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Trimethylsilyl Ylides

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Distillable ylides with α-trimethylsilyl groups have been synthesized by the reaction of onium salts with butyllithium in ether. $(CH_3)_3P^+{-}^-CHSi(CH_3)_3$, $(CH_3)_3P^+{-}^-C[Si(CH_3)_3]_2$, $(CH_3)_3As^+{-}^-CHSi(CH_3)_3$, and $(CH_3)_2S^+{-}^-CHSi(CH_3)_3$ are colorless liquids with low freezing points and high boiling points (about 180°). They are strong, reactive bases which fume in air and liberate hydroxide ion from water. $(CH_3)_3P^+{-}^-CHSi(CH_3)_3$ is thermally stable at temperatures above 100°.

Introduction

The recently discovered ylide $(CH_3)_3P^+{-}^-CHSi(CH_3)_3$ is novel in that it is volatile, highly reactive, yet thermally stable.[1] A study has therefore been initiated to determine how these properties are structurally related and to determine what other compounds of similar nature might be synthesized.

The term, ylide, refers to the class of polar compounds with an onioum-type atom adjacent to a trigonal carbon, so named because the extreme valence bond form shows a zwitterion structure having a methylide carbanion, as in triphenylphosphinomethylide, A.

$$\underset{\text{A}}{(C_6H_5)_3P^+{-}^-CH_2 \longleftrightarrow (C_6H_5)_3P{=}CH_2}$$

More often A is named triphenylphosphinemethylene, emphasizing another valence bond extreme of the structure.[2] This class of compounds was demonstrated first by Staudinger and Meyer[3] and also by Coffman and Marvel. The subsequent discovery by Wittig[4] that the phosphorus-containing ylides react with carbonyl compounds to exchange methylene for oxygen of the carbonyl compound led to the syntheses of many kinds of ylides, since the reaction is a valuable method for preparing certain olefins. Usually the ylide is prepared *in situ* and is not isolated because of high reactivity. Those that have been isolated have the carbanion carbon conjugated with a π-electron system, and they are usually found to be colored solids. The first ylide, triphenylphosphinediphenylmethylene, is one such isolable ylide.

The silyl-substituted ylides reported by Gilman and Tomasi[5] were not isolated and were not characterized. They were inferred to be present in dark-colored reaction mixtures. They did not undergo the normal Wittig reaction with benzophenone.

Several α-trimethylsilyl-substituted ylides of the type

$$(CH_3)_nE^+{-}^-CHSi(CH_3)_3 \qquad n = 2, 3; \quad E = P, As, S$$

have now been obtained in good yields by the direct reaction of butyllithium with onium salts. The chemical reactivity of these compounds is found to be strongly dependent on the onium element, E.

Experimental

Reagent grade solvents were used. Ether was dried over sodium wire. The n.m.r. spectra were obtained on Varian A-60 instruments. Vapor pressure and molecular weight measurements were made using immersible tensimeters[6] constructed so that the sample is in contact only with glass, mercury, Teflon, and Viton A. Pressures were measured with a cathetometer capable of 0.1-mm. precision. The tensimeters were thermostated to ±0.1° in a mineral oil bath. Temperatures were obtained with calibrated thermometers, and corrections were made for emergent stem.

Trimethylphosphine was prepared from phosphorus tribromide and excess methylmagnesium bromide in ether according to a standard method.[7] It was isolated and purified *via* the silver iodide complex. Traces of water were removed by allowing it to contact calcium hydride for several days and then distilling (under vacuum).

Trimethylarsine was prepared from methylmagnesium bromide and arsenic trichloride in ether. The product was isolated as the silver iodide complex.[7b] Small amounts of water were removed by contact with calcium hydride. The purified material had a 100-mm. vapor pressure at 0° (100 mm. reported[7b]). The yield of purified product was 28%.

Chloromethyltrimethylsilane was prepared by standard procedures[8] from chlorotrimethylsilane. The over-all yield of pure chloromethyltrimethylsilane, b.p. 96–98°, based on chlorotrimethylsilane was 46%.

Trimethylphosphinetrimethylsilylmethylene (I).—Trimethylsilylmethyltrimethylphosphonium chloride (II), $(CH_3)_3SiCH_2P(CH_3)_3{}^+Cl^-$, was prepared by heating equimolar amounts of chloromethyltrimethylsilane and trimethylphosphine in a closed system at 40° for several days. The unreacted materials were removed under vacuum to give the substituted phosphonium salt as a white crystalline solid in a yield better than 50%.

Anal.[9] Calcd. for $(CH_3)_3SiCH_2P(CH_3)_3{}^+Cl^-$: C, 42.3; H, 10.1; Cl (ionic), 17.8. Found: C, 42.3; H, 10.1; Cl (ionic), 17.9.

A small amount of the chloride salt was converted to the PF_6^- salt (III) by dissolving it in water and adding saturated NH_4PF_6 solution until precipitation was complete. The white precipitate was recrystallized from hot water acidified with hydrochloric acid, keeping the temperature below 70°, since $(CH_3)_3SiCH_2P(CH_3)_3{}^+$ is cleaved rapidly in boiling water to form $(CH_3)_3SiOSi(CH_3)_3$ and tetramethylphosphonium ion.

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[1] N. E. Miller, *J. Am. Chem. Soc.*, **87**, 390 (1965).

[2] In this paper both names are employed. The ylide nomenclature is more easily used in discussing compounds with different onium atoms. This avoids such specific parent names as phosphorane.

[3] (a) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919); (b) D. D. Coffman and C. S. Marvel, *J. Am. Chem. Soc.*, **51**, 3496 (1929).

[4] G. Wittig and H. Laib, *Ann.*, **580**, 57 (1953).

[5] H. Gilman and R. A. Tomasi, *J. Org. Chem.*, **27**, 3647 (1962).

[6] Design is to be published.

[7] (a) M. Halmann, *Spectrochim. Acta*, **16**, 407 (1960); (b) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

[8] (a) R. H. Krieble and J. R. Elliott, *ibid.*, **67**, 1810 (1945); (b) F. C. Whitmore, L. H. Sommer, and J. Gold, *ibid.*, **69**, 1976 (1947).

[9] Microanalyses were obtained from Weiler and Strauss Microanalytical Laboratory, A. Bernhardt Microanalytical Laboratory, and Schwarzkopf Microanalytical Laboratory.

TABLE I

VAPOR PRESSURE $(CH_3)_3SiCHP(CH_3)_3$[a]

T, °C.	25.5[b]	52.3	54.6[b]	65.4[b]	68.7	74.5	82.5	90.8	92.8[b]	95.8	99.9	104.8	110.3	114.3
P, mm. (obsd.)	1.5	6.0	7.2	11.9	13.4	17.8	25.3	35.5	39.7	44.3	52.3	63.6	77.0	88.9
P, mm. (calcd.)[c]	1.3	6.1	6.8	11.7	13.6	17.8	25.4	33.7	39.1	44.1	51.9	62.5	76.9	89.1

[a] Constants derived from the vapor pressure equation $\log P(\text{mm.}) = -2371.1/T + 8.0695$; $\Delta H_{\text{vap}} = 10.8$ kcal./mole; b.p. 184° (extrapolated 70°). [b] Measurements obtained after maintaining sample at higher temperature listed for at least 1 hr. [c] Calculated values obtained from equation of best line determined by graphical inspection.

Anal. Calcd. for $(CH_3)_3SiCH_2P(CH_3)_3{}^+PF_6{}^-$: C, 27.3; H, 6.5; P, 20.1. Found: C, 28.0; H, 6.6; P, 19.2.

The n.m.r. spectrum of II in deuterioacetonitrile is a slightly unequal doublet, small singlet, and large singlet located at −1.80 (A_{PCH} = 15 c.p.s.), −1.37 and −0.25 p.p.m. from internal tetramethylsilane. The predicted spectrum is a large doublet, a small doublet, and a singlet with the intensity ratio of 9:2:9 due to PCH_3, CH_2, and $SiCH_3$ protons, respectively. If it is assumed that the large doublet and small doublet overlap, excellent agreement is obtained between the predicted and observed spectra. The ratio of intensities observed is (starting at low field) 4.5:5.3:1:8.6, and that expected if overlap had occurred is 4.5:5.5:1:9. Since the high-field peak of the doublet is noticeably asymmetrical (shoulder on the low-field side), and since the PCH coupling constant (18 c.p.s.) is reasonable for CH_2 protons, it is believed that assignment assuming overlap is properly made.

A 15.1-g. portion (0.076 mole) of II was slurried in 63 ml. of dry ether, and 63 ml. (0.074 mole) of 1.18 *M* butyllithium in ethyl ether was added dropwise with stirring over a 45-min. period. Nearly all the solid dissolved. After stirring another 30 min. at room temperature, the ether was removed under vacuum to leave a white solid residue. The residue was slowly heated under vacuum to about 100°, at which temperature considerable material was caught in a U-trap cooled to −78°. Heating was continued (finally at 170°) until no more material volatilized. The trap contents were transferred (condensed) into a short-pass still and distilled to give 12.0 g. (99% based on butyllithium used) of II, boiling at 63–66° (9–11 mm.). Another sample, prepared in a different way, with identical properties was analyzed.

Anal. Calcd. for $(CH_3)_3SiCHP(CH_3)_3$: P, 19.1; Si, 17.3. Found: P, 18.5; Si, 17.7.

The carbon and hydrogen values by combustion analysis were uniformly low, possibly the result of rapid combustion. In an attempt to bring about slow combustion the sample exploded.

Anal. Calcd.: C, 51.8; H, 11.8. Found: C, 48.6, 49.9, 50.0; H, 11.2, 11.8, 11.7.

Vapor pressure measurements were made over a 90° range, and the data are collected in Table I. Since the measurement was reproducible on cooling, no significant decomposition had occurred at the higher temperatures.

A gas-phase molecular weight determination indicated a monomeric composition. In a 306.5-ml. volume, 18.5 mg. of I exerted a pressure of 22.6 mm. at 88.4° to give an experimental molecular weight of 165.3 (calcd. 162.3).

Reaction of II with water gave a clear, basic solution. Addition of saturated ammonium hexafluorophosphate solution caused the precipitation of a white crystalline solid, the infrared spectrum of which could be completely assigned to bands of III and $(CH_3)_4P^+PF_6{}^-$ (the latter in minor amounts).

Reaction of I with excess methyl iodide in ethyl ether produced a white, ether-insoluble solid. This solid dissolved completely in water. Addition of saturated ammonium hexafluorophosphate solution caused the precipitation of a white, solid $PF_6{}^-$ salt, $(CH_3)_3SiCH(CH_3)P(CH_3)_3{}^+PF_6{}^-$ (IV). The infrared spectrum shows P–F absorption and is quite different from the spectrum of III. A sample was recrystallized from hot water for analysis.

Anal. Calcd. for $(CH_3)_3SiCH(CH_3)P(CH_3)_3{}^+PF_6{}^-$: C, 29.8; H, 6.9; P, 19.2. Found: C, 30.1; H, 7.0; P, 19.1.

The ^1H n.m.r. spectrum of IV in deuterioacetonitrile contains a large doublet and singlet and two smaller unequal singlets. The doublet results from the PCH_3 protons and is found at −1.72 p.p.m. from internal tetramethylsilane, with a coupling constant of 14 c.p.s.; and the large singlet at −0.20 p.p.m. is due to the $SiCH_3$ protons. Whether both the two small peaks at −1.40 and −1.15 p.p.m. are characteristic of IV is not known, and one might be an impurity peak. Integrated intensities observed were in the ratio 9 (for doublet):1.8:0.8:7.6. A somewhat large radiofrequency field had to be used because of instrumental difficulties, and some saturation may have occurred. If the small peaks observed are assumed to be C–CH_3 peaks, the ratio of intensities is not far from that expected, 9:2.6:7.6 compared with 9:3:9.

Reaction of I with Trimethylboron.—A 49.0-mg. (0.303 mmole) sample of I was condensed with 0.434 mmole of trimethylboron in a bulb attached to the vacuum line. On warming to a temperature above −78°, a white solid formed. The solid was white and chalky as contrasted to the prismatic crystalline character of I, which is also a solid at low temperatures. The excess volatiles at room temperature were measured as 0.14 mmole and had vapor pressure properties similar to trimethylboron. Thus the stoichiometry of the trimethylboron adduct was established as 1:1 (1:0.96 measured) within experimental error. The adduct melted at 28–29.5°, and it very readily supercooled.

An elemental analysis of a sample of another experiment was made. The sample had been heated rather strongly (above 100°) during the transfer and may have been partly decomposed.

Anal. Calcd. for $(CH_3)_3SiCH[B(CH_3)_3]P(CH_3)_3$: C, 55.0; H, 12.9; P, 14.2; B, 5.0. Found: C, 56.8; H, 13.4; P, 13.5; B, 4.5.

Trimethylarsinetrimethylsilylmethylene (V).—A mixture of 5.1 g. (0.042 mole) of trimethylarsine and 9.9 ml. (8.5 g., 0.06 mole) of chloromethyltrimethylsilane was heated at 100–130° for 4 days in a 50–75 ml. sealed ampoule. Volatile materials remaining after the heating period were removed under vacuum to leave 7.6 g. (74%) of trimethylsilylmethyltrimethylarsonium chloride (VI), $(CH_3)_3SiCH_2As(CH_3)_3{}^+Cl^-$, a white solid.

Anal. Calcd. for $(CH_3)_3SiCH_2As(CH_3)_3{}^+Cl^-$: C, 34.6; H, 8.4; As, 30.9. Found: C, 34.6; H, 8.8; As, 30.6.

A slurry of 4.4 g. (0.018 mole) of V in 15 ml. of dry ether was allowed to react with 15.4 ml. (0.018 mole) of 1.18 *M* butyllithium and worked up as in the preparation of I. The white residue after ether evaporation liberated volatiles at 120–140°. Distillation of the crude product in a short-pass still gave 2.0 g. (54%) of V as a clear liquid boiling at 69° (6 mm.) which fumed in air and smelled strongly of trimethylarsine.

Anal. Calcd. for $(CH_3)_3SiCHAs(CH_3)_3$: C, 40.8; H, 9.3; As, 36.3. Found: C, 42.3; H, 9.2; As, 35.2.

The rather poor analysis may again be attributed to an analytical difficulty, since the sample was shown to be ylide V by chemical methods.

Proof of Composition of V by Reaction with Dry HCl.—A 63.6-

mg. sample of V was exposed to 0.38 mmole of HCl gas. A white solid immediately formed. After long standing, to ensure complete reaction, the volatile material at room temperature was removed and found to be 0.08 mmole of gas which was essentially HCl with traces of hexamethyldisiloxane (from traces of water). The hydrogen chloride equivalent weight of V was thus determined to be 212, within experimental error of the value (206) expected of V from eq. 1.

$$\mathrm{HCl} + \underset{\mathrm{V}}{(\mathrm{CH_3})_3\mathrm{SiCHAs}(\mathrm{CH_3})_3} \longrightarrow \underset{\mathrm{VI}}{(\mathrm{CH_3})_3\mathrm{SiCH_2As}(\mathrm{CH_3})^+\mathrm{Cl}^-} \quad (1)$$

The solid reaction residue dissolved completely in water. Addition of excess saturated ammonium hexafluorophosphate solution precipitated 68.7 mg. of white solid, the infrared spectrum of which was identical with that of the PF_6^- salt obtained by metathesis of VI.

Reaction of V with Methyl Iodide.—A small quantity (about 250 mg.) of V was dissolved in dry ether, and an excess of methyl iodide was added. An off-white precipitate formed and was collected by filtration. It dissolved completely in water, and its solution was treated with excess ammonium hexafluorophosphate. The insoluble white salt was collected and recrystallized from hot water. Its infrared spectrum was different from that of $(CH_3)_3SiCH_2As(CH_3)_3{}^+PF_6^-$, but it clearly showed $Si(CH_3)_3$ by absorption at 1260 cm.$^{-1}$ and the PF_6^- ion by the strong PF absorption at 850 cm.$^{-1}$. It analyzed for $(CH_3)_3SiCH(CH_3)As(CH_3)_3{}^+PF_6^-$ (VII).

Anal. Calcd. for $(CH_3)_3SiCH(CH_3)As(CH_3)_3{}^+PF_6^-$: C, 26.2; H, 6.1; As, 20.4. Found: C, 27.0; H, 6.2; As, 20.9.

Reaction of Butyllithium with Trimethylsilylmethyltrimethylammonium Chloride (VIII).—Trimethylsilylmethylammonium chloride (VIII) was prepared by heating a mixture of 7.22 g. (0.0586 mole) of chloromethyltrimethylsilane with 4.42 g. (measured as 0.075 mole of gas) of trimethylamine in a sealed ampoule for 10 days at 150°. Volatiles remaining were removed under vacuum to leave 9.0 g. (85%) of VIII as white crystalline flakes. A small portion was dissolved in water and metathesized to $(CH_3)_3SiCH_2N(CH_3)_3{}^+PF_6^-$ (IX) with NH_4PF_6. The white precipitate was recrystallized twice from hot water.

Anal. Calcd. for $(CH_3)_3SiCH_2N(CH_3)_3{}^+PF_6^-$: C, 28.9; H, 6.9; N, 4.8. Found: C, 28.9; H, 6.5; N, 5.1.

A slurry of 5.0 g. (0.0275 mole) of VIII in 30 ml. of ether was stirred at 0°, and 23 ml. (0.0274 mole) of 1.18 *M* butyllithium was added dropwise over a 0.5-hr. period. There was no visible change during the addition, so the mixture was stirred at room temperature for 4 hr. After the first 0.5 hr. at room temperature the solid in the slurry had noticeably changed its consistency. Ether was removed under vacuum, and the white solid residue left was heated under vacuum. At 120° there was a sudden violent evolution of volatile material which was caught in a U-trap cooled to −78°. The volatile material was redistilled to give 2.0 g. (50%) of 1-dimethylaminoethyltrimethylsilane (X) boiling at 71° (88 mm.) and a small amount of yet unidentified, higher boiling material.

Anal. Calcd. for $(CH_3)_2NCH(CH_3)Si(CH_3)_3$: C, 57.8; H, 13.2; N, 9.6. Found: C, 57.9; H, 13.1; N, 9.5.

The silylamine X dissolved quietly in dilute hydrochloric acid to give a solution from which a sparingly soluble PF_6^- salt could be prepared by metathesis with ammonium hexafluorophosphate as usual. The PF_6^- salt (XI) was isolated as a white crystalline solid, the infrared spectrum of which shows a strong NH absorption.

Anal. Calcd. for $(CH_3)_2N^+HCH(CH_3)Si(CH_3)PF_6^-$: C, 28.8: H, 6.9; N, 4.8; P, 10.6. Found: C, 29.6; H, 7.3; N, 4.6; P, 9.4.

The reaction of X with excess methyl iodide in dry ether caused the precipitation of the water-soluble iodide salt, 1-(trimethylsilyl)ethyltrimethylammonium iodide (XII).

Anal. Calcd. for $(CH_3)_3SiCH(CH_3)N^+(CH_3)I^-$: C, 33.4; H, 7.7; N, 4.9; I, 44.2. Found: C, 32.9; H, 7.3; N, 4.8; I, 43.2.

Preparation of Trimethylsilylmethylsulfonium Iodide (XIV).—There was no observed reaction between chloromethyltrimethylsilane and dimethyl sulfide in a sealed tube at 120° for several days. Therefore, the similar reaction using the corresponding iodomethylsilane was employed.

Iodomethyltrimethylsilane was prepared by a standard procedure[10] involving reflux of chloromethyltrimethylsilane with an equimolar amount of sodium iodide in acetone for several hours. The solid mixture was filtered, and the insoluble salt was extracted with ether. The ether extracts and the acetone filtrate were concentrated under a water-pump vacuum. As distillation slackened, heat was applied until the temperature of the liquid was 100°. The colorless, clear liquid residue of iodomethyltrimethylsilane was used without further purification.

A 29-g. (0.135 mole) portion of iodomethyltrimethylsilane was heated for 1 week at 100–125° with 10 ml. (8.5 g., 0.137 mole) of dimethyl sulfide in a sealed tube. The amount of solid present seemed to decrease at the higher temperature (125°), so the mixture was heated at 80° for an additional 5 days. The tube was opened, and the solid present was separated by filtration and washed with dry ether. The solid amounted to 14.4 g. and was identified as trimethylsulfonium iodide (107% based on eq. 8). The filtrate and washings were concentrated to 10 g. of yellow oil under water pump vacuum. The oil was treated with more than an equal volume of methyl iodide and then diluted several times with ether. Flaky, yellowish crystals of $(CH_3)_3SiCH_2S(CH_3)_2{}^+I^-$ (XIV) formed. In all, 10.6 g. (56% based on eq. 8) was obtained.

Anal. Calcd. for $(CH_3)_3SiCH_2S(CH_3)_2{}^+I^-$; C, 26.1; H, 6.2; S, 11.6; I, 45.9. Found: C, 26.8; H, 6.1; S, 11.3; I, 45.3.

The ^{1}H n.m.r. spectrum of XIV in deuterioacetonitrile is three singlets (and some small impurity peaks) at −2.82, −2.70, 0.0 p.p.m. from external 5% tetramethylsilane. The integrated intensity ratio was 6:2:7.5, compared to 6:2:9 predicted for XIV. Due to instrumental difficulties a radiofrequency field of 0.2 mgauss was used. Saturation, which would cause deviation from expected intensities, may have occurred.

Dimethyl Sulfide–Trimethylsilylmethylene (XV).—A slurry of 3 g. (0.0105 mole) of XIV in 9 ml. of ether was stirred at 0° while 9.2 ml. (0.0108 mole) of 1.18 *M* butyllithium was added dropwise. The addition required 15 min., at which time nearly all of the solid had dissolved. Ether was removed under vacuum, and the white residue formed was heated under vacuum at 100–110°. Volatile material liberated on heating was caught in a −78° trap. Redistillation separated the ylide XV from about an equal amount of ether. The ylide boiled at 51–53° (12 mm.). Care was taken to keep the pot temperature less than 70°.

Proof of Composition of XV by Reaction with HCl.—A 255-mg. portion of XV was allowed to react with 4.37 mmoles of HCl gas in a bulb on the vacuum line. A white solid formed immediately and partially dissolved in the presence of excess HCl. Volatiles from the reaction were removed and fractionally distilled from a −78° trap to a −196° trap. The −196° trap contained 2.58 mmoles of HCl (by infrared analysis). The residue, a soft white solid, weighed 234 mg. and had an infrared spectrum nearly identical with that of XIV. This solid was confirmed to be $(CH_3)_3SiCH_2S(CH_3)_2{}^+Cl^-$ (XVI) by converting it to the PF_6^- salt, XVII. The infrared spectrum of XVII was identical with that of a sample prepared by metathesis from XIV.

Trimethylphosphine–Bis(trimethylsilyl)methylene (XVII).—An excess over an equimolar quantity of $(CH_3)_3SiCHP(CH_3)_3$ (I) was condensed onto trimethylchlorosilane in ether. On warming to room temperature, the mixture deposited a white precipitate. Most of the ether was removed by rapid vacuum evaporation, and the less volatile portion was then fractionated through a −78° trap. The poorly volatile liquid stopped at −78° was confirmed by infrared analysis to be identical with $[(CH_3)_3Si]_2$-

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[10] J. Roberts and S. Dev, *J. Am. Chem. Soc.*, **73**, 1879 (1951).

[11] N. E. Miller, to be published.

$CP(CH_3)_3$ prepared by a pyrolytic reaction.[11] The analysis of the sample obtained by pyrolysis is given.

Anal. Calcd. for $[(CH_3)_3Si]_2P(CH_3)_3$: C, 51.2; H, 11.6; P, 13.2. Found: C, 51.2; H, 12.7; P, 13.5.

The white solid residue was confirmed to be $(CH_3)_3SiCH_2P(CH_3)_3^+Cl^-$ (II) by its infrared spectrum.

A small amount of XVII was treated with methyl iodide in ether. The iodide salt isolated was converted to the PF_6^- salt (XVIII) which was recrystallized from hot water and analyzed.

Anal. Calcd. for $[(CH_3)_3Si]_2C(CH_3)P(CH_3)_3^+PF_6^-$: C, 33.5; H, 7.7; P, 15.7. Found: C, 33.6; H, 7.9; P, 15.7.

The ^1H n.m.r. spectrum of XVIII consists of a doublet, two small peaks, and a large singlet. The doublet centered at -1.80 p.p.m. from internal tetramethylsilane can be assigned to the PCH_3 protons (PCH coupling constant, 12 c.p.s.), and the large singlet at -0.30 p.p.m. can be assigned to the $SiCH_3$ protons. Whether the smaller peaks are characteristic of XVIII or not is not known. The predicted spectrum for first-order effects would be a doublet, a singlet, and a singlet having intensities in the ratio of 3:1:6. If the two smaller peaks (at -1.21 and -1.56 p.p.m.) could be assigned to $C-CH_3$ protons, the ratio of the observed resonances, 3:1.16:5.5, is in fair agreement with the predicted ratio.

Proof of Structure of XVIII.—The salt XVII was shown by hydrolytic cleavage to have both $(CH_3)_3Si$ groups bonded to an ethyl group. Basic hydrolysis proceeded according to the equation

$$H_2O + [(CH_3)_3Si]_2C(CH_3)P(CH_3)_3^+ \xrightarrow{OH^-} C_2H_5P(CH_3)_3^+ + [(CH_3)_3Si]_2O \quad (2)$$

A 25-mg. sample was dissolved by boiling in 1 ml. of water made basic with one drop of 6 *M* sodium hydroxide. On cooling, the white precipitate which formed was collected by filtration. This precipitate was identified as $C_2H_5P(CH_3)_3^+PF_6^-$ (5.4 g., 36% based on eq. 2) since it had an infrared spectrum identical with that of an authentic sample which was prepared by reaction of trimethylphosphine with ethyl iodide in ether (the iodide was collected and then converted into the hexafluorophosphate salt in the usual way).

Results and Discussion

The ylides $(CH_3)_3SiCHP(CH_3)_3$, $(CH_3)_3SiCHAs(CH_3)_3$, and $(CH_3)_3SiCHS(CH_3)_2$ were prepared in good yields by the reaction of butyllithium in ethyl ether with α-trimethylsilyl-substituted onium salts. There is some evidence also for the transitory existence of the nitrogen analog $(CH_3)_3SiCHN(CH_3)_3$. Table II lists the physical properties of the ylides. In general, they are highly refractive, mobile liquids with room temperature vapor pressures of about 1 mm. or less.

TABLE II
PHYSICAL PROPERTIES OF YLIDES

	M.p., °C.	B.p., °C.
$(CH_3)_3SiCHP(CH_3)_3$ (I)	-36	66 (11 mm.)
$[(CH_3)_3Si]_2CP(CH_3)_3$ (XVI)	14 to 18	45–50 (<1 mm.)
$(CH_3)_3SiCHAs(CH_3)_3$ (IV)	-29 to -27.7	69 (6 mm.)
$(CH_3)_3SiCHS(CH_3)_2$ (XIV)	-51 to -47	53 (12 mm.)

A structure can be proposed in which the silicon d orbitals participate in the delocalization of the π electrons. The resonance hybrids of the valence bond description of the arsenic-containing ylide can be written

$$(CH_3)_3As^+{-}^-CHSi(CH_3)_3 \longleftrightarrow (CH_3)_3As{=}CHSi(CH_3)_3 \longleftrightarrow (CH_3)_3As^+CH{=}^-Si(CH_3)_3$$

This structure does agree with the results of a preliminary study of the base strengths of the phosphorus-containing ylides, as explained herein. Certainly, involvement of silicon d orbitals in silicon chemistry is not unknown.[12] Furthermore, the isolation of stable ylides, while not necessarily implying the existence of resonance, at least harmonizes with the fact that the ylides which are stable in the pure state are resonance stabilized.[13]

Preliminary results of a study of the base strengths of the ylides indicate that steric factors are important for large acids. Whereas $(CH_3)_3PCHSi(CH_3)_3$ forms a very strong complex with trimethylboron, $(CH_3)_3PC[Si(CH_3)_3]_2$ does not form a complex at room temperature. Even though these ylides are formally analogous to di-*t*-butylamine and the yet unknown tri-*t*-butylamine, the steric strain due to crowding at the back of the molecule (B strain[14]) ought to be markedly reduced because of the long Si–C and P–C bonds. A classic example of how long bonds change steric factors is found in the methylphosphines. Even toward such bulky acids as trimethylboron the order of decreasing base strength is $(CH_3)_3P > (CH_3)_2PH > CH_3PH_2 > PH_3$, while the order of decreasing base strength of the corresponding amines is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ toward the tiny proton.[15] Thus the inductive effect of the methyl groups governs the basicity of the methylphosphines, but a combination of inductive effect modified by B-strain governs that of the methylamines.

That $[(CH_3)_3Si]_2CP(CH_3)_3$ is a weaker base than $(CH_3)_3SiCHP(CH_3)_3$ toward the proton can be inferred from the synthesis reactions

$$(CH_3)_3SiCHP(CH_3)_3 + (CH_3)_3SiCl \longrightarrow \underset{B}{[(CH_3)_3Si]_2CHP^+(CH_3)_3Cl^-}$$

$$B + (CH_3)_3SiCHP(CH_3)_3 \longrightarrow [(CH_3)_3Si]_2CP(CH_3)_3 + II \quad (3)$$

This reaction may be viewed as the competition of $[(CH_3)_3Si]_2CP(CH_3)_3$ and $(CH_3)_3SiCHP(CH_3)_3$ for a proton, hence $[(CH_3)_3Si]_2CP(CH_3)_3$ is the weaker base.

The apparent order of base strength of the phosphorus-containing ylides toward the proton is $RCH_2 > R_2CH > R_3C$, where R is $(CH_3)_3P$ or $(CH_3)_3Si$. Such an order cannot result from steric factors alone since the order for the more highly strained *t*-butylamines is $(t\text{-}C_4H_9)_2NH > t\text{-}C_4H_9NH_2$.[16] An increasing participation of the empty d orbitals of silicon in the series RCH_2, R_2CH, R_3C would make the basic pair less available and lead to the observed trend.

The ylides are all assumed to be monomeric on the basis of molecular weight data obtained for $(CH_3)_3PCHSi(CH_3)_3$. The somewhat high Trouton constant

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[12] A detailed account is given by C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960.

[13] (a) A. J. Speziale, G. J. Marco, and K. W. Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960); (b) A. J. Speziale and K. W. Ratts, *ibid.*, **84**, 854 (1962); (c) F. Ramirez and S. Levy, *J. Org. Chem.*, **21**, 488 (1956); (d) S. Tripett and D. M. Walker, *J. Chem. Soc.*, 1266 (1961).

[14] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).

[15] H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

[16] F. Klages and H. Sitz, *Ber.*, **96**, 2394 (1963).

TABLE III

^{1}H N.M.R. DATA: CHEMICAL SHIFT[a]

	$Si(CH_3)_3$	CH	$E(CH_3)_n$	Integrated intensities[c]
$(CH_3)_3SiCHP(CH_3)_3$ (I)	0.27	1.03 (8)[b]	−1.20 (13)[b]	9:1:9 (9:1:9)
$[(CH_3)_3Si]_2CP(CH_3)_3$ (XVI)	0.13		−1.27 (12)[b]	2.1:1 (2:1)
$(CH_3)_3SiCHAs(CH_3)_3$ (IV)	0.13	0.55	−1.27	9.4:1:9 (9:1:9)
$(CH_3)_3SiCHS(CH_3)_2$ (XIV)	0.25	−0.13	−2.27	8.3:1:6 (9:1:6)

[a] Referred to external tetramethylslaine, in p.p.m. [b] PCH coupling constant, in c.p.s. [c] Integrated intensities predicted by first-order effects included in parentheses.

for $(CH_3)_3PCHSi(CH_3)_3$ suggests there is association in the liquid phase, which is not surprising for a compound that must certainly be considerably polar.

The ^{1}H n.m.r. spectra (Table III) support the ylide structures. It is seen that the resonances of the CH protons of $(CH_3)_3SiCHP(CH_3)_3$ and $(CH_3)_3SiCHAs(CH_3)_3$ are shifted to the high-field side of the $Si(CH_3)_3$ proton resonance. A decreased electronegativity of the methylenic carbon compared with the normal CH_2 carbon as well as the magnetic anisotropy of the methylenic carbon atom in the ylides could account for the upfield shift. The peak due to the CH proton of the sulfur-containing ylide is on the low-field side of the $Si(CH_3)_3$ proton resonance, apparently because of the inherent lower shielding of methylenic protons adjacent to sulfur. The separation of the SCH_3 protons and the methylenic proton (112 c.p.s.) is similar to that of the corresponding hydrogen atoms in the arsenic-containing ylide (110 c.p.s.), but less than that for $(CH_3)_3SiCHP(CH_3)_3$. The PCH coupling constants of I and XVI are essentially the same as that in triethylphosphine.[17]

The high-field shift of methylenic protons adjacent to two poorly electronegative groups was reported recently by Schmidbaur[18] for compounds such as $[(CH_3)_3Si]_2CH_2$. These compounds are isoelectronic with the ylides reported herein. It appears, however, that the upfield shift of the ylides is primarily the consequence of the "unshared" electron pair and not due to the adjacent groups, since the shielding in the corresponding onium cations, $(CH_3)_3SiCH_2P(CH_3)_3^+$, for example, is more nearly normal.

Chemical Properties.—The α-trimethylsilyl ylides react vigorously (producing smoke) on contact with air or water. Reaction of I with aqueous acid produced $(CH_3)_3SiCH_2P(CH_3)_3^+$ and traces of hexamethyldisiloxane and tetramethylphosphonium ion. This reaction, depicted by eq. 4, supports the proposed structures of the ylides. The tetramethylphosphonium ion is the product of a cleavage reaction of $(CH_3)_3SiCH_2P(CH_3)_3^+$ at the C–Si bond, shown in eq. 5. The cleavage proceeds rapidly in boiling water and almost instantaneously in hot base. This type of Si–C cleavage is not unusual and has been reported by Seyferth and Grim[19] to be so facile as to make the isolation of $(CH_3)_3SiCH_2P(C_6H_5)_3^+$ nearly impossible. In the absence of acid, the cleavage reaction predominates and a basic solution of tetramethylphosphonium ion results. The arsenic-containing ylide produced $(CH_3)_4As^+$ but no $(CH_3)_3SiCH_2As(CH_3)_3^+$ on reaction with aqueous acid, indicating greater lability of the Si–C bond.

$$(CH_3)_3SiCHP(CH_3)_3 + H_3O^+ \longrightarrow (CH_3)_3SiCH_2P(CH_3)_3^+ + H_2O \quad (4)$$

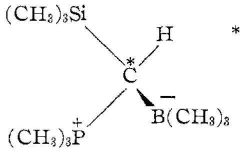
$$2(CH_3)_3SiCH_2P(CH_3)_3^+ + H_2O \xrightarrow{OH^-} 2(CH_3)_4P^+ + (CH_3)_3SiOSi(CH_3)_3 \quad (5)$$

Adduct formation is a general reaction. The addition of gaseous hydrogen chloride or methyl iodide produces salts. These reactions were employed in support of the proposed structures of the ylides. Equations 6 and 7 show their use in structure proofs.

$$[(CH_3)_3Si]_2P(CH_3)_3^+ + CH_3I \xrightarrow{(C_2H_5)_2O} [(CH_3)_3Si]_2CCH_3P(CH_3)_3^+I^- \xrightarrow{OH^-} (CH_3)_3PC_2H_5^+ \quad (6)$$

$$(CH_3)_3SiCHS(CH_3)_2 + HCl \longrightarrow (CH_3)_3SiCH_2S(CH_3)_2^+Cl^- \quad (7)$$

The more hindered Lewis acid, trimethylboron, also forms a 1:1 adduct with $(CH_3)_3SiCHP(CH_3)_3$. The structure of this adduct must be the zwitterion model (C) proposed for analogous adducts of other ylides and Lewis acids.[20] This adduct is quite stable in contrast to the reported nonexistence of an adduct between triphenylphosphinemethylene and trimethylboron.[21] The difference may indicate lower basicity in triphenylphosphinemethylene. Steric factors must be important for larger acids. Indeed, it was observed in this study that there was no adduct formed between $[(CH_3)_3Si]_2CP(CH_3)_3$ and trimethylboron. However, in the attempt of Seyferth and Grim to make the trimethylboron adduct of triphenylphosphinemethylene there were two acids present, trimethylboron and alkali or alkaline earth salts. It could be that the alkali metal ion is a stronger acid than trimethylboron toward the ylide base, a suggestion supported by the observation of strong adducts of α-trimethylsilyl-substituted ylides with lithium halides.



* Optically active site

C

The ylides have been observed to react readily with a large variety of halides and ketones, sometimes exceedingly vigorously. Results of the detailed study of the reaction of the ylides will be the subject of a future communication.

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[17] S. L. Tafford and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **83**, 4473 (1961).

[18] H. Schmidbaur, *Ber.*, **97**, 270 (1964).

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

[20] M. W. Hawthorne, *ibid.*, **83**, 367 (1961).

[21] D. Seyferth and S. O. Grim, *ibid.*, **83**, 1615 (1961).

TABLE IV

INFRARED DATA[a] (CM.$^{-1}$)

$(CH_3)_3SiCHP(CH_3)_3$ (I), liquid

2950 m, 2900 w, 1440 m, 1310 w, 1285 m, 1235 m, 1150 s, 1000 s, 930 m, 850 s, 750 m, 710 w, 675 w, 630 w

$(CH_3)_3SiCHAs(CH_3)_3$ (V), liquid

2950 m, bd, 1420 m, bd, 1230 m, 1110 m, 900 s, 830 s, 750 w, 670 w

$(CH_3)_3SiCHS(CH_3)_2$ (XV), liquid

2950 m, 2910 w, 1425 m, bd, 1250 m, 1010 w, 980 w, 955 w, 850 s, 755 m, 700 w

$[(CH_3)_3Si]_2CP(CH_3)_3$ (XVII), liquid

2950 m, 2900 w, 1420 w, 1310 w, 1280 m, 1250 m, 1160 s, 950 s, 850 s, 755 m, 710 w, 675 m

$(CH_3)_3SiCH(CH_3)N(CH_3)_2$ (X), liquid

2950 m, 2900 w, 2850 w, 2810 w, 2780 w, 1460 m, 1370 w, 1300 s, 1160 w, 1100 w, 1045 m, 850 s, 760 m, 690 w

$(CH_3)_3SiCH_2P(CH_3)^+Cl^-$ (II), N

1460 w, 1305 m, 1300 m, 1250 m, 1150 m, 980 s, bd, 890 s, 850 s, bd, 780 m, 770 w, 700 w

$(CH_3)_3SiCH_2P(CH_3)_3{}^+PF_6{}^-$ (III), N

1450 m, 1375 w, 1330 w, 1310 w, 1260 m, 1140 m, 990 m, 970 m, 890 m, 850 s, bd, 780 w, 775 w

$(CH_3)_3SiCH_2P(CH_3)_3{}^+PF_6{}^-$ (IV), N

1430 w, 1330 w, 1315 m, 1260 m, 1155 w, 1015 m, 980 m, 940 m, 850 s, bd, 780 w, 770 w

$[(CH_3)_3Si]_2CCH_3P(CH_3)_3{}^+PF_6{}^-$ (XVIII), N

1410 w, 1320 w, 1300 m, 1260 m multiplet, 1080 w, 1070 w, 975 m, 965 m, 850 s, bd, 770 w, 700 w multiplet

$(CH_3)_3SiCH_2As(CH_3)_3{}^+Cl^-$ (VI), N

1425 w, 1250 m, 1025 w, 950 s, 850 s multiplet, 775 m, 755 m, 695 w, 650 m

$(CH_3)_3SiCH_2As(CH_3)_3{}^+PF_6{}^-$, N

1425 m, 1260 m, 1125 m, 940 m, 850 s, bd, 780 w, 770 w, 750 w, 705 w, 650 w

$(CH_3)_3SiCHCH_3As(CH_3)_3{}^+PF_6{}^-$ (VII), N

1425 w, 1280 w, 1260 m, 1005 w, 935 m, 845 s, bd, 765 w, 725 w, 700 w, 650 w

$(CH_3)_3SiCH_2S(CH_3)_2{}^+I^-$ (XIV), N

1420 w, 1340 w, 1255 s, 1180 w, 1155 w, 1060 w, 1005 m, 980 w, 945 w, 850 s, 800 w, 775 w, 715 w

$(CH_3)_3SiCH_2N(CH_3)_3{}^+Cl^-$ (VIII), N

1490 m, 1425 w, 1405 w, 1265 m, 995 w, 980 w, 970 w, 950 w, 860 s, 775 w, 720 w, 705 w

$(CH_3)_3SiCHCH_3N(CH_3)_3{}^+I^-$ (XII), N

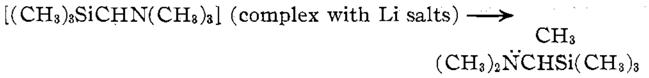
1420 w, 1260 m, 1050 w, 985 w, 960 w, 880 m, 850 s, 775 m, 705 w, 660 w

[a] Obtained with a Perkin-Elmer 237B grating spectrometer. Where indicated (N), the sample was run as a mineral oil mull. Absorptions in common with or masked by mineral oil are not included. Abbreviations: s, strong; m, moderate; w, weak, bd, broad. Very weak bands were not included in the tabulations. Of many bands present only the stronger ones are listed. About one-half of the bands of the spectrum are not listed.

The range of thermal stability of the ylides, P > As > S (>N?), would seem to indicate that the onium atom is more important in determining the properties than is the trimethylsilyl group. The phosphorus compound is completely stable in the absence of air at 120°, but the sulfur compound is decomposed slowly at room temperature. Speculations upon the reasons for the observed trend will not be meaningful until more data are obtained on the chemical properties of these compounds.

Synthesis.—The synthesis reaction of butyllithium and the onium salt is rapid between 0° and room temperature, and the resulting products are all soluble in ether. (The product of $(CH_3)_3SiCH_2N(CH_3)_3{}^+Cl^-$ and butyllithium was not soluble.) Ether is removed under vacuum to leave a solid, stable complex of the ylide with lithium salts. The composition and structure of the complexes have not been determined, but their stability is known to be high since the ylides are liberated only by heating them to about 100° under vacuum. The liberated ylide is essentially free of ether and is purified further by distillation. In the one example where the onium iodide instead of the chloride salt was used, substantial amounts of ether were also liberated along with the ylide.

In an attempt to prepare the nitrogen-containing ylide, 1-dimethylaminoethyltrimethylsilane was isolated as a major product. This product is believed to result from methyl migration when the intermediate (not isolated) ylide was liberated from a salt complex.



$$[(CH_3)_3SiCHN(CH_3)_3]\ \text{(complex with Li salts)} \longrightarrow (CH_3)_2\ddot{N}\overset{CH_3}{C}HSi(CH_3)_3$$

The onium salts employed in the synthesis were prepared by heating the proper bases with chloromethyltrimethylsilane in sealed tubes. However, the synthesis of a $(CH_3)_3SiCH_2S(CH_3)_3{}^+$ salt was not as simple. The reaction of dimethyl sulfide with chloromethyltrimethylsilane was almost negligible, even at 100°. When the more reactive iodomethyltrimethylsilane was used, a quite different reaction took place, apparently due to solubility phenomena, and trimethylsulfonium iodide was the salt isolated. An equilibrium process shown in eq. 8 is assumed to occur. The desired

$$(CH_3)_3SiCH_2I + (CH_3)_2S \longrightarrow [(CH_3)_3SiCH_2S(CH_3)_2{}^+I^- \xrightarrow{(CH_3)_2S} (CH_3)_3S^+I^- + CH_3SCH_2Si(CH_3)_3 \quad (8)$$

onium salt was then prepared by reaction of CH_3SCH_2-$Si(CH_3)_3$ with methyl iodide. It was found that the infrared spectrum was a better characterization property than the melting point for the salts. Infrared data for the salts and ylides are collected in Table IV.

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