15 ml of anhydrous 1,2-dimethoxyethane was prepared at −78° in a dry, 150-ml, round-bottom flask, equipped with a nitrogen inlet, a magnetic stirrer, and a side arm sealed with a rubber septum. Using a syringe, 4.2 g (20 mmol) of dipentylzinc dissolved in 10 ml of tetrahydrofuran was injected into the suspension of ylide. The reaction mixture was warmed to room temperature and stirred vigorously for 24 hr during which time no observable change occurred.

The contents of the reaction flask were placed in two dry centrifuge tubes, which were then sealed with rubber septums, and centrifuged. The liquid layers were decanted into a 100-ml, round-bottom flask. The solid material in the centrifuge tubes was slurried with 20 ml of fresh tetrahydrofuran and centrifuged again. The liquid layers were added to the 100-ml, round-bottom flask, and the insoluble material in the tubes was dried. A qualitative analysis for zinc on a sample of the dried solid in slightly alkaline solution using hydrogen sulfide indicated that no zinc ions were present in the solution.

The 100-ml flask containing the combined liquid layers obtained from centrifuging was now attached to the vacuum line. The liquid was distilled by heating to 100° into another flask cooled to −196° in liquid nitrogen leaving a slightly yellow solid coating the walls of the flask. The solid was found to consist mainly of lithium bromide and contained no zinc compounds (negative hydrogen sulfide test).

The distillate was hydrolyzed with 20 ml of 2% sulfuric acid. The solution was saturated with sodium carbonate and extracted with three 20-ml portions of diethyl ether. The ether extract was dried over anhydrous magnesium sulfate and analyzed by gas chromatography using a 5-ft alumina column, packed with 20% adiponitrile, supported on 60–80 mesh Chromosorb W, at 30°. Using *n*-heptane as an internal standard, the yield of *n*-pentane was found to be 35.5 mmol (88% recovery of dipentylzinc) but no *n*-hexane was detected.

The reaction was repeated using "ylide solution" instead of a suspension of "solid ylide," but again no *n*-hexane could be detected in the hydrolyzed reaction mixture and no solid zinc compound could be found.

Reaction with Diphenylmercury.—Into a dry 25-ml reaction tube fitted with a standard-tapered joint was placed 2.5 g (7.1 mmol) of diphenylmercury and 5 ml of anhydrous tetrahydrofuran under a nitrogen atmosphere. To this solution was added 14 ml of 0.5 *N* "ylide solution." The tube was sealed with a glass stopper and placed on a shaker and shaken vigorously for 3 days.

Initially the reaction mixture was light brown, but as shaking continued, it became cloudy and a reddish brown precipitate began to form. After 3 days, the solution was brown and contained much fine, tan precipitate. The solution was centrifuged to settle the precipitate, and the tube was opened in the drybox where the liquid layer was decanted from the brown solid. The solid was slurried with 20 ml of fresh tetrahydrofuran, and the mixture was filtered. The solid in the filter was washed with 30 ml of anhydrous tetrahydrofuran and with 50 ml of anhydrous diethyl ether. Drying the solid under high vacuum gave 2.1 g of a tan, light-sensitive solid which decomposed in a melting point tube at 260–265° giving off mercury. The solid was insoluble in ethereal, hydrocarbon, and chlorinated hydrocarbon solvents. It dissolved partially in methanol, ethanol, and water, but only gray resins could be recovered.

The infrared spectrum of the solid (KBr pellet) showed strong absorption bands centered at 3040 (aromatic C=C), 2975, 2920 (C—H), 1600, 1450 (C—N$^+$), 1300 (C=C), 1110, 980, 775, 725, and 690 cm^{-1}. Pyrolysis of a sample of the solid under high vacuum at 300° gave trimethylamine, methyl bromide, and benzene, which were identified by their infrared spectra, as well as mercury, which was observed visually. *Anal.* Calcd for $C_{10}H_{16}BrHgN$: C, 27.9; H, 3.72. Found: C, 29.5; H, 4.15.

The tetrahydrofuran solution which was decanted from the solid after centrifuging and the filtrates from washing the solid were combined and hydrolyzed with 3 ml of water. The hydrolyzed solution was dried over anhydrous magnesium sulfate and analyzed by gas chromatography using a 10-ft aluminum column packed with 20% 1,2,3-tris(2-cyanoethoxy)propane, supported on 60–80 mesh firebrick at 90°. Using 1-bromobutane as an internal standard, the yield of benzene was found to be 4.6 mmol (66% yield of exchange product based on "ylide solution").

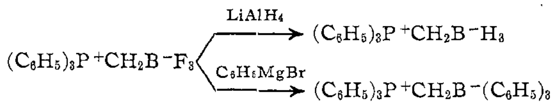
The reaction was repeated exactly as described above except that excess "ylide solution" was used instead of excess diphenylmercury. In this case, 2.5 g (7.1 mmol) of diphenylmercury was treated with 32 ml of 0.5 *N* "ylide solution" and allowed to shake for 5 days. The solid which formed was filtered, washed with 50 ml each of tetrahydrofuran and diethyl ether, and dried under vacuum giving 2.2 g of solid product. The filtrate and wash solvents were hydrolyzed with water and dried over magnesium sulfate. Gas chromatographic analysis of the dried solution showed the yield of benzene to be 9.9 mmol (70% yield of exchange product based on diphenylmercury).

The infrared spectrum (KBr pellet) of the solid product showed strong absorption bands centered at 3000, 2940, (C–H), 1600, 1485 (C–N$^+$), 950, and 850 cm^{-1}. The solid had no definite melting point but began to decompose at about 250° giving off mercury. All attempts to recrystallize the solid were unsuccessful since no solvent could be found in which it dissolved without decomposition. Partial dissolution occurred in methanol and water, but only brown or gray resins could be recovered from solution.

Pyrolysis of a 0.45-g sample of the impure solid at 300° for 24 hr under high vacuum gave a total of 2.3 mmol of trimethylamine and methyl bromide, identified by their infrared spectra, and significant amounts of metallic mercury. *Anal.* Calcd for $C_8H_{22}BrHgN_2$: C, 19.0; H, 4.3. Found: C, 21.4; H, 4.9.

Discussion and Results

Reaction with Boron Halides.—Seyferth and Grim[10] described the reaction of methylenetriphenylphosphorane with boron trifluoride in ether to give the ether-insoluble adduct triphenylphosphinemethylene–trifluoroborane. This material could be reduced to the B-trihydro adduct by the use of lithium aluminum hydride and arylated to the B-triphenyl adduct with either phenyllithium or phenylmagnesium bromide



$$(C_6H_5)_3P^+CH_2B^-F_3 \begin{array}{l} \xrightarrow{\text{LiAlH}_4} (C_6H_5)_3P^+CH_2B^-H_3 \\ \xrightarrow{C_6H_5\text{MgBr}} (C_6H_5)_3P^+CH_2B^-(C_6H_5)_3 \end{array}$$

Treatment of boron trichloride with methylenetriphenylphosphorane gave what appeared to be an adduct but this adduct was somewhat unstable and could not be purified.

The reaction of boron trifluoride with trimethylammonium methylide gave a product whose properties were consistent with those expected for trimethylaminomethyltrifluoroborane. Pyrolysis in a sealed tube at 275° gave ethylene and trimethylaminotrifluoroborane

$$(CH_3)_3N^+CH_2B^-F_3 \xrightarrow{275°} (CH_3)_3NBF_3 + CH_2{=}CH_2$$

The infrared spectrum (KBr pellet) of the ylide adduct showed absorption bands which were consistent with the proposed structure. The nmr spectrum in nitromethane or deuterium oxide was not as easily interpreted, owing to the presence of a diffuse triplet centered at δ 1.77. This triplet seemed to indicate that the adduct had ionized in solution to give a fluoride ion and a substituted tetramethylammonium ion

$$(CH_3)_3N^+CH_2B^-F_3 \xrightarrow{CH_3NO_2} (CH_3)_3N^+CH_2BF_2 + F^-$$

Spin coupling of the two hydrogens of the methylene group with the two remaining fluorine atoms bound to boron in the ionized adduct may give rise to a triplet with a resultant broadening of the peaks caused by ^{10}B and ^{11}B nuclei having spins of 3 and $^3/_2$, respectively. Line broadening in the triplet could also be caused by slow exchange of fluoride ions in solution or quadruple interactions from the boron nuclei. The ^{11}B nmr spectrum in nitromethane showed only a singlet. No splitting of the boron signal due to the fluorine atoms was observed.

Further evidence for ionization of the adduct in solution was found by comparing the specific conductance of nitromethane solutions of the adduct with that of betaine and tetramethylammonium fluoride at similar concentrations. If the adduct is not ionized in solution, its conductivity would be expected to be similar to that of an internal salt of similar structure (betaine). If the adduct is ionized in solution, it may be expected to have a conductivity similar to that of tetramethylammonium fluoride. Inspection of Table I shows that the specific conductances of solutions of the adduct compare more favorably with the conductances of solutions of tetramethylammonium fluoride than with similar solutions of betaine, suggesting that the adduct is a 1:1 electrolyte. The consistently lower values of specific conductance observed for solutions of the adduct compared with those of tetramethylammonium fluoride at similar concentrations suggest the presence of either an equilibrium between ionized and un-ionized species in solution or ion pairing. Although these results suggest that ionization of the adduct occurs in solution, they do not preclude the possibility that the adduct is not ionized in the solid state.

Attempts to alkylate the boron trifluoride adduct with butyllithium as reported by Seyferth[10] with the phosphorus ylide adduct of boron trifluoride were unsuccessful. If alkylation had occurred to give the B-trialkyl adduct, it would be expected that, upon oxidation of this product with alkaline hydrogen peroxide, 1-butanol could be found as well as some 1-pentanol arising from rearrangement.[27] Neither of these alcohols could be detected in the reaction mixture after oxidation.

TABLE I[a]

CONDUCTIVITIES IN NITROMETHANE SOLUTIONS AT 25°

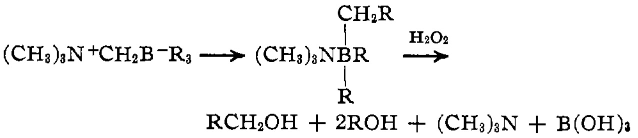
Compound	Concn, *M*	Sp conductance
Betaine	1.37×10^{-3}	4.27
	6.85×10^{-4}	4.45
	3.43×10^{-4}	4.70
	1.71×10^{-4}	5.12
Boron trifluoride adduct	1.28×10^{-3}	50.2
	6.37×10^{-4}	51.5
	3.19×10^{-4}	52.5
	1.60×10^{-4}	53.0
Tetramethylammonium fluoride	9.95×10^{-4}	64.2
	4.97×10^{-4}	65.0
	2.48×10^{-4}	65.6
	1.24×10^{-4}	66.2

[a] The data were obtained using the apparatus and technique described in the Ph.D. thesis of M. S. Hussain, University of California, Davis, Calif., 1968.

The reaction of boron trichloride with trimethylammonium methylide in 1,2-dimethoxyethane afforded a boron-containing material having the properties expected of an adduct of the ylide with boron trichloride, although it could not be satisfactorily purified. All attempts to recrystallize the initially obtained product resulted in formation of intractable resins. However, the infrared and nmr spectra were consistent with a compound of the proposed structure. The material decomposed in water and absorbed water from the atmosphere giving insoluble resins. Thus the unstable nature of the boron trichloride adduct is similar to that of the phosphorus analog.[10]

Reaction with Borane and Organoboranes.—Seyferth and Grim[10] demonstrated that the trialkylborane adducts of methylenetriphenylphosphorane were unstable and could not be isolated. Faced with the possibility of inherent instability of trialkylborane adducts of the nitrogen ylide, we attempted to demonstrate the existence or formation of such adducts, not by isolation of the adduct itself, but rather by isolation of the reaction products whose formation may be most easily rationalized by a mechanism involving the initial formation of an ylide–borane adduct.

In an earlier study[27] we reported that the reaction of nitrogen ylides with organoboranes led to a rearrangement in which the methylene group of the ylide was inserted into the B–C bond of the organoborane. Comparison studies with several organoboranes indicated that secondary alkyl groups bonded to boron migrated more easily than primary alkyl groups. No evidence for a migration of a hydrogen atom from boron to carbon was noted.



$$(CH_3)_3N^+CH_2B^-R_3 \longrightarrow (CH_3)_3N\overset{\overset{\displaystyle CH_2R}{|}}{\underset{\underset{\displaystyle R}{|}}{B}}R \xrightarrow{H_2O_2} RCH_2OH + 2ROH + (CH_3)_3N + B(OH)_3$$

Using similar techniques of reaction and isolation of products, Tufariello and Lee[28] demonstrated the generality of alkyl migration from boron to carbon in reactions of trialkylboranes with ylides, using the sulfur ylide dimethyloxosulfonium methylide. These workers also favor a mechanism involving initial coordination of the ylide with the borane followed by migration and displacement of a good leaving group, which in their case was dimethyl sulfoxide. Recently, Köster and Rickborn[29] reported that the migration of

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[27] W. K. Musker and R. R. Stevens, *Tetrahedron Letters*, **11**, 995 (1967).

[28] J. J. Tufariello and L. T. C. Lee, *J. Am. Chem. Soc.*, **88**, 4757 (1966).

[29] R. Köster and B. Rickborn, *ibid.*, **89**, 2782 (1967).

a phenyl group in methylenetriphenylphosphorane–triphenylborane can be induced if the adduct is dissolved in decalin and heated to 205° for 15 min.

Since we observed that hydrogen migrated so poorly, we attempted to isolate the borane adduct of the ylide. Although numerous attempts were made to isolate the adduct, no pure material uncontaminated with lithium bromide was isolated. Recently Bickelhaupt and Barnick[30] isolated the triphenylborane adduct of trimethylammonium methylide by treating the lithium bromide adduct with triphenylborane in tetrahydrofuran. In this case the lithium bromide impurity could be washed out of the adduct with water—a technique which is impossible with the borane adduct owing to solvolysis. Cleavage of the triphenylborane adduct with hydrochloric and acetic acids gave a boronic acid $[(CH_3)_3N^+CH_2B(OH)_2]$. This boronic acid is extremely acidic (pK = 5.6) when compared with common boronic acids (p$K \approx$ 10–11) and ionizes to give a species isoelectronic with betaine $[(CH_3)_3N^{\oplus}\text{-}CH_2COO^{\ominus}]$. This boronate ion is also isoelectronic with the ionic form of the BF_3 adduct described earlier and its stability lends additional credibility to the suggestion that the BF_3 adduct should be formulated as $[CH_3N^+CH_2BF_2]F^-$.

Reaction with Trihexyl- and Trimethylaluminum.—Like trialkylboranes, trialkylaluminum compounds are good Lewis acids, which combine readily with such donors as amines, phosphines, ethers, and thioethers to give tetrahedral four-coordinated complexes that are relatively more stable to dissociation than the corresponding trialkylborane complexes.[31] Because the investigation of the reactions of trialkylboranes with trimethylammonium methylide indicated the intermediate existence of ylide–borane adducts, it was expected that trialkylaluminum compounds might react in a similar manner to give ylide–trialkylaluminum adducts. If the adducts were stable, they could presumably be isolated and, if unstable, might rearrange by alkyl group migration from aluminum to carbon giving rearrangement products similar to those found in the reactions of trialkylboranes with the ylide.

The reaction of trihexylaluminum with trimethylammonium methylide was carried out using the same procedure reported for the reaction of the ylide with trihexylborane. An analysis of the reaction mixture by gas chromatography after hydrolysis with 10% sulfuric acid failed to detect any *n*-heptane, indicating that either an alkylaluminum–ylide adduct did not form or a stable adduct formed but no alkyl group migration occurred. Hydrolysis of the reaction solution after removal of most of the solvent and precipitation of all salts by addition of *n*-pentane gave an 85% recovery of *n*-hexane available from the original trihexylaluminum reactant, indicating that very little, if any, adduct formation between the ylide and the trialkylaluminum had occurred.

Since steric factors are known[31] to have great influence on the stability of complexes formed between trialkylaluminum compounds and Lewis bases, it seemed likely that the failure of trihexylaluminum to form the adduct with trimethylammonium methylide may have been due to steric interference by the rather bulky hexyl groups. When trimethylaluminum, a compound having a much smaller steric requirement, was treated with a tetrahydrofuran solution of the ylide, the expected adduct was obtained. The adduct decomposed slowly at room temperature under nitrogen or under vacuum giving methane and ethylene and was rapidly hydrolyzed by water to give methane. The most significant observation concerning the structure of the adduct was the nmr spectrum in methylene chloride, which corresponded exactly to that expected for the trimethylaluminum adduct of trimethylammonium methylide. It is also noted that the analogous phosphorus ylide adduct of trimethylaluminum has recently been prepared by Schmidbaur and Jonas[32]

$$(CH_3)_3P^+C^-H_2 + (CH_3)_3Al \longrightarrow (CH_3)_3P^+CH_2Al^-(CH_3)_3$$

Since the trialkylborane adducts of trimethylammonium methylide,[27] methylenetriphenylphosphorane,[29] and dimethyloxosulfonium methylide[28] apparently undergo rearrangement by alkyl group migration, it was of interest to investigate the possibility of causing a similar rearrangement of the trimethylaluminum adduct of trimethylammonium methylide. A sample of the alkylaluminum adduct was heated to 160° for 12 hr under high vacuum. During this time the sample partially decomposed giving methane and ethylene in small yield. The undecomposed material was then hydrolyzed with 2 N HCl, giving a relatively large yield of hydrocarbon gases shown by mass spectrometry to be a mixture of 77.7% methane, 19.2% ethane, and 2.9% propane, indicating that methyl group migration had occurred.

A calculation taking into account that the maximum yield of ethane possible in such a rearrangement is 33% shows that about 60% rearrangement took place. This is comparable to the yield of rearrangement product obtained in the reactions of boron alkyls with the ylide.[27] The formation of propane is consistent with similar data obtained by Tufariello and Lee[28] in the reaction of dimethyloxosulfonium methylide with organoboranes. For example, these workers found that treatment of trihexylborane with the sulfur ylide gave, after oxidation, 68% hexanol and 26% heptanol, as well as 6% octanol.

An explanation for the formation of propane may involve the establishment of an equilibrium between trimethylammonium methylide and trimethylaluminum in the melted adduct at 160°. This would allow interaction of initially formed dimethylethylaluminum with the free ylide, effecting a second alkyl group migration to give dimethylpropylaluminum, which upon hydrolysis would yield propane.

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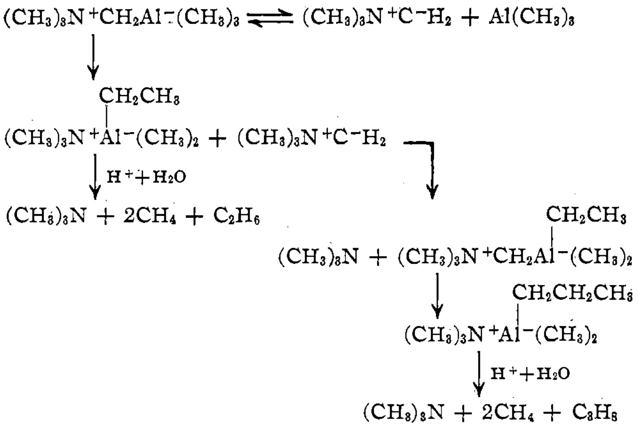
[30] F. Bickelhaupt and J. W. F. K. Barnick, *Rec. Trav. Chim.*, **87**, 188 (1968).

[31] F. G. A. Stone, *Chem. Rev.*, **58**, 100 (1958).

[32] H. Schmidbaur and G. Jonas, *Angew. Chem.*, **79**, 412 (1967).



Reaction with Trimethyl-Substituted Group IV Metal Bromides.—Previous studies of the reaction of methylenetriphenylphosphorane with trimethylbromosilane, triphenylbromogermane, and trimethylbromostannane indicated that displacement of bromide ion occurred in each case yielding a substituted phosphonium salt.[10] In order to obtain data which could be compared with these results, reactions of trimethylammonium methylide with trimethylbromosilane, trimethylbromogermane, and trimethylbromostannane were carried out.

$$(C_6H_5)_3P^+C^-H_2 + R_3MBr \longrightarrow [(C_6H_5)_3P^+CH_2MR_3]X^- \quad (M = Si, Ge, Sn)$$

The reaction of trimethylbromosilane with trimethylammonium methylide produced the expected product, trimethyl[(trimethylsilyl)methyl]ammonium bromide. All physical and chemical properties of the product obtained from the reaction were identical with those of an authentic sample of trimethyl[(trimethylsilyl)methyl]ammonium bromide prepared by reaction of trimethylamine and trimethylbromomethylsilane.

Pyrolysis of trimethyl[(trimethylsilyl)methyl]ammonium bromide at 275° under high vacuum caused demethylation at nitrogen giving methyl bromide and dimethylaminomethyltrimethylsilane.

$$[(CH_3)_3N^+CH_2Si(CH_3)_3]Br^- \xrightarrow{280°} (CH_3)_2NCH_2Si(CH_3)_3 + CH_3Br$$

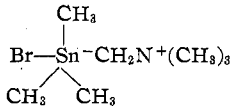
The reaction of trimethylammonium methylide with trimethylbromogermane produced a white crystalline product whose infrared and nmr spectra are consistent with those expected for trimethyl[(trimethylgermyl)methyl]ammonium bromide. The material had physical properties very similar to those of the analogous silicon compound. Pyrolysis of this salt also caused demethylation at nitrogen giving methyl bromide and dimethylaminomethyltrimethylgermane

$$[(CH_3)_3N^+CH_2Ge(CH_3)_3]Br^- \xrightarrow{280°} (CH_3)_2NCH_2Ge(CH_3)_3 + CH_3Br$$

Trimethylbromostannane appeared to react with trimethyalmmonium methylide just as the silicon and germanium trimethyl halides, giving trimethyl[(trimethylstannyl)methyl]ammonium bromide. Here again the physical properties of the isolated salt were very similar to those of the analogous silicon salt. However, pyrolysis of the tin salt did not yield products analogous to those obtained from pyrolysis of the similar silicon and germanium salts. Heating the tin compound to 210° under high vacuum caused rapid decomposition giving trimethylamine, trimethylbromostannane, and an insoluble amorphous residue thought to be polymethylene

$$[(CH_3)_3N^+CH_2Sn(CH_3)_3]Br^- \xrightarrow{210°} (CH_3)_3N + (CH_3)_3SnBr + (CH_2)_n$$

The different products obtained from pyrolysis of the material prepared by treatment of trimethylbromostannane with trimethylammonium methylide may indicate that the tin compound may not be structurally the same as the corresponding compounds prepared from trimethylbromosilane and trimethylbromogermane. In the silicon and germanium compounds the bromine atom appears to have been displaced, as expected, by the strongly nucleophilic ylide. When the germanium and silicon products were heated a nucleophilic attack at carbon occurs to give the N-demethylated product without attack on silicon or germanium. In the case of the product obtained from treatment of trimethylbromostannane with the ylide, the formation of a coordination complex between tin and the carbanionic ylide may have taken place leaving the bromine atom still bonded to tin



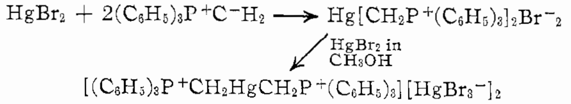
Heating such a complex would not be expected to cause demethylation at nitrogen by bromide ion but would cause dissociation of the complex; in this case, giving trimethylbromostannane and the free ylide which would decompose to trimethylamine and polymethylene. Alternatively, the nucleophilic attack of bromide on tin may provide for an activated complex of lower energy leading to decomposition rather than attack at the N-methyl group.

In summary, it appears that the reactions of trimethylammonium methylide with trimethyl-substituted group IV metal bromides are exactly the same as the reaction of methylenetriphenylphosphorane, at least in the cases of trimethylbromosilane and trimethylbromogermane. There remains some doubt, however, about the similarity of the products obtained from the reaction of the ylides with trimethylbromostannane. The phosphorus ylide is reported to cause displacement of bromide from the tin compound, whereas the nitrogen ylide may form a complex of similar stoichiometry, but without the displacement of bromide ion.

Reaction with Dipentylzinc.—Dialkylzinc compounds where zinc has two empty p orbitals might be expected to be rather good Lewis acids which would coordinate readily with donors having an easily available pair of electrons. This is indeed found in the stable adducts of a variety of zinc alkyls with tertiary amines and polydentate ethers which have been prepared and isolated.[33-35] Since zinc alkyls coordinate to a number of Lewis bases, we attempted to prepare an adduct of a dialkylzinc with trimethylammonium methylide. If the adduct was unstable and decomposed by alkyl group migration, its existence as an intermediate could be demonstrated by isolation of migration products as in the case of organoboranes. However, when dipentylzinc was treated with trimethylammonium methylide, no evidence for the formation of an adduct was found. Perhaps the failure of dipentylzinc to react with the ylide may be attributed to the steric requirement of the solvated dialkylzinc reagent. Recall that trihexylaluminum failed to react with the ylide but trimethylaluminum reacted easily. Thus lower homologs of the zinc alkyls may be required for effective coordination.

Reaction of Diphenylmercury.—Daniel and Paetsch[7] have carried out a reaction of the lithium bromide complex of trimethylammonium methylide with diphenylmercury in order to clarify the structure of the ylide in solution. Previously Gilman and Jones[36] as well as Salinger and Dessy[37] had demonstrated that, in a solution containing both lithium and mercury alkyls, an equilibrium is established in which the organic carbanions of the two alkyls are exchanged. Daniel and Paetsch,[7] therefore, attempted to show that phenyllithium would be formed in a reaction between the ylide and diphenylmercury and thereby demonstrate that the ylide in solution reacts simply as a lithium alkyl. The reaction went as expected and yields of phenyllithium as high as 65% were obtained, but no attempt was made to isolate the mercury-exchange product.

It may be noted that such a compound is reported to form when mercuric bromide is treated with the phosphorus ylide methylenetriphenylphosphorane.[14] Although the actual displacement product of the reaction was not isolated, recrystallization of the initial amorphous product from a hot, concentrated methanolic solution of mercuric bromide gave a product of the proper stoichiometry



$$HgBr_2 + 2(C_6H_5)_3P^+C^-H_2 \longrightarrow Hg[CH_2P^+(C_6H_5)_3]_2Br^-_2 \xrightarrow{HgBr_2\text{ in }CH_3OH} [(C_6H_5)_3P^+CH_2HgCH_2P^+(C_6H_5)_3][HgBr_3^-]_2$$

When the reaction between diphenylmercury and trimethylammonium methylide was repeated as described by Daniel,[7] a 66% yield of phenyllithium was obtained along with a large amount of brown, amorphous solid thought to be a material having the structure $[(CH_3)_3N^+CH_2HgC_6H_5]Br^-$. Although the isolated material could not be purified owing to its insolubility, the crude product did exhibit some properties expected of an organomercurial. For instance, the infrared spectrum (KBr pellet) showed bands characteristic of the C_6H_5Hg group at 3090, 725, and 690 cm^{-1} as well as strong, wide bands centering at 1620 and 1450 cm^{-1} which are characteristic of alkylammonium salts. Pyrolysis of a sample of the solid gave methyl bromide, trimethylamine, benzene, and mercury as expected of a compound having the postulated structure, although not in stoichiometric amounts or ratios.

Since the mercury-containing product from the reaction of the ylide with an equimolar amount of diphenylmercury could not be satisfactorily identified, an attempt was made to isolate the product from a reaction in which the amount of ylide used was slightly more than twice the molar amount of diphenylmercury. Here again, the product isolated after washing to remove unreacted diphenylmercury was an amorphous, brown, light-sensitive solid which defied solution and decomposed in water and air. The solid did, however, have several properties which might be expected of a compound having the structure $[(CH_3)_3N^+CH_2HgCH_2N^+(CH_3)_3]Br^-_2$. The infrared spectrum of this product showed very strong, wide absorption bands centering at 1600 and 1450 cm^{-1} characteristic of alkylammonium salts but the bands characteristic of the phenyl groups in diphenylmercury at 3010, 775, 725, and 690 cm^{-1} were conspicuously absent. The material did not have a well-defined melting point but began to decompose at 260° giving off mercury. Pyrolysis of a sample of the solid at 300° under high vacuum produced nonstoichiometric amounts of trimethylamine, methyl bromide, and mercury but no benzene, suggesting that both phenyl groups of diphenylmercury had been replaced. From the observed results, it appears that the expected compounds of mercury may be formed, but they precipitate in an unstable or polymeric form which defies purification.

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[33] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1064 (1966).

[34] J. G. Noltes and J. W. G. van der Kirk, *J. Organometal. Chem.* (Amsterdam), **1**, 377 (1964).

[35] K. H. Thiele and P. Zdunneck, *Organometal. Chem. Rev.*, **1**, 331 (1966).

[36] H. Gilman and R. Jones, *J. Am. Chem. Soc.*, **63**, 1439 (1941).

[37] R. Salinger and R. Dessy, *Tetrahedron Letters*, 729 (1963).