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# PHOSPHINE AND ARSINE DERIVATIVES OF MONOSILANE

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**Abstract**—The reaction of silyl iodide with phosphorus, phosphine, arsenic and the arsenides of potassium and mercury has been studied. The compounds $P(SiH_3)I_2$ and $As(SiH_3)I_2$ have been isolated and characterized. Both decompose below 100°. Evidence is presented for the existence of the compounds $P(SiH_3)_2I$, $P(SiH_3)_3$, $P(SiH_3)_4I$, $As(SiH_3)_2I$, $As(SiH_3)_3$ and $As(SiH_3)_4I$ which, however, have not yet been fully characterized. Silyl iodide forms 1 : 1 addition compounds with trimethylamine, triethylamine, trimethyl phosphine, triethylphosphine and trimethyl arsine. The first four are only slightly dissociated, but the arsenic compound dissociates readily. Silyl iodide also forms a compound $SiH_3I \cdot 1{\cdot}8\ N(CH_3)_3$ in its reaction with trimethylamine under pressure. This compound gives a non-conducting solution in acetonitrile, whereas the compounds with one mole of trimethylamine and triethylphosphine give conducting solutions and are therefore salt-like. These results are related to current theories of the formation by silicon of compounds with co-ordination number in excess of four, and of the utilization of *d* orbitals in bond formation.

The alteration in the properties of an organic compound on substitution of silicon for one or more of the carbon atoms can often be explained in terms of a few fundamental points of difference between the two elements. Thus the covalently bound silicon atom is larger than the carbon atom and can therefore be thought of as more exposed to attack. Silicon is also more electropositive than carbon. The most far-reaching consequence of this difference is the presumed reversal of the polarity of the bond dipole in the Si—H and C—H bonds, which renders the silanes and their partially substituted derivatives much more liable to polar attack by nucleophilic reagents. In addition, silicon can attain a maximum covalency of six, whereas carbon is restricted to four. This provides a mechanism for the readier reaction of silicon compounds, and also accounts for the formation of some of their adducts.

The above differences are to some extent interdependent and, largely because of the greater size of the silicon atom, $p_\pi$—$p_\pi$ bonding cannot be strong, so that normal double or triple bonds between silicon or silicon and carbon atoms are unknown.(1) There is, however, considerable evidence for the existence of double bond character in bonds involving the silicon atom in certain types of compound. Thus, although the trialkyl silyl group sometimes exhibits an electron releasing effect, as for instance in its influence on the strength of the substituted amines(2, 3) or fatty acids,(4) it may exhibit the opposite behaviour. Thus, electron attraction is found in the nucleophilic substitution of chlorine by iodine in $Me_3SiCH_2Cl$,(5) and in the reduced dipole moments and ionization constants of compounds such as *p*-trimethylsilyl aniline.(6, 7)

Recently, a new theoretical analysis has confirmed that double bonds of the $\pi$ type can be formed in some circumstances between silicon and other atoms. Craig, Maccoll, Nyholm, Orgèl, and Sutton, have shown(8) that the overlap between a vacant $d_\pi$ orbital on a silicon atom and a fully occupied $p_\pi$ on an atom to which the

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(1) Pitzer, *J. Amer. Chem. Soc.* **70**, 2140 (1948).

(2) Sommer & Rockett, *J. Amer. Chem. Soc.* 73, 5130 (1951).

(3) Noll, Daubert, & Speier, *ibid.*, 3871.

(4) Sommer, Gold, Goldberg, & Marans, *ibid.* 71, 1509 (1949).

(5) Cooper & Prober, *ibid.* **76**, 3943 (1954).

(6) Soffer & de Vries, *ibid.* **73**, 5817 (1951).

(7) Benkeser & Krysiak, *ibid.* **75**, 2421 (1953).

silicon is already bound by a $\sigma$ bond is sufficient to confer double bond character on the bond. The bonds between silicon and the elements of Groups 5, 6, and 7 can therefore be expected to show a double bond character which will be stronger the more electronegative the element providing the $p_\pi$ orbital.(8) In many compounds this double bond effect should oppose the effect of the greater electropositivity of silicon.

Hitherto, relatively few compounds have been described which are suitable for estimating the actual importance of this effect. That silicon-halogen bonds possess some double bond character is shown by the fact that the dipole moments of the simple halogenated silanes are generally smaller, rather than larger, than those of the corresponding carbon compounds.(9) The Si—Cl and Si—F bonds are shorter than would be expected for single bonds. On the other hand the Si—I bond is of the same length in $SiH_3I$ as in $SiI_4$.(10) The silicon-oxygen bond in the silicones is also shorter than is required for a single bond.

The only known compounds containing the Si—N bond which are suitable for testing the extent of double bond character are trisilylamine and the methyl silylamines. The absence of base forming properties in the former was observed by Stock and Somieski.(11) This was adduced as evidence of double bond character in the Si—N bond by Craig *et al.*(8) Burg and Kuljian(12) also found that boron trifluoride and trichloride gave addition compounds with trisilylamine and methyl disilylamine, whereas diborane did not. Had the donor properties of the nitrogen atom been unimpaired a borine derivative should have been formed, as in the case of trimethylamine. These authors suggest that the unexpectedly high volatility of $(SiH_3)_2NB_2H_5$ and $(SiH_3)(CH_3)NB_2H_5$ may be due to a reduction of the dipole by charge migration associated with the double bond character. Another result of this bonding is the unusual planar configuration of the $(SiH_3)_3N$ molecule (Hedberg, *vide* Craig *et al.*(8) This double bonding is often referred to as back co-ordination.

Notwithstanding this evidence of the reduction in the availability of the electron pair in amines containing a Si—N bond, a quaternary compound, $N(CH_3)_3SiH_3Cl$, containing this linkage has been found.(13) The salt-like character of the compound was demonstrated by showing that its solution in acetone could be electrolyzed. If the silyl chloride-trimethylamine compound were not quaternary in character it would presumably be a compound of penta- or hexa-covalent silicon.(14) The possibility that silicon can exceed a covalency of four in molecules containing Si—Cl bonds has been questioned by Schumb and Cook,(15) although similar compounds containing Si—F bonds have long been known. However, the existence of Harden's pyridine adduct of silicon tetrachloride(15a) has been confirmed.(16)

(8) *J. Chem. Soc.*, 332 (1954).

(9) Brockway and Coop, *Trans. Faraday Soc.* **34**, 1429 (1938).
Lewis and Smythe, *J. Amer. Chem. Soc.* **61**, 3063 (1939).
Malatesta and Pizzotti, *Gazzetta* **73**, 143 (1943).
Spanschus, Mills, Scott, and McKenzie, *J. Amer. Chem. Soc.* **72**, 1377 (1950).

(10) Sharbaugh, Heath, Thomas, and Sheridan, *Nature* **171**, 87 (1953).

(11) *Ber.* **54B**, 740 (1921).

(12) *J. Amer. Chem. Soc.* **72**, 3103 (1950).

(13) Emeléus and Miller, *J. Chem. Soc.*, 819 (1939).

(14) Sujishi and Witz, *J. Amer. Chem. Soc.* **76**, 4630 (1954).

(15) *J. Amer. Chem. Soc.* **75**, 5133 (1953).

(15a) *J. Chem. Soc.* **51**, 40 (1887).

(16) Piper and Rochow, *J. Amer. Chem. Soc.* **76**, 4318 (1954).

The assessment of the importance of back co-ordination and the question of the existence of derivatives containing penta- and hexa-covalent silicon call for the study of a wider range of silicon compounds, and the purpose of this investigation was the preparation of derivatives containing bonds between silicon and the elements of Groups 5 and 6. Some results on the nitrogen, phosphorus, and arsenic derivatives are described below. The compounds of the elements of Group 6 will be considered in a subsequent paper. At the time when this investigation was commenced no derivatives containing the Si—P and Si—As bonds had been described. FRITZ has, however, recently described the preparation of monosilyl phosphine by the pyrolysis of a mixture of monosilane and phosphine.(17) No details of the chemical properties of this substance have been given. Very recently SUJISHI and WITZ(18) have shown that mono- and dimethyl-phosphine give 1 : 1 adducts with silyl bromide and iodide at low temperatures. Both compounds were extensively dissociated at 0°, much more so than methyl phosphonium iodide and bromide or the compound between triethylamine and silyl bromide. No reaction was observed with phosphine. The authors found that the 1 : 1 dimethyl phosphine adduct reacted with more dimethyl phosphine. Decomposition reactions also occurred with liberation of monosilane. It was concluded that the compounds were not phosphonium salts.

Silyl iodide was found to react with phosphorus much more readily than does methyl iodide. In a series of experiments at temperatures between 20–100° the only product isolated in a pure state was silyl diiodo phosphine, $SiH_3PI_2$. There was evidence that $(SiH_3)_2PI$ and $P(SiH_3)_3$ were also produced. The former could not be separated from silylene iodide, $SiH_2I_2$, which is formed by the disproportionation of silyl iodide, and phosphorus trisilyl appears to have a similar volatility to silyl iodide. It also reacted with silyl iodide to form a readily dissociated 1 : 1 adduct. The reaction of silyl iodide with arsenic gave similar products, but only $As(SiH_3)I_2$ was isolated in a pure state. There was again evidence for the formation of a 1 : 1 arsenic trisilyl-silyl iodide adduct. The compound $SiH_3PI_2$ and its arsenic analogue both decomposed slowly at room temperature, forming a mixture of products which included hydrogen, hydrogen iodide, silyl iodide and phosphine, or arsine, and decomposition was rapid at 80°. There was evidence that the other silyl derivatives of these two elements were also unstable, and were thus sharply differentiated from the disilyls of sulphur and selenium.(19)

Although it did not prove possible to isolate in a pure state the trisilyls of phosphorus and arsenic and to study in detail the quaternary compounds which they form, several related adducts of silyl iodide were isolated. Thus, solid compounds were obtained by the combination of equimolecular quantities of silyl iodide and trimethylamine or triethylamine. Both had a dissociation pressure at room temperature of $<1$ mm, compared with the dissociation pressure of 3 cm for the chloro-compound, $N(CH_3)_3SiH_3Cl$. (EMELÉUS and MILLER.(13)) The compound $N(CH_3)_3SiH_3I$ was not spontaneously inflammable in air, underwent only superficial oxidation, and could be handled in a dry-box. The compounds $P(CH_3)_3SiH_3I$ and $P(C_2H_5)_3SiH_3I$ were prepared by reaction of the alkyl phosphines with silyl iodide at room temperature, and had also very low dissociation pressures, the ethyl compounds being

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(17) *Z. Naturforsch.* **8b**, 776 (1953).

(18) Rept. No. 1, March 1954, Office of Ordnance Research Control DA-11-OLL. ORD 1264.

(19) EMELÉUS, MCDIARMID, and MADDOCK, *J. Inorg. Nucl. Chem.* **1**, 195 (1955).

less volatile than the methyl compounds. All these compounds lost monosilane very slowly at room temperature and formed involatile products. Trimethyl arsine also formed a 1 : 1 adduct, $As(CH_3)_3SiH_3I$, which dissociated more readily, and reversibly. From measurements of the dissociation pressure the value of $\Delta H_{273}$ from liquid $SiH_3I$ and $AsMe_3$ was—9,700 cals.

The action of excess of trimethylamine on the compound $(CH_3)_3NSiH_3I$ led to some decomposition and silane production, but the main product had a composition approximating to the formula $[(CH_3)_3N]_2SiH_3I$. The conductivities of the compounds $(CH_3)_3NSiH_3I$, $(C_2H_5)_3PSiH_3I$, and $[(CH_3)_3N]_2SiH_3I$ were measured in acetonitrile solution. The first two gave readily conducting solutions and were therefore represented as salt-like substituted ammonium and phosphonium compounds. The 2 : 1 compound was likewise readily soluble in acetonitrite but did not give an appreciable increase in conductance. It is likely therefore that this compound differs in type from the quaternary compounds and it may well be a derivative of hexa covalent silicon.

## EXPERIMENTAL

Silyl iodide was prepared by the reaction of monosilane with hydrogen iodide in presence of aluminium iodide.(20) Monosilane was prepared by the method of FINHOLT, BOND, WILZBACH, and SCHLESINGER(21) in an apparatus similar to that used by PEAKE, NEBERGALL, and YUN TI CHEN.(22) The separation and characterization of volatile substances was done in an all-glass vacuum apparatus of the type described by STOCK, using taps in place of mercury float valves. In some cases, where it was necessary to avoid contact with tap grease, taps were replaced by thin glass diaphragms, which were broken electromagnetically as required.

*Reaction of silyl iodide with phosphorus*—In a series of experiments varying quantities of white phosphorus were sealed with measured quantities of silyl iodide in a 500 ml bulb in which the phosphorus had first been heated in vacuum so as to produce a large surface. The bulb was fitted with a diaphragm and magnetic breaker to enable the reaction products to be returned to the vacuum system for separation and identification. Reaction occurred below 0°, giving a red solid. The orange-red liquid gradually disappeared as the reaction proceeded. In most cases the bulb was heated to 100° for a time. In one such experiment silyl iodide (11·076 g) was heated with phosphorus (43·06 g) for 18 hr at 100°. The volatile products identified were hydrogen (63 ml), monosilane (0·35 g), silylene iodide and about 0·6 g of a liquid which was identified as phosphorus silyl diiodide (Found: P, 9·0; Si, 8·8; H, 0·87; I, 81·3 per cent; M, 321, 317. Calc. for $PSiH_3I_2$: P, 9·8; Si, 8·9; H, 0·96; I, 80·4; M, 316). The compound melted sharply at $-1·8°$. Vapour pressures measured with a spoon-gauge in the range 20–109° gave the following values.

| Temp° | 0 | 10·1 | 19·0 | 36 | 52 | 70 | 94 | 109 |
|---|---|---|---|---|---|---|---|---|
| V.p, mm | 1·2 | 2·2 | 3·5 | 75 | 88 | 133 | 207 | 299 |

The b.p. was 190° ± 0·5°, the latent heat of vaporisation 9300 cals/g-mol and TROUTON's constant 20·5. The approximate liquid density was 2·9 ± 0·2 g/ml at 20°. Decomposition was fairly rapid above about 80° and appreciable in a few days at room temperature. The decomposition products identified were hydrogen, hydrogen iodide, silyl iodide, and phosphine. A red solid was also formed. In a similar experiment with silyl iodide (10·14 g) and phosphorus (21 g) heated for 12 hr at 80° the above products were again identified and in addition a small liquid fraction (0·15 g), which condensed in the fractional condensation at $-46°$, was isolated. It had a molecular weight of 256 ($SiH_2I_2$, 284; $P(SiH_3)_2I$, 220). It was shown by hydrolysis to contain phosphorus, silicon, hydrogen (as Si—H), and iodine and was thought to be a mixture of silylene iodide, $SiH_2I_2$, and phosphorus disilyl iodide, $P(SiH_3)_2I$. Numerous attempts to obtain this compound in a pure condition were unsuccessful. Fractions such as the above yielded, on standing for several days at room temperature, silyl iodide, phosphine, hydrogen and phosphorus silyl diiodide. The latter was characterized by molecular weight determination and vapour pressure measurements.

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(20) EMELÉUS, MADDOCK, and REID, *J. Chem. Soc.* 353 (1941).

(21) *J. Amer. Chem. Soc.* **69**, 2692 (1949).

(22) *Ibid.* **74**, 1526 (1952).

Reaction at room temperature was incomplete, probably because of the limited phosphorus surface available. In a typical experiment silyl iodide (7·615 g) and phosphorus (26·8 g) were allowed to react for 18 hr at 20°. The products were roughly fractionated and all the material condensed in a trap cooled to −96° (i.e. unchanged $SiH_3I$ and reaction products other than hydrogen and monosilane) were resealed with fresh phosphorus (15 g) for a further 18 hr. The products then identified were hydrogen, phosphine, disilane, unreacted silyl iodide, a trace of silylene iodide and a pale buff-coloured solid which had a vapour pressure at 19° of 2 cm. This solid could be distilled in the vacuum apparatus. It passed through a trap cooled to −64° but was held by one at −96°. Approximate determinations of molecular weight at room temperature gave values of 151, 152, and 145 (Calc. for $SiH_3I$, 158; Calc. for $P(SiH_3)_3$, 124). These approximate values were consistent with the solid being the compound $P(SiH_3)_4I$, which dissociated in the vapour phase. A quantity of the solid was hydrolyzed by 15 per cent alkali. The hydrogen evolved and the iodide in the hydrolysate were measured. (Found: $H_2$ : I, 12 : 1. Calc. for $P(SiH_3)_4I$. $H_2$ : I, 12.) The solid did not react with trimethylamine or triethylamine.

*Reaction of silyl iodide with phosphine*—When silyl iodide (2·993 g) and phosphine (0·950 g) were sealed together in a tube a very small amount of buff-coloured solid was formed; 2·906 g of silyl iodide and 0·921 g of phosphine were recovered, together with 50 mg of a solid (v.p. 2 cm at 20°) which was shown qualitatively to contain phosphorus, silicon, iodine, and hydrogen. The unreacted silyl iodide and phosphine were distilled back to the reaction tube with an excess of triethylamine (which would yield $NEt_3SiH_3I$, which could react further with phosphine). A white solid was formed at room temperature. The volatile products were $H_2$ (21·7 ml), unreacted phosphine (160 ml), excess triethylamine and a liquid (0·15 ml) which was spontaneously inflammable and liberated phosphine with water. It was possibly a mixture of phosphorus trisilyl and triethylamine (Found: M, 116. Calc. for $P(SiH_3)_3$, 124. Calc. for $N(C_2H_5)_3$, 101).

In a further experiment silyl iodide (1·901 g) was mixed with excess of trimethylamine to form the quaternary compound $N(CH_3)_3SiH_3I$. Excess of the amine was removed and phosphine (0·842 g) added. The tube was heated for 7·5 hr at 65°. The products were $H_2$ (24 ml), $PH_3$ (139 ml) and two small fractions which were held during separation by fractional condensation by baths at −134° and −96°, respectively. The former yielded phosphine on hydrolysis with water and contained phosphorus, silicon, and hydrogen (as Si—H), but no iodine. The molecular weight (67·6) suggested that it was silyl phosphine (M, 64). The substance held at −96° (v.p. at 0°, 8·3 cm) was shown qualitatively by hydrolysis to contain phosphorus, silicon, and hydrogen (as Si—H), but no iodine. It had a molecular weight of 122 (calc. for $P(SiH_3)_3$, 124). The compound was shown not to react with carbon disulphide.

*Reaction of silyl iodide with arsenic*—Reaction between silyl iodide and powdered arsenic occurred on gently heating. The same type of apparatus was used as in the reaction with phosphorus. Arsenic (30·2 g) and silyl iodide (8·08 g) were kept for 9 weeks at room temperature and then heated for 14 hrs at 72°. The products were hydrogen (176 ml), silyl iodide (1·510 g), and fractions which, from molecular weight determinations, were identified as arsine, hydrogen iodide, monosilane, and silylene iodide. In addition impure arsenic silyl diiodide (0·7 g) was isolated. During purification by repeated fractional condensation this passed a trap cooled to 0° but was held at −36°. (Found: H, 0·79; I, 71·0 per cent; M, 354. Calc. for $AsSiH_3I_2$: H, 0·83; I, 70·6 per cent; M, 360.) Arsenic and silicon were also present in the hydrolysate. The m.p. was −4·0° ± 0·5°. Vapour pressure measurements with a spoon gauge in the range 20°–108° gave the following values:

| Temp° | 21·0 | 34·8 | 59 | 63 | 71·7 | 83·7 | 100·6 | 107·9 |
|---|---|---|---|---|---|---|---|---|
| V.p., mm | 4·5 | 14 | 50 | 70 | 74 | 109 | 190 | 238 |

The extrapolated b.p. was 210° ± 5°, the latent heat of vaporisation 9200 cals/g-ml and TROUTON's constant 19.3

In a further experiment arsenic (16·65 g) and silyl iodide (11·37 g) reacted for 5 days at room temperature. The tube contents were red-brown in colour. The volatile products were hydrogen (266 ml), unchanged silyl iodide (4·11 g, 36·1 per cent), disilane, hydrogen iodide and a small amount of a liquid which was held during fractionation by a trap cooled to −64°. It had a molecular weight of 167 (calc. for $As(SiH_3)_3$, 168) and 18·1 mg on hydrolysis with alkali gave 21·6 ml of $H_2$ and 6·1 mg of $AsH_3$ (M, 79. Calc. for $AsH_3$; M, 78). These figures represent 99·5 per cent and 73 per cent respectively of the amounts expected from the hydrolysis of this weight of arsenic trisilyl. In a further experiment using arsenic (27·4 g) and silyl iodide (6·94 g) with a reaction time of 7 weeks the products identified were $H_2$ (181 ml), disilane (0·194 g), hydrogen iodide (0·405 g) and silyl iodide (2·56 g) with a liquid (0·49 g, M, 276–285) which was mainly silylene iodide. A further small fraction which passed a trap cooled to −112° but which was held at −134° had M, 113 and 31·5 mg gave, on hydrolysis with alkali, 10·8 ml of $H_2$ (Calc. for $As(SiH_3)H_2$; M, 108. Hydrogen on hydrolysis, assuming each Si—H bond gives $H_2$ is 11.0 ml). The hydrolysate contained silicon and arsenic, but no iodide.

*Reaction of silyl iodide with potassium and mercuric arsenides*—Potassium arsenide was prepared by the reaction of powdered arsenic (51 g) with molten potassium (55 g). The product was powdered in a nitrogen-filled dry box, and 20 g of it was sealed with silyl iodide (5·562 g) and allowed to react at 20° for 3 days. The products were $H_2$ (7·4 ml), silyl iodide (2·05 g), $SiH_4$, $Si_2H_6$, and a very small less volatile fraction which condensed during the fractionation in a trap at −46°. It was treated with silver powder to remove traces of free iodine. The product (14·0 mg) had M, 168 (Calc. for $As(SiH_3)_3$; M, 168). It was shown qualitatively to contain arsenic, silicon and hydrogen (as Si—H bonds), but no iodine. A similar small fraction was isolated in a repeat experiment during which the reactants were heated at 85° for 5 hrs. It had a v.p. at 0° of 1·7 cm and evolved hydrogen at room temperature.

Mercuric arsenide, prepared by the method of DUMESNIL[23] was dried in vacuum for 48 hrs and 5 g of the dry material was mixed with an equal weight of powdered glass and placed in a horizontal reaction tube (20 mm diam.). Silyl iodide (2·174 g) was streamed repeatedly (12 times) in vacuum through this tube, the contents of which became warm, with production of mercuric iodide. A small amount of hydrogen was removed after each pass. The products included arsine and monosilane, which were separated by fractionation and identified by molecular weight determinations. A volatile cream-coloured solid was also formed (v.p. at 21°, 1·6 cm). This lost silyl iodide and hydrogen at room temperature, the former being characterized by its molecular weight. A fresh sample on hydrolysis with aqueous alkali evolved hydrogen and gave a solution containing arsenic, silicon, and iodide (Found: $H_2$ evolved: I, 11·2 : 1. Calc. for $As(SiH_3)_4I$ : $H_2$ : I, 12 : 1).

*Reaction of silyl iodide with tertiary amines*—These reactions were studied in small bulbs (50 ml) attached to the vacuum system. Known weights of the reactants were distilled in and the bulbs were sealed off with the reactants frozen in liquid nitrogen. The volatile reaction products were taken back into the vacuum system for identification. Silyl iodide (0·379 g) reacted with trimethylamine (0·143 g) forming a white solid. Excess trimethylamine (0·069 g) was the only volatile material remaining. There was thus a reaction ratio of $SiH_3I : N(CH_3)_3$ of 1 : 1·01. The v.p. of the solid was very low, since a 50 ml sample required 12 hrs for its complete vaporization in high vacuum at room temperature. When a sample was heated in a sealed tube to 150° the only volatile product was a very small amount of monosilane and hydrogen. The solid was decomposed slowly in moist air. In a second experiment silyl iodide (0·688 g) reacted with trimethylamine (0·216 g). Excess of silyl iodide (0·106 g) was recovered, leading to a reaction ratio, $SiH_3I : N(CH_3)_3$, of 1 : 0·994. A portion (0·448 g) of this solid was hydrolyzed with 15 per cent sodium hydroxide solution (Found: H, 1·30; I, 58·9 per cent. $N(CH_3)_3SiH_3I$ requires: H, 1·39; I, 58·5 per cent). In a similar experiment silyl iodide (0·461 g) reacted with triethylamine (0·273 g), giving a white solid of very low volatility. Silyl iodide (0·030 g) was recovered, giving a reaction ratio, $SiH_3I : N(C_2H_5)_3$, of 1 : 0·992. No other volatile products were formed. [Found: H, 1·12; I, 49·2 per cent. $N(C_2H_5)_3SiH_3I$ requires: H, 1·17; I, 49·0 per cent.]

*Reaction of silyl iodide with tertiary phosphines*—Silyl iodide (2·534 g) reacted with trimethylphosphine, giving a white solid. Silyl iodide (0·204 g) was recovered, giving a combining ratio, ($SiH_3I : P(CH_3)_3$, of 1 : 0·98. The compound was hydrolyzed by aqueous alkali with evolution of hydrogen [Found: H, 1·31; I, 54·8 per cent. $P(CH_3)_3SiH_3I$ requires: H, 1·29; I, 54·2 per cent]. Similarly, silyl iodide (1·308 g) reacted with triethylphosphine (0·882 g) to form a white solid and 0·135 g of silyl iodide was recovered [$SiH_3I : P(C_2H_5)_3$, 1 : 1·01. Found: H, 1·04; I, 46·1 per cent. $P(C_2H_5)_3SiH_3I$ requires: H, 1·10; I, 46·0 per cent]. This compound and that with trimethylphosphine had a very low volatility in vacuum.

*Reaction of silyl iodide with trimethylarsine*—Silyl iodide (0·770 g) and trimethylarsine (0·795 g) reacted at low temperatures to form a solid which melted just below room temperature. Excess of trimethyl arsine (0·216 g) was pumped off at −64°, giving a combining ratio, $SiH_3I : As(SiH_3)_3$, of 1 : 0·99. The m.p. of the solid was in the range 8·1–9·6°. A sample was analyzed by hydrolysis with 20 per cent sodium hydroxide solution (Found: H, 1·05; I, 45·4 per cent. $As(CH_3)_3SiH_3I$ requires:

[23] *Compt. rend.* **152**, 868 (1911).

H, 1·09; I, 45·7 per cent). The v.p. of three samples of the compound was measured in the range −40° to 21° with a sensitive spoon gauge. Typical data are:

| Temp° | −34° | −26·4 | −19·7 | −15 | −9 | −0·7 | 5·1 | 12·0 | 15·0 | 21·0 |
|---|---|---|---|---|---|---|---|---|---|---|
| V.p., mm | 6·5 | 13 | 24·5 | 39 | 64 | 105 | 140·5 | 189 | 212 | 665 |

At temperatures above about 5° these data corresponded with values calculated from the partial pressures of an equimolecular mixture of silyl iodide and trimethyl arsine. At lower temperatures the vapour pressure became progressively lower than those calculated on this basis. Thus at −39·3° the measured vapour pressure was 3·0 mm, whereas an equimolecular mixture of $As(CH_3)_3$ and $SiH_3I$ should have a vapour pressure of 13·8 mm. Approximate determinations of vapour density at −24° and 0° gave values of 131 and 133, compared with calculated values of 136 and 142, assuming complete dissociation of the vapours to $As(CH_3)_3$ and $SiH_3I$. The slope of a plot of $\log p$ versus $1/T$ showed that the heat of dissociation of the compound was 23,400 cals at 0°. Assuming the vapour was completely dissociated the heat of formation of the complex from the liquid components at 0° must be 9,700 cals, since the heat of volatilization of silyl iodide at 0° is 7,040 cals (EMELÉUS, MADDOCK, and REID(22)) and of trimethyl arsine is 6,600 cals.(24)

*Reaction of silyl iodide with excess of trimethylamine under pressure*—Two bulbs of approximately 50 ml capacity were connected by a long wide reaction tube. In one bulb was placed 0·986 g of silyl iodide and in the other 1·232 g of trimethylamine ($SiH_3I : N(CH_3)_3 = 1 : 3{\cdot}5$). The volume of the apparatus was such as to give a pressure of 5 atm if no reaction occurred. The two reactants, each frozen initially in liquid nitrogen, were allowed to warm up so that the two vapours met mainly in the connecting reaction tube. A white solid separated. The apparatus, containing excess of methylamine, was kept at room temperature for 14 hrs. The volatile products were: $H_2$ (7·9 ml), $SiH_4$ (6·0 mg, M, 31·3) and residual trimethylamine (0·631 g). Thus the combining ratio $SiH_3I : N(CH_3)_3$, was 1 : 1·63. The tube was filled with dry nitrogen and a sample of the powder was removed in a nitrogen-filled dry box and weighed. This was analysed by hydrolysis with 30 per cent potassium hydroxide solution (Found: H, 1·05; I, 47·8 per cent. $SiH_3I \cdot 1{\cdot}83\ N(CH_3)_3$ requires: H, 1·13; I, 47·7 per cent). The discrepancy between this result and the experimentally determined combining ratio may be accounted for by the fact that during the mixing process some of the more volatile amine reacted with liquid silyl iodide and the solid product of this reaction was not included in the sample taken. The white solid analyzed was very little changed on exposure for several days to moist air.

*Conductivity measurements*—Freshly-distilled acetonitrile (boiling range 81–83°) was allowed to stand successively over anhydrous potassium carbonate and phosphorus pentoxide and then further purified by vacuum distillation. The material used as solvent had a resistance of about 1·5 megohms in a cell of constant 4·6 $cm^{-1}$, corresponding to a specific conductivity of $1{\cdot}80 \times 10^{-6}$ $ohm^{-1}\ cm^{-1}$.

The 1 : 1 addition compound of silyl iodide and trimethylamine (0·0992 g, 457 micromoles) was transferred to the bulb of the conductivity cell in a nitrogen-filled dry box. Approx. 25 ml of acetonitrile was distilled into the cell in vacuo and the solid dissolved readily. The resistance of the solutions at 25° changed from 630 ohms after 15 mins to 690 ohms after 90 mins, indicating a very slow decomposition. This resistance corresponds to a specific conductivity for the solution of $7{\cdot}30 \times 10^{-3}$ $ohm^{-1}\ cm^{-1}$. The solvent was distilled out of the cell in vacuum and its specific conductivity was found to be $7{\cdot}81 \times 10^{-6}$ $ohm^{-1}\ cm^{-1}$.

In a similar way 0·0143 g of the 1 : 1·83 silyl iodide—trimethylamine compound was mixed with approx. 25 ml of acetonitrile. It dissolved readily. The specific conductivity of the pure solvent was $1{\cdot}24 \times 10^{-6}$ $ohm^{-1}\ cm^{-1}$, that of the solution $1{\cdot}80 \times 10^{-6}$ $ohm^{-1}\ cm^{-1}$, and that of the solvent after recovery, as before, $3{\cdot}22 \times 10^{-6}$ $ohm^{-1}\ cm^{-1}$. The 1 : 1 silyl iodide-triethylphosphine compound (0·0623 g, 226 micromoles) was likewise dissolved in 25 ml of acetonitrile, which had an initial specific conductivity of $2{\cdot}43 \times 10^{-6}$ $ohm^{-1}\ cm^{-1}$. The specific conductivities of the solution and the solvent recovered from it were $4{\cdot}95 \times 10^{-3}$ and $6{\cdot}80 \times 10^{-6}$ $ohm^{-1}\ cm^{-1}$, respectively.

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(24) ROSENBAUM and SANDBERG, *J. Amer. Chem. Soc.* **62**, 1622 (1940).