before any evidence of a reaction between $H_2B_2O_3$ and diborane is found. This effect was also found when diborane and $H_2B_2O_3$ were allowed to react under electrical discharge conditions.[5] In the absence of B_2H_6, oxygen was found to react photochemically with $H_2B_2O_3$ to produce boric acid type products. This reaction accounts for the observation that in the photochemical reaction of B_2H_6 and O_2 the ratio of O_2 to B_2H_6 used is greater than the stoichiometric value of 2.[6]

As the concentration of B_2H_6 was increased relative to the concentration of $H_2B_2O_3$, the rate of the reaction was decreased. This suggests that B_2H_6 acts as a light filter and, therefore, the primary photochemical step is the excitation of $H_2B_2O_3$. This is also supported by subsequent experiments (discussed below) that show that the $H_2B_2O_3$ ring is fragmented in the reaction.

Mass spectral patterns obtained from the photochemical reaction of ^{16}O–^{18}O isotopically labeled samples of $H_2B_2O_3$ with B_2H_6 are shown in Figure 5. The ratios of $^{16}O_3$, $^{16}O_2{}^{18}O$, $^{16}O^{18}O_2$, and $^{18}O_3$ in the $H_2B_2O_3$ ring were calculated using the known mass spectrum of $H_2B_2O_3$ with the natural isotopic abundances.[2] The nonstatistical calculation for $H_2B_2O_3$ was obtained from the "normal" mass spectral pattern assuming the ^{16}O–^{18}O ratios given in Figure 5. This would be the expected pattern if there were no fragmentation of the $H_2B_2O_3$ ring. The statistical calculation was obtained from the ratio $^{16}O:^{18}O$ = 0.459:0.541. By comparison of the observed and calculated mass spectral patterns for $H_3B_3O_3$, it is evident that the $H_2B_2O_3$ ring must be fragmented in the reaction. Thus, the photochemical reaction between $H_2B_2O_3$ and B_2H_6 cannot be viewed as a simple insertion of a BH group into the $H_2B_2O_3$ ring at the O–O bond, but must involve fragmentation of the ring and subsequent reaction with B_2H_6. In order to obtain the complete statistical scrambling found in boroxine, it is necessary that intermediates containing single oxygen atoms be formed. The complexity of the reaction suggests that it proceeds by a surface mechanism with possible intermediates like HBO.

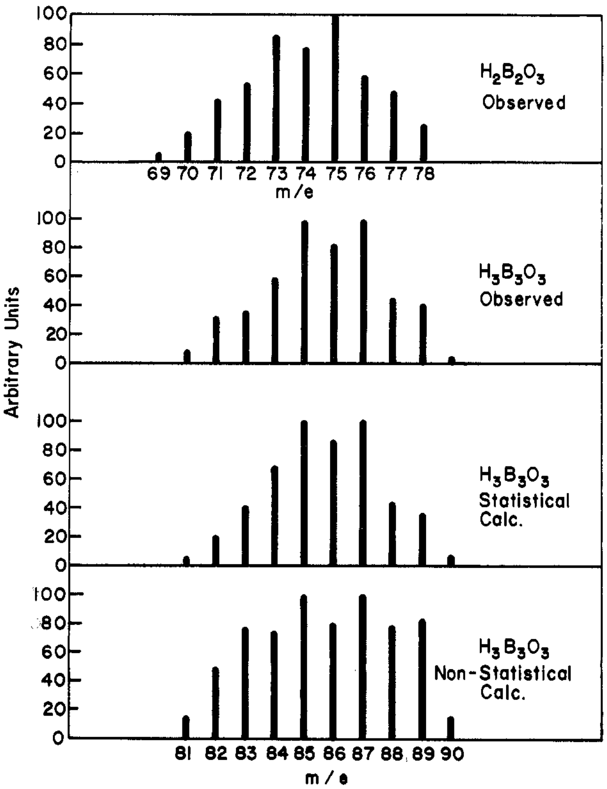

Figure 5.—Observed and calculated mass spectral patterns from the isotopic labeling experiments in the $H_2B_2O_3$–B_2H_6 reaction. Starting ratios of $H_2B_2O_3$ were $H_2B_2{}^{16}O_3$:$H_2B_2{}^{16}O_2{}^{18}O$:$H_2B_2{}^{16}O{}^{18}O_2$:$H_2B_2{}^{18}O_3$ = 0.195:0.261:0.270:0.274.

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Chemistry of Trimethylsilyl Ylides. Reactions of Trimethylsilylmethylenetrimethylphosphorane with Halogen Compounds

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A study of the reactions of trimethylsilylmethylenetrimethylphosphorane with a broad scope of halogen compounds was made. Nucleophilic substitution of alkyl halides was examined and found to proceed only with *n*-alkyl halides. New stable ylides have been uncovered, one of which is the dibasic ylide $(CH_3)_3SiC\ddot{P}(CH_3)_2P(CH_3)_3$.

Of the known isolable ylides with trimethylsilyl substitution,[2] trimethylsilylmethylenetrimethylphosphorane, $(CH_3)_3SiCHP(CH_3)_3$ (1), was chosen for initial investigation because of its good thermal stability and relatively convenient synthesis. It is believed that a detailed study of this class of ylides will contribute to the understanding of substituent effects upon structure and chemistry of ylides. Such a study would have the further practical value of determining

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(2) N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965).

the potential of these compounds in synthesis and in the search for new structures in phosphorus and silicon chemistry.

Results and Discussion

Alkyl Halides.—The nucleophilic displacement of halide ions from primary alkyl halides by **1** occurs rapidly to form substituted phosphonium salts **2**

$$\underset{\mathbf{1}}{(CH_3)_3SiCHP(CH_3)_3} + RCH_2X \longrightarrow \underset{\mathbf{2}}{(CH_3)_3SiCH(CH_2R)P(CH_3)_3{}^+X^-} \quad (1)$$

where R = H, CH_3, or C_2H_3 and X = I or Br. These salts undergo cleavage of the Si–C bond in aqueous solution, even in the presence of acid, and this cleavage reaction is used in structure proofs of **2**.

Quite a different reaction course is observed for the reaction of **1** with isopropyl bromide and *t*-butyl bromide. Proton abstraction and halide elimination produce the olefins, propylene, and isobutylene, respectively, in near quantitative yields. Substitution, if it occurs, is too small to detect (less than 1–5%). These elimination reactions are not rapid, and some heating is necessary.

Thus it appears that nucleophilic substitution occurs only with *n*-alkyl halides wherein the crowding in the transition state is still not unfavorable.

Hindered organic halides without β hydrogens either do not react, as observed for phenyl iodide, or undergo a complex reaction, as is observed for benzyl bromide which gives moderate amounts of stilbene as the only characterizable nonsalt product. In this latter reaction, there is not enough evidence to permit a choice between a carbanion and a carbene mechanism for the stilbene formation.

The alkyl-substituted phosphonium salts **2** are used to prepare new stable ylides by treatment with butyllithium. The ylides are isolable as distillable colorless or yellow liquids similar to **1**. Their physical characterization data are collected in Table I. It should be noted that those ylides which are alkyl derivatives of **1** have nearly the same thermal stability, and it may be therefore concluded that steric crowding has little if any destabilizing effect.

While reactions of organic and organometallic monohalides proceed smoothly to the substituted phosphonium salt, the reactions with "positive" polyhalides CH_2Cl_2, $CHCl_3$, CCl_4, and CBr_4 are complex, and the products have not been characterized.

Organometallic Halides.—The observed facile substitution reactions of **1** with trimethylsilyl chloride and trimethylstannyl chloride contrast markedly with the inactivity of **1** toward the analogous *t*-butyl chloride. The greater polarity and accessibility of the metal–halogen bond in the organometallic chlorides compared to that of carbon–halogen bonds undoubtedly accounts for the differences in the substitution rates.

Low yields are sometimes encountered in these substitutions. To account for such behavior, particularly in the specific example of the preparation of $[(CH_3)_3Si]_2CHP(CH_3)_3{}^+Cl^-$ from **1** and trimethylsilyl chloride, an explanation based on transylidation is suggested. Since the bis-silyl phosphonium salt is the conjugate acid of the bis-silyl ylide, $[(CH_3)_3Si]_2CP(CH_3)_3$, which is known to be a weaker base than **1**,[2] it is conceivable that some bis-silyl ylide is also formed during reaction. The following equations illustrate the process

$$\underset{\mathbf{1}}{(CH_3)_3SiCHP(CH_3)_3} + (CH_3)_3SiCl \longrightarrow [(CH_3)_3Si]_2CHP(CH_3)_3{}^+Cl^-$$

$$[(CH_3)_3Si]_2CHP(CH_3)_3{}^+Cl^- + \mathbf{1} \longrightarrow [(CH_3)_3Si]_2CP(CH_3)_3 + (CH_3)_3SiCH_2P(CH_3)_3{}^+Cl^- \quad (2)$$

In fact, only a poor yield (40%) of the bis-silyl phosphonium salt is obtained when the reaction is carried out at room temperature.[3] Nearly quantitative yields, however, are obtained at slightly higher temperature (40°) with longer reaction time. The enhancement of yield could result from the continuing reaction of trace amounts of **1** (in equilibrium with the bis-silyl ylide in the mixture) and unreacted trimethylsilyl chloride. As **1** reacts, more is formed at the expense of the bis-silyl ylide until the latter ylide or trimethylsilyl chloride is exhausted.

The reaction of **1** with dimethylphosphorus chloride gives $(CH_3)_3SiCH\ddot{P}(CH_3)_2P(CH_3)_3{}^+Cl^-$, which when treated with butyllithium yields a new ylide, $(CH_3)_3SiC\ddot{P}(CH_3)_2P(CH_3)_3$, **3**. This ylide has two adjacent strongly basic sites. It is a colorless liquid and, like **1**, is monomeric in the vapor state.

The difference in the basicity of the two basic sites in **3** is illustrated in its reactions with Lewis acids. Trimethylboron forms a 1:1 complex only, whereas diborane forms a 1:2 ylide–BH_3 adduct. In view of the inability of the sterically similar $[(CH_3)_3Si]_2CP(CH_3)_3$ to form a complex with trimethylboron, the 1:1 **3**–trimethylboron adduct obviously has P–$B(CH_3)_3$ bonding. As expected 1 mole of diborane reacts with the trimethylboron complex slowly to form the 1:2 borane adduct. The 1:2 borane complex itself loses 0.5 mole of diborane upon heating near 125° under vacuum, forming a 1:1 adduct which probably has C–BH_3 bonding.

Surprisingly, the reaction of **3** with methyl iodide leads to loss of the trimethylsilyl group under the mild condition of heating at 40° in the absence of a solvent. The product is a 2+ cation, either $[(CH_3)_3P]_2CHCH_3{}^{2+}$ or $[(CH_3)_3P]_2C(CH_3)_2{}^{2+}$. Facile loss of trimethylsilyl iodide could be explained by low activation energy for five-coordinate silicon owing to the 2+ charge of the cation. A reaction sequence (3) may be postulated. Unfortunately, it is not possible

$$(CH_3)_3SiC\ddot{P}(CH_3)_2P(CH_3)_3 + 2CH_3I \longrightarrow (CH_3)_3SiCCH_3[P(CH_3)_3]_2{}^{2+}2I^-$$

$$\longrightarrow (CH_3)_3SiI + [(CH_3)_3P]_2C(CH_3){}^+I^-$$

$$[(CH_3)_3P]_2C(CH_3){}^+I^- + CH_3I \longrightarrow [(CH_3)_3P]_2C(CH_3)_2{}^{2+}2I^- \quad (3)$$

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(3) The bis-silyl salt was not isolated. It was used *in situ* to form the bis-silyl ylide by the salt–butyllithium reaction. Yields of the salt were inferred from the amount of bis-silyl ylide finally isolated.

to decide between one and two C-methyl groups from the analyses. Both commercial analysis and analyses in our laboratory give carbon values intermediate between those expected for one and two methyl groups but closer to that expected for two. Explosions during combustion analyses, evidenced by bright light flashes, cannot be eliminated even by slow heating. The $\mathrm{H^1}$ nmr spectrum of the salt is not helpful in determining the number of C-methyl groups since the protons of the C-methyls appear to be strongly coupled to phosphorus and hidden under the broad base of the $\mathrm{P{-}CH_3}$ doublets. Large PCCH coupling constants are also known for other compounds, for example, $\mathrm{(H_2P)_2C(CH_3)_2}$, which has a PCCH coupling constant of 12 cps.[4] The present evidence is considered to favor strongly the cation $\mathrm{[(CH_3)_3P]_2C(CH_3)_2{}^{2+}}$.

The same dication is obtained by methylation of $\mathrm{(CH_3)_3SiCH\ddot{P}(CH_3)_2P(CH_3)_3{}^+Cl^-}$ with methyl iodide. If the product is the di-C-methylated cation preferred above, then the C–H must be replaced by $\mathrm{C{-}CH_3}$. One could argue that this occurs by loss of HI from a dication, $\mathrm{[(CH_3)_3P]_2CHCH_3{}^{2+}}$, which is a good Brønsted acid

$$\mathrm{(CH_3)_3SiCH\ddot{P}(CH_3)_2P(CH_3)_3{}^+Cl^- + 2CH_3I \longrightarrow [(CH_3)_3P]_2CHCH_3{}^{2+}2I^- + (CH_3)_3SiCl}$$

$$\mathrm{[(CH_3)_3P]_2CHCH_3{}^{2+}2I^- + CH_3I \xrightarrow{-HI} [(CH_3)_3P]_2C(CH_3)_2{}^{2+}2I^-} \quad (4)$$

The crude methylation product here is deeply orange, in contrast to the clear white crude product from methylation of **3**. Decomposition of the HI to form iodine would give a colored product because of the $\mathrm{I_3^-}$ ion. Support for these conjectures is the report that the methylenic protons on the analogous bissulfonium dication, $\mathrm{[(CH_3)_2S]_2CH_2{}^{2+}}$, are weakly acidic, $\mathrm{p}K_\mathrm{a} = 9$.[5]

In other nucleophilic reactions with organometallic halides the methylmercury-substituted cation, $\mathrm{(CH_3)_3SiCH(HgCH_3)P(CH_3)_3{}^+}$, and the trimethylstannyl-substituted ylide, $\mathrm{(CH_3)_3SiCP(CH_3)_3Sn(CH_3)_3}$, are also obtained. The vapor pressures of the trimethylstannyl-substituted ylide and $\mathrm{[(CH_3)_3Si]_2CP(CH_3)_3}$ are remarkably similar.

Transition Metal Halides.—In reactions with transition metal halides, complexes with $\mathrm{HgI_2}$, $\mathrm{AgI_3}$, and CuI were obtained. The mercury and silver complexes lose the trimethylsilyl group on work-up with acetonitrile, probably from hydrolysis caused by adventitious water. The hydrolyzed complexes appear to be $\mathrm{(CH_3)_3PCH_2HgI_2}$ and $\mathrm{(CH_3)_3PCH_2AgI_3}$ on the basis of analytical and degradation data.

Basicity.—It is apparent from some of the foregoing discussions that the basicity of ylides is one of the more important of their chemical properties. However, it has not yet been possible to ascertain a scale of basicities which has physical significance. In this connection it is of value to report that **1** reacts with cyclopentadiene in ether solution to form the insoluble, white, highly reactive salt $\mathrm{(CH_3)_3SiCH_2P(CH_3)_3{}^+C_5H_5{}^-}$. Unfortunately, no suitable solvent for this salt has been found so that a comparison between the basicities of **1** and the cyclopentadienide ion could be made. While the crystal lattice energy is a complication here and operates to make the phosphonium ion a weaker acid, it should be noted that the pK of the phosphonium ion must be greater than that for the conjugate acids of trimethylammonium cyclopentadienylide and pyridinium cyclopentadienylide ylides which have an aqueous $\mathrm{p}K_\mathrm{a}$ of 10.[6]

Experimental Section

Diethyl ether, hexane, and acetonitrile were dried with sodium, sulfuric acid, and $\mathrm{P_4O_{10}}$, respectively, and were stored over calcium hydride. Unless otherwise stated reagents used were of reagent grade commercial quality.

Diborane was prepared according to literature directions[7] from sodium borohydride and iodine in tetraglyme solution.[8]

Vapor pressure and molecular weight determinations were made with a tensimeter[9] in which the sample contacts only mercury, glass, and small amounts of Teflon and Viton A (Du Pont trademarks for fluorocarbon polymers). Pressure measurements, corrected for expansion of mercury, had precision better than ±0.03 mm. The vapor pressure measurements were fitted with the best straight line graphically.

Melting points were uncorrected for emergent stem. Freezing points were obtained with an alcohol thermometer calibrated with an iron–constantan thermocouple.

Trimethylsilylmethylenetrimethylphosphorane was prepared from the phosphonium chloride salt, $\mathrm{(CH_3)_3SiCH_2P(CH_3)_3{}^+Cl^-}$, as described previously.[2]

Dimethylchlorophosphine was prepared[10] according to literature procedures from $\mathrm{PCl_3}$, dimethylamine, and methylmagnesium bromide.[11] A 93% yield for the last step, based upon $\mathrm{(CH_3)_2N{-}P(CH_3)_2}$, was obtained. The product was a water-white liquid with 0° vapor pressure of 35. 0 mm (lit.[11] 34.6 mm).

Reaction with Methyl Iodide or Ethyl Bromide.—Either equimolar amounts of **1** and the alkyl halide or an excess of alkyl halide was used. Either the reagents were condensed together and allowed to warm to room temperature, or the alkyl halide was dissolved in ether and added dropwise at 0° with stirring. The resulting slurry of white solid was then stirred for about 1 hr and the volatiles were removed under high vacuum pumping. The product from the methyl iodide reaction was identical with (1-trimethylsilylethyl)trimethylphosphonium iodide[2] by infrared analysis. The product from the ethyl bromide reaction was assigned the structure of (1-trimethylsilylpropyl)-trimethylphosphonium bromide on the basis of its infrared absorption which showed both $\mathrm{PCH_3}$ and $\mathrm{SiCH_3}$ deformations. This structure assignment was confirmed by hydrolytic cleavage. An aqueous solution of 20.7 mg (0.91 mmole) of the bromide salt was made weakly basic and heated to 60°. After cooling, a saturated solution of ammonium hexafluorophosphate was added to precipitate 19.7 mg of white crystalline solid. This solid was shown to be propyltrimethylphosphonium hexafluorophosphate by infrared comparison with a known sample prepared from trimethylphosphine and propyl bromide. The yield for the cleavage reaction was 95%.

$\mathrm{(CH_3)_3SiCCH_3P(CH_3)_3}$.—To a slurry of 1.5 g (5.0 mmoles) of (1-trimethylsilylethyl)trimethylphosphonium iodide in 15.0 ml of anhydrous ether was added 3.8 ml (1.23 *M*) of butyllithium in anhydrous ether dropwise, under nitrogen with stirring over a

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(8) The authors are indebted to R. J. Rowatt for this preparation.

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TABLE I

PHYSICAL PROPERTIES OF $(CH_3)_3SiCRP(CH_3)_3$ YLIDES

Compound	Mp, °C	Bp,[a] °C (p, mm)	Vapor pressure eq[b] A	Vapor pressure eq[b] B	ΔH_v,[c] kcal/mole	Mol wt[d]	Temp threshold,[e] °C
$(CH_3)_3SiC(CH_3)P(CH_3)_3$	−61 to −69	72 (8)	...	...	...	...	...
$(CH_3)_3SiC(C_2H_5)P(CH_3)_3$	−46	68–70 (10)	...	...	...	...	...
$(CH_3)_3SiC(CH_2CHCH_2)P(CH_3)_3$ (yellow liquid, mol wt 202.3)	−48	64–65 (3)	2215	7.498	10.10 (207)	198 (84.4)	88
$[(CH_3)_3Si]_2CP(CH_3)_3$ (mol wt 234.2)	19–21	49–50 (1)	2771.4	8.2925	12.64 (239)	251 (125.4)	110
$(CH_3)_3SiC[Sn(CH_3)_3]P(CH_3)_3$	18–21	63 (1)	2725.7	8.2871	12.43 (231)	...	120
$(CH_3)_3SiC[\ddot{P}(CH_3)_2]P(CH_3)_3$ (mol wt 222.3)	−2–0	54 (0.1)	2735.8	7.2864	12.48 (233)	220 (110.2)	115

[a] Boiling point in short-path still. [b] Log p(mm) = $-(A/T) + B$. [c] Derived from vapor pressure equation. Extrapolated normal boiling point (°C) in parentheses. [d] By vapor density at temperature (°C) indicated in parentheses. [e] Temperature at which decomposition was noticeable in tensimeter.

TABLE II

YLIDE–BORON ACID COMPLEXES

Compound[a]	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% B Calcd	% B Found	% P Calcd	% P Found	Hydrolytic hydrogen,[b] mmole/mg × 10³ Calcd	Hydrolytic hydrogen,[b] mmole/mg × 10³ Found
$(CH_3)_3SiCHBH_3P(CH_3)_3$ Chalk white solid; sublimes at 90–95°	121–122	47.7	48.0	12.5	12.5	6.1	6.0	17.6	17.4		
$(CH_3)_3SiCHBF_3P(CH_3)_3$ White solid; sublimes at 100–110°		36.5	36.5	8.2	7.9	4.7	4.6	13.5	13.8		
$(CH_3)_3SiC(CH_3)BH_3P(CH_3)_3$ White solid; distils at 80°	59.5–60	50.3	50.7	12.6	12.3	5.6	5.6	16.2	16.3		
$[(CH_3)_3Si]_2CBH_3P(CH_3)_3$ White solid; distils at 70–85°	70.5	48.4	48.5	12.1	11.9	4.4	4.4	12.5	12.3		
$[(CH_3)_3Si]_2CBF_3P(CH_3)_3$ White solid; sublimes at 100–105°		39.6	38.8	8.9	8.6	3.6	3.7	10.3	11.3		
$(CH_3)_3SiC(BH_3)P(CH_3)_2BH_3P(CH_3)_3$ Sticky white solid											
$(CH_3)_3SiC(BH_3)P(CH_3)_2P(CH_3)_3$ Soft, white solid; distils at 125°										12.7	12.7
$(CH_3)_3SiCP(CH_3)_3B(CH_3)_3P(CH_3)_3$ Viscous, clear liquid											
$(CH_3)_3PCH_2BH_3$ White solid; distils at 124°										28.9	29.3

[a] Distillation or sublimation was conducted while pumping with a two-stage mercury diffusion pump. [b] From measurement of hydrogen produced in acid solution in presence of platinum black.

15-min period at 0°. The mixture was stirred at 0° for an additional 30 min. Evaporation of ether left a white residue which was heated slowly to 100° under vacuum to liberate the ylide. Considerable volatile material was caught in a U trap cooled to −78°. Heating was continued to 125° until no more material volatilized, whereupon the trap content was transferred (condensed) into a short-path still and distilled to give 0.310 g of ylide (37% based on butyllithium) boiling at 72.5° (7.5 mm). The colorless liquid melted over a range of −61 to −59°.

A small sample was treated with hydrogen chloride and the resulting chloride salt was converted to the hexafluorophosphate salt by metathesis.

Its infrared spectrum was identical with that of a known sample[2] of $(CH_3)_3SiCHCH_3P(CH_3)_3{}^+PF_6{}^-$.

$(CH_3)_3SiC(C_2H_5)P(CH_3)_3$ was prepared in a manner similar to that of the C-methyl homolog. The ylide was obtained in 66% yield. Its properties are summarized in Table I.

Boron Acid Complexes.—Borane and trifluoroborane adducts were prepared for a number of the ylides mentioned herein. These are all new compounds. Some of their properties and characterization data are given in Table II.

A typical preparation is that for $(CH_3)_3SiC(CH_3)BH_3P(CH_3)_3$. A mixture of 257.1 mg (1.46 mmoles) of (1-trimethylsilylethylidene)trimethylphosphorane in 3.0 ml of anhydrous ether and 1.45 mmoles of diborane (passed through a −135° trap for purification) was pepared by condensing them together in a bulb attached to the vacuum line. A white solid formed on warming to near 0°. The slurry was stirred for 1 hr at 0°, whereupon volatiles were removed, leaving an oily residue which was heated under vacuum at 50° to remove any traces of ether present. The oil slowly crystallized at 0° to give a sticky solid which was sublimed at 80° to yield 210 mg of trimethylphosphinemethyltrimethylsilylmethyleneborane (76.2%). The white solid was soluble in chloroform and had a melting point of 59.5–60°.

$(CH_3)_3SiC(CH_2CHCH_2)P(CH_3)_3$.—A solution of 296 mg (1.83 mmoles) of **1** in 5.0 ml of dry ether and 139.7 mg (1.83 mmoles) of freshly distilled allyl chloride (bp 46°) were condensed together in a bulb attached to the vacuum line. A reaction occurred

TABLE III

INFRARED SPECTRA[a]

$(CH_3)_3PCH(CH_3)Si(CH_3)_3{}^+I^-$, N	1440 m, 1320 w, 1295 s, 1257 s, 1145 m, 987 s, 940 s, 935 s, 890 m, 870 m, 848 m, b, 805 m, 777 m, 775 m, 699 w
$(CH_3)_3PCH(CH_3)Si(CH_3)_3{}^+PF_6{}^-$, N	1425 m, 1328 w, 1311 m, 1260 m, 1150 w, 1010 w, 980 m, 968 m, 885 s, 840 s, b, 799 w, 763 w, 744 w, 725 w, 704 w
$(CH_3)_3PC(CH_3)Si(CH_3)_3$(1)	2975 m, 2948 m, 2939 w, 1477 w, 1436 m, 1402 w, 1322 m, 1308 m, 1271 m, 1260 m, 1208 w, 1166 s, 1060 m, 1040 m, 1020 m, 990 m, 948 m, 922 w, 870 s, 854 s, 827 s, 758 m, 677 w, 670 m
$(CH_3)_3PCH(C_2H_5)Si(CH_3)_3{}^+PF_6{}^-$, N	1430 s, 1325 w, 1308 m, 1299 m, 1252 m, 1123 w, 1048 w, 975 m, 962 m, 912 w, 875 w, 835 s, 774 m, 738 w, 700 w
$(CH_3)_3PC(CH_3)(CH_2CH{=}CH_2)Si(CH_3)_3{}^+Cl^-$, N	1644 m, 1425 m, 1300 m, 1253 s, 1163 m, 1050 s, 998 s, 975 s, 848 s
$(CH_3)_3PC_3H_7{}^+PF_6{}^-$, N	1461 s, 1329 w, 1310 s, 1086 w, 1063 m, 987 s, b, 961 s, 848 s, b, 780 m, 745 w
$(CH_3)_3PCH(CH_2CH_3)Si(CH_3)_3{}^+Br^-$, N	1302 m, 1252 m, 1149 w, 1055 w, 988 s, 975 s, 880 m, 845 s, b, 776 m
$(CH_3)_3PCH(BF_3)Si(CH_3)_3$, N	1320 w, 1300 m, 1268 w, 1258 m, 1250 m, 1143 m, 1078 s, 1026 s, 962 s, 938 s, 887 m, 860 m, 850 m, 770 w, 762 w, 694 w
$(CH_3)_3PCH(BH_3)Si(CH_3)_3$, N	2341 w, 2252 s, 2222 m, 1289 s, 1250 w, 1239 m, 1138 s, 1026 m, 980 s, 958 m, 949 s, 884 s, 846 s, 830 s, 800 w, 769 w, 755 w, 684 w
$(CH_3)_3PC(CH_3)(BH_3)Si(CH_3)_3$, N	2258 s, 2213 m, 1308 w, 1292 m, 1242 m, 1137 s, 1125 m, 1023 m, 967 s, 948 m, 883 m, 845 s, 834 s, 768 w
$(CH_3)_3PCH_2BH_3$, N	2322 m, 2211 s, b, 1395 w, 1285 s, 1150 s, 1139 s, 1118 w, 983 s, 956 s, 847 s, 777 m
$(CH_3)_3PCH(HgCH_3)Si(CH_3)_3{}^+PF_6{}^-$, N	1438 m, 1326 m, 1306 m, 1300 m, 1270 w, 1260 m, 1132 m, 980 s, 960 s, 888 s, 838 s, b, 765 m, 744 w, 698 w, 652 w
$(CH_3)_3PC(BF_3)[Si(CH_3)_3]_2$	1327 w, 1306 m, 1300 m, 1270 w, 1252 m, 1100 m, 1075 m, 1058 s, 1028 s, 995 m, 960 s, 926 s, 899 m, 860 m, 840 m, 682 w
$(CH_3)_3PC(BH_3)[Si(CH_3)_3]_2$, N	2350 w, 2260 s, 2256 s, 2224 m, 1288 m, 1254 m, 1242 s, 1147 s, 995 s, 980 m, 954 s, 946 s, 879 m, 946 s, 835 s
$(CH_3)_3PCH[P(CH_3)_2]Si(CH_3)_3{}^+Cl^-$, N	2845 s, 1294 s, 1250 m, 1055 w, 990 s, 969 s, 926 m, 907 m, 845 m, 777 w
$(CH_3)_3PC[\ddot{P}(CH_3)_2]Si(CH_3)_3$(1)	2945 s, 2897 s, 2805 m, 1418 m, 1303 w, 1283 m, 1255 m, 1238 m, 1150 w, 1046 s, b, 1000 w, 960 s, 927 m, 842 m, 825 s
$(CH_3)_3PC(BH_3)[P(CH_3)_2]Si(CH_3)_3$, N	2275 s, b, 2223 m, 1296 s, 1245 m, 1144 s, 1073 w, 1030 m, 985 s, 957 s, 885 s, 850 s, 831 s, 758 w, 685 w
$(CH_3)_3PC(CH_3)_2P(CH_3)_3{}^{2+}2(I^-)$, N	1437 m, 1320 w, 1308 s, 1300 m, 1061 s, 1008 s, 964 s, b, 879 w, 845 s, b, 780 w
$(CH_3)_3PC(CH_3)_2P(CH_3)_3{}^{2+}2(PF_6{}^-)$, N	1431 s, 1326 w, 1309 m, 1300 m, 1025 s, 978 s, 949 m, 840 s, b
$(CH_3)_3PCH_2Si(CH_3)_3{}^+(C_5H_5)^-$, N	3032 w, 3021 s, 2802 s, 1413 m, 1290 s, 1275 m, 1254 m, 1244 m, 1238 m, 1146 m, 1127 m, 1000 s, 975 s, 952 s, 927 m, 882 s, 840 s, 775 m, 768 m, 762 w, 700 s, 1340 m, multiplet

[a] Absorptions are listed in wave numbers (cm^{-1}) and are qualitatively described as strong (s), moderate (m), weak (w), or broad (b). Many very weak absorptions are not listed. Where indicated with N the sample was run as a mineral oil mull, and the absorptions in common with or masked by those of the mineral oil are not included.

slowly at room temperature. The solution was stirred at 40° for 1 hr. Volatile material was removed under vacuum leaving a white residue. To this was added 1.47 ml (1.18 *M*) of butyllithium solution in ethyl ether, dropwise at 0° over a period of 30 min. The yellow liquid ylide was isolated in the usual way, in a yield of 77%; bp 64–65° (2.8 mm).

A small sample on treatment with methyl iodide produced a phosphonium salt having an infrared spectrum nearly identical with that of a sample of phosphonium salt prepared from allyl chloride and $(CH_3)SiC(CH_3)P(CH_3)_3$. Both salts decomposed in moist air and could not be recovered from acidified water without loss of the trimethylsilyl group. They gave identical $PF_6{}^-$ salts, presumably $(CH_3)_3PCH(CH_3)CH_2CHCH_2{}^+PF_6{}^-$. The isolation of the same cation by two routes supports the structure assignment.

The molecular weight of the ylide was determined from its vapor density. A 44.606-mg sample in a 306.6-ml tensimeter exerted 16.34 mm pressure at 84.4°.

Vapor pressure data are collected here and compared with that calculated from the graphically fitted straight line. T (°C), p_{obsd} (mm), p_{calcd} (mm): 58.7, 6.65, 6.65; 64.7, 8.75, 8.71; 70.05, 11.21, 11.10; 75.10, 13.72, 13.72; 79.6, 16.49, 16.49.

$[(CH_3)_3Si]_2CP(CH_3)_3$.—A mixture of 1.91 g (11.8 mmoles) of **1** and 6.0 ml of dry ether was frozen in a bulb equipped with a side arm having a serum cap and attached to the vacuum line. Onto this was condensed 1.28 g (11.7 mmoles) of trimethylsilyl chloride. After warming to 0°, a slurry of white solid formed. After stirring for 2.5 hr at a temperature near 40°, 9.94 ml of 1.18 *M* butyllithium in ether solution was added over a 15-min period and the mixture was stirred an additional hour at 0°. Volatile material at room temperature was removed, leaving a white solid residue. On slowly heating this residue under vacuum to about 100°, considerable material was caught in a U trap cooled to −78°. Heating was continued to 130° until no more material volatilized. The trap content was transferred (condensed) into a short-path still and distilled to give 2.73 g of bis(trimethylsilyl)methylenetrimethylphosphorane (94.3% based on butyllithium); bp 49–51° (1 mm), mp 19–21°.

The vapor density molecular weight was calculated to be 252 from the 5.18 mm pressure exerted by a 15.583-mg sample in a 306.6-ml tensimeter at 125.2°. This value agrees reasonably well with the theoretical monomeric weight of 234.2.

Vapor pressure measurements were made over an 80° range. As the oil bath was cooled, several vapor pressure measurements were run to check reproducibility of measurements. If the temperature was kept below 130°, no significant decomposition resulted. The experimental data are given along with pressures calculated from the straight line fitted graphically. T (°C), p_{obsd} (mm), p_{calcd} (mm): 66.2, 1.34, 1.34; 73.0, 1.98, 1.93; 80.9, 2.92, 2.92; 86.7, 3.84, 4.13; 91.7, 4.94, 4.97; 96.8, 6.34, 6.33; 100.9, 7.66, 7.66; 107.9, 10.60, 10.50; 113.5, 13.32, 13.35; 119.7, 17.23, 17.35; 125.4, 21.70, 21.82; 129.5, 25.67, 25.76; 135.0, 31.86, 31.81; 137.6, 35.34, 35.28; 142.8, 42.82, 42.76.

$(CH_3)_3Si\ddot{P}(CH_3)_2P(CH_3)_3$ (3) was prepared several times. A typical preparation is described.

A sample of 2.103 g (0.013 mole) of trimethylsilylmethylenetrimethylphosphorane in 30.0 ml anhydrous ether and 1.12 g

(0.012 mole) of dimethylchlorophosphine were condensed together in a bulb, fitted with a serum cap adaptor, attached to the vacuum line. On warming to room temperature, a solid slowly formed. The slurry was stirred for another 30 min at room temperature and 3 hr at 48°. Then 11.0 ml of 1.18 *M* butyllithium in ethyl ether was added dropwise with stirring at 0°. The slurry was stirred at room temperature for 30 min and volatiles were removed under vacuum leaving a white residue. Upon slowly heating the residue to 90°, considerable material was caught in a U trap cooled to −78°. Heating was continued to 150° until no more material volatilized. The content of the U trap was transferred by condensation to a short-path still and distilled to give 1.245 g of **3** (70.5% based on butyllithium) boiling at 54° (0.1 mm). The colorless liquid had a melting point of −20° (temperature corrected for emergent stem).

Vapor pressure measurements are given here. T (°C), p_{obsd} (mm), p_{calcd} (mm): 78.6, 3.50, 3.42; 83.9, 4.27, 4.28; 88.0, 5.07, 8.13; 92.2, 6.05, 6.07; 98.9, 7.91, 7.94; 103.5, 9.76, 9.52; 104,5, 9.86, 9.89; 110.1, 12.22, 12.24; 115.2, 14.80, 14.25; 120.9, 18.07, 18.02; 125.4, 21.13, 21.16.

To confirm the structure of the ylide, a 239.8-mg (1.08-mmole) sample was treated with 1.16 mmoles of hydrogen chloride in a bulb attached to the vacuum system. After standing for 30 min at room temperature, 0.10 mmole of gas was removed (the ir spectrum of which showed only $(CH_3)_3SiCl$ bands). The infrared spectrum of the white solid residue was the same as that of the salt $(CH_3)_3SiCH\ddot{P}(CH_3)_2P(CH_3)_3{}^+Cl^-$, obtained from 1 and dimethylchlorophosphine.

A 0.135-mmole portion of ylide was condensed with 0.176 mmole of trimethylboron. Reaction was observed only when the mixture was warmed above room temperature. The gaseous products were removed and identified as 0.027 mmole of trimethylboron and 0.03 mmole of hexamethyldisiloxane by infrared spectral analysis. The disiloxane apparently was produced from traces of water. Thus, the nonvolatile liquid adduct which remained in the reaction flask was inferrred to have 1:1 stoichiometry (1:1.1 measured). To this adduct was added 0.130 mmole of diborane. After heating the mixture at 70°, the only gaseous material recovered was 0.13 mmole of trimethylboron (by infrared analysis). Thus a 1:2 ylide–BH_3 adduct must have formed. Sublimation of this adduct at 125° under high-vacuum pumping led to loss of diborane and formation of a 1:1 ylide–BH_3 adduct whose composition was confirmed by hydrolytic hydrogen analysis (see Table II).

The same 1:2 and 1:1 ylide–borane adducts were also obtained directly from the ylide and diborane.

$(CH_3)_3SiCH(HgCH_3)P(CH_3)_3{}^+Cl^-$.—A sample of 50.1 mg (0.308 mmole) of 1 was condensed onto a slurry of 77.0 mg (0.307 mmole) of methylmercury chloride in 2.0 ml of anhydrous ether in a bulb attached to the vacuum line. A white solid formed on warming the solution to 0°. After removal of the ether under vacuum, 89.3 mg of (methymercuritrimethylsilylmethyl)trimethylphosphonium chloride (71% based on methylmercury chloride used) was isolated. A portion of the chloride salt was dissolved in water acidified with 6 *M* hydrochloric acid and an excess of a saturated solution of ammonium hexafluorophosphate was added. The white precipitate that formed was recrystallized from hot acidic water (temperature kept below 60° to avoid decomposition) as (methylmercuritrimethylsilylmethyl)trimethylphosphonium hexafluorophosphate. *Anal.* Calcd for $(CH_3)_3SiCH(HgCH_3)_3{}^+PF_6{}^-$: C, 18.45; H, 4.21. Found: C, 18.54; H, 3.94.

$(CH_3)_3SiCH_2P(CH_3)_3{}^+C_5H_5{}^-$.—A 120.4-mg (0.743-mmole) sample of 1 was condensed into a bulb attached to the vacuum line which contained 0.06 ml of freshly distilled cyclopentadiene (bp 42°). On warming to near 0°, a white solid formed. Virtually no volatile material was found when the system was evacuated. The 1:1 adduct decomposed to a black, tarry material on exposure to air. Attempts to dissolve the solid in tetrahydrofuran or acetonitrile failed. The solid reacted vigorously with solvents containing an active group (*e.g.*, halogens, hydroxyl groups).

Structural assignment of the 1:1 adduct as a cyclopentadienide salt was supported by reaction with gaseous hydrogen chloride. Addition of 0.515 mmole of HCl onto 0.51 mmole of adduct liberated cyclopentadiene and $(CH_3)_3SiCH_2P(CH_3)_3{}^+Cl^-$, identified by infrared spectroscopy, as the only products.

Hydrolysis of $(CH_3)_3SiCHBH_3P(CH_3)_3$ and Synthesis of $(CH_3)_3PCH_2BH_3$.—$(CH_3)_3SiCHBH_3P(CH_3)_3$ was stable to 6 *M* sodium hydroxide up to 80° even for 12 hr. However, aqueous 6 *M* sodium hydroxide or methanolic potassium hydroxide cleaved the trimethylsilyl group on heating at 85° for 76 hr in a sealed ampoule. The insoluble, off-white solid product from the hydrolysis was recrystallized from a strongly basic aqueous solution and sublimed at 145°. It was determined to be $(CH_3)_3PCH_2BH_3$ by its hydrolytic hydrogen content; yield, 54% (see Table II).

AgI, HgI_2, and CuI Reactions.—A slurry of 127.6 mg (0.785 mmole) of 1 and 262.8 mg (0.894 mmole) of silver iodide in 4.0 ml of tetrahydrofuran slowly turned brown-black at room temperature. Solvent was removed and the residue recrystallized from acetonitrile to give 167 mg of red-brown solid. *Anal.* Calcd for $(CH_3)_3PCH_2Ag^+I_3{}^-$: C, 8.2; H, 1.9; P, 5.3. Found: C, 8.3; H, 1.9; P, 4.7. Upon heating this solid in aqueous 6 *M* NaOH for several hours, tetramethylphosphonium cation was isolated from the solution (as the $PF_6{}^-$ salt).

A slurry of 254.8 mg (1.570 mmoles) of 1 and 269.0 g (1.39 mmoles) of cuprous iodide in dry ether reacted to form a dark green oil. After solvent removal and leaching with acetonitrile, a dark green solid remained. For characterization a small sample was treated with excess gaseous hydrogen chloride. The yellow solid which resulted was extracted with methanol and the solution was evaporated to dryness. The residue was taken up in acidified water. Metathesis with ammonium hexafluorophosphate gave white $(CH_3)_3SiCH_2P(CH_3)_3{}^+PF_6{}^-$, identified from its infrared spectrum.

A 204.1-mg (1.250-mmole) sample of 1 was condensed into a bulb attached to the vacuum line containing 571.0 mg (2.510 mmoles) of mercuric iodide dissolved in 1.5 ml of tetrahydrofuran. The solvent was removed under vacuum. The solid was recrystallized from hot acetonitrile (temperature kept below 45° to avoid decomposition) yielding 161.0 mg of material believed to be iodo(trimethylphosphinemethylene)mercury iodide (37%, based on 1), mp 135.6°. *Anal.* Calcd for $(CH_3)_3PCH_2HgI^+I^-$: C, 8.80; H, 2.02; P, 5.69. Found: C, 9.62; H, 2.08; P, 4.06.

$(CH_3)_3SiC[Sn(CH_3)_3]P(CH_3)_3$.—A mixture of 1.050 g (6.50 mmoles) of 1, 0.684 g (3.43 mmoles) of trimethyltin chloride, and about 4 ml of ether was prepared in a vessel attached to the vacuum line. White solid was formed and the mixture was stirred 2 hr at room temperature. Volatile materials were passed through a −40° trap. The only material stopped by the trap was produced after the residue in the reaction flask was heated with a soft flame. Distillation gave a liquid boiling at 63° (1 mm); mp 18–21°. *Anal.* Calcd for $(CH_3)_3SiC[Sn(CH_3)_3]P(CH_3)_3$: C, 36.9; H, 8.4. Found: C, 36.1; H, 8.3.

A small sample reacted vigorously with methyl iodide and the white salt product was taken up in water and metathesized to the hexafluorophosphate which in turn was recrystallized. *Anal.* Calcd for $(CH_3)_3SiCCH_3[Sn(CH_3)_3]P(CH_3)_3{}^+PF_6{}^-$: C, 27.2; H, 6.2. Found: C, 27.7; H, 6.2.

For characterization, a 60.2-mg sample was treated with excess ethanol (1 ml) and allowed to stand several hours. To this was added 1 mmole of gaseous hydrogen chloride. On warming to room temperature, a white slurry formed. Volatiles were fractionated through traps at −30 and −196°. The −30° trap stopped 10.3 mg (0.050 mmole) of $(CH_3)_3SnCl$, identified by its melting point (37–38°) and odor. Thus, 25% of the tin theoretically present was recovered as $(CH_3)_3SnCl$.

Another sample of ylide was treated with dilute nitric acid and tested for Cl^- with silver nitrate. No chloride was detected, and thus it was concluded that the product had no codistilling $(CH_3)_3SnCl$ present.