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Abstract

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SYNTHESIS OF ELEMENT-ELEMENT-ORGANIC COMPOUNDS IN WHICH SILICON OR TIN IS BONDED DIRECTLY TO PHOSPHORUS OR ARSENIC

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At the present time, only a small number of organic compounds of silicon and tin are known in which the indicated elements are bonded directly to phosphorus or arsenic. Attempts have been made (^{1}) to obtain organophosphorus compounds containing a P—Si bond by the action of alkylhalosilanes on trialkyl phosphites, by a reaction of the Arbuzov rearrangement type, or by the interaction of alkylhalosilanes with sodium dialkyl phosphite. However, later, upon more detailed investigation, it was shown that as a result of these reactions compounds are formed in which silicon is bonded to phosphorus through oxygen (^{2}-^{4}),

$$R_3SiX + P(OR')_3 \rightarrow R_3SiOP(O)(OR')R' + R'X.$$

Later, papers appeared on the interaction of alkylhalosilanes (^{5}) and alkoxyhalosilanes (^{6}) with sodium derivatives of dialkyl phosphite, as a result of which, in the authors' opinion, compounds with an Si—P bond are formed. However, these results are insufficiently convincing in light of the above-mentioned works of B. Arbuzov et al. (^{4}) and Malatesta (^{2},^{3}).

The preparation of trimethylsilyldiphenylphosphine and triethyltin-diphenylphosphine by the action of trimethylchlorosilane or bromotriethyltin on sodium diphenylphosphine, respectively, has also been described (^{7},^{8}).

Recently a publication appeared in which the preparation of mono-, bis-, and tris-trimethylsilylphosphines by the action of trimethylchlorosilane on lithium phosphide was described (the latter was obtained by passing phosphine into an ethereal solution of butyllithium (^{9})).

Inorganic compounds in which silicon is bonded to phosphorus or arsenic have also been described. Thus, as a result of the interaction at 500° of silane with phosphorous hydrogen, silylphosphine $H_3Si—PH_2$ was obtained (^{10}-^{12}). In the interaction of white phosphorus with silyl iodide at a temperature of 20-100°, a mixture of unstable, spontaneously inflammable products is formed, from which diiodosilylphosphine $H_3Si—PJ_2$ was isolated (^{13}-^{16}). In the same work there is an indication that arsenic, like phosphorus, reacts with silyl iodide; diiodosilylarsine $H_3Si—AsJ_2$ was isolated from the reaction mixture.

In the present work, the reaction between the hydrophosphide, alkylhydrophosphide, or hydroarsenide of alkali metals and monohaloalkyl derivatives of silicon and tin was studied with the aim of obtaining element-element-organic compounds in which an element of Group IV would be bonded directly to an element of Group V of the periodic system. This route could make it possible to obtain element-element-organic compounds containing hydrogen or alkyl and aryl radicals at both elements.

$$\mathrm{R_3E^{IV}X + MeE^{V}R'_2 \rightarrow R_3E^{IV}E^{V}R'_2 + MeX} \quad (1)$$

$$\mathrm{E^{IV} = Si,\ Sn;\quad R = H,\ CH_3\ \text{and others};\quad Me = Li,\ Na,\ K;\quad E^{V} = P,\ As;\quad X = F,\ Cl,\ Br;}$$

$$\mathrm{R' = H,\ CH_3, C_6H_5\ \text{and others}.}$$

1. Compounds with an Si–P bond. Study of the indicated route of synthesis showed that, in the reaction of potassium (sodium) hydro- or alkylhydrophosphides with trimethylchloro- or bromosilanes, only a very small amount of silylphosphines is formed. This reaction proceeds considerably better when alkylfluorosilanes are used. Thus, on the action of trimethylfluorosilane on potassium (sodium) dihydrophosphide, a mixture of bis- and tris-trimethylsilylphosphines is obtained with a total yield of 40-50%.

$$\mathrm{5(CH_3)_3SiF + 5KPH_2 \rightarrow ((CH_3)_3Si)_2PH + ((CH_3)_3Si)_3P + 5KF + 3PH_3.} \quad (2)$$

One of the possible reasons for the different action of trimethylfluorosilane and trimethylchlorosilane on potassium (sodium) hydrophosphide may be the greater electron affinity of fluorine, owing to which formation of the P–Si bond is facilitated when potassium alkylhydrophosphides act on alkylfluorosilanes.

The formation of secondary and tertiary silylphosphines in the reaction mixture can be explained by the following intermediate processes, which take place in the reaction of trimethylfluorosilane with potassium dihydrophosphide:

$$\mathrm{(CH_3)_3SiF + KPH_2 \rightarrow (CH_3)_3Si - PH_2 + KF;}$$

$$\mathrm{(CH_3)_3Si - PH_2 + KPH_2 \rightarrow (CH_3)_3Si - PHK + PH_3;}$$

$$(CH_3)_3Si-PHK+FSi(CH_3)_3 \rightarrow ((CH_3)_3Si)_2PH+KF;$$

$$((CH_3)_3Si)_2PH+KPH_2 \rightarrow ((CH_3)_3Si)_2PK+PH_3;$$

$$((CH_3)_3Si)_2PK+FSi(CH_3)_3 \rightarrow ((CH_3)_3Si)_3P+KF.$$

The amount of phosphine evolved during the reaction almost quantitatively corresponds to equation (2), which may, to some extent, serve as confirmation of the scheme given above. It should be noted that the process was carried out under conditions excluding hydrolysis of the reaction products, during which phosphine might have been evolved.

The structure of the synthesized silylphosphines is confirmed by the following data: upon hydrolysis of tris-trimethylsilylphosphine with water or an aqueous alkali solution, phosphine and hexamethyldisiloxane are isolated according to the equation

$$2((CH_3)_3Si)_3P+6H_2O \rightarrow 2PH_3+6(CH_3)_3SiOH$$

$$\downarrow -3H_2O$$

$$3(CH_3)_3Si-O-Si(CH_3)_3$$

In the IR spectrum of bis-trimethylsilylphosphine ($[(CH_3)_3Si]_2PH$), a band at ~ 2500 cm^{-1}, characteristic of the stretching vibration of P—H, was found; in tris-trimethylsilylphosphine ($[(CH_3)_3Si]_3P$) such a band is absent. The mass spectrum of tris-trimethylsilylphosphine was studied; in it an ion with mass 59 was found, which can be interpreted as the Si + P bond ($m = 28+31$)[*].

Tris-trimethylsilylphosphine readily adds elemental sulfur with formation of tris-trimethylsilylthiophosphate ($[(CH_3)_3Si]_3PS$), which testifies to the trivalence of phosphorus in silylphosphine.

Study of the reaction of trimethylfluorosilane with potassium methylhydrophosphide showed that in this case also a mixture of mono- and bis-trimethylsilylmethylphosphines is formed, with a total yield of about 55%.

$$3(CH_3)_3SiF+3KPH(CH_3) \rightarrow (CH_3)_3Si-PH(CH_3)+((CH_3)_3Si)_2PCH_3+3KF+CH_3PH_2. \tag{3}$$

[*] The IR spectra and mass spectrum were studied by N. Rodionova, S. Dubov, A. Khokhlova, and V. Fedotova.

II. **Compounds with an Si–As bond.** Previously only one compound, and that an inorganic one, was known that contained a direct arsenic–silicon bond (^{8}). By the action of trimethylfluorosilane on potassium dihydroarsenide, we obtained bis- and tris-trimethylsilylarsines, in 25% yield.

$$5(CH_3)_3SiF + 5KAsH_2 \rightarrow ((CH_3)_3Si)_2AsH + ((CH_3)_3Si)_3As + 5KF + 3AsH_3.$$

It should be noted that compounds having an arsenic–silicon bond proved to be less stable than the corresponding compounds with a phosphorus–silicon bond.

III. **Compounds with an Sn–P bond.** Tin halogen derivatives, in contrast to analogous silicon compounds, are known not to undergo the ammonolysis reaction; therefore, the reaction between sodium (potassium) dihydrophosphide and tin halogen derivatives was carried out in liquid ammonia.

Owing to the solubility of these components in liquid ammonia, the reaction proceeds considerably more readily than in ether, and there is no need to use tin fluoro derivatives.

On interaction of trimethyltin bromide with sodium hydrophosphide, tris-trimethylstannylphosphine was obtained in about 65% yield.

$$3(CH_3)_3SnBr + 3NaPH_2 \rightarrow ((CH_3)_3Sn)_3P + 3NaBr + 2PH_3.$$

Experimental Part

1. **Preparation of bis- and tris-trimethylsilylphosphines.** Finely ground potassium dihydrophosphide, 14.42 g, was covered with anhydrous ether (150 ml), and with vigorous stirring at −20°, 35.8 g of trimethylfluorosilane was condensed into this mixture. The temperature of the reaction mixture was gradually raised to room temperature (reflux condenser cooled to −20–−25°), and the mixture was stirred for 12-18 h; then the temperature was raised to 30°, and the mixture was stirred for an additional 6 h. During the reaction a gas was evolved containing up to 50-70% phosphine.

The reaction mixture was siphoned off from the precipitate. The precipitate was washed with ether 2-3 times. Volatile products and ether were distilled off, and the remaining liquid was subjected to vacuum distillation. All operations were carried out in an atmosphere of oxygen-free nitrogen. The following were obtained: bis-trimethylsilylphosphine, b.p. 60-61° (20 mm); d_4^{20} 0.8188; 2.5 g of substance was obtained (about 8.0% of theoretical).

$C_6H_{19}Si_2P$.	Found %:	Si + P 48.6
	Calculated %:	Si + P 48.9

Tris-trimethylsilylphosphine, b.p. 66.8-67° (2 mm); d_4^{20} 0.8670; 10 g was obtained (33% of theoretical).

$C_9H_{27}Si_3P$.	Found %:	C 43.6;	H 11.3;	Si + P 45.6
	Calculated %:	C 43.2;	H 10.9;	Si + P 46.0

Molecular weight: found 258.0, calculated 250.6. The substances ignite spontaneously in air.

2. **Preparation of mono- and bis-trimethylsilylmethylphosphines.** Mono- and bis-trimethylsilylmethylphosphines were obtained under the same conditions as bis- and tris-trimethylsilylphosphines. By the interaction of potassium methylhydrophosphide (15.43 g) with trimethylfluorosilane (22 g), 4.0 g of mono-trimethylsilylmethylphosphine was obtained (13.9% of theoretical); b.p. 54-55° (153 mm); d_4^{20} 0.7969, and 9.3 g of bis-trimethylsilylmethylphosphine (40.6% of theoretical);

b.p. 75-76° (20 mm); d_4^{20} 0.8433.

$C_4H_{13}SiP$.	Found, %:	C 39.0;	H 10.8;	Si + P 49.1
	Calculated, %:	C 40.0;	H 10.9;	Si + P 49.1

$C_7H_{21}Si_2P$.	Found, %:	C 43.3;	H 11.4;	Si + P 45.0
	Calculated, %:	C 43.70;	H 11.0;	Si + P 45.30

The substances ignite spontaneously in air.

3. Preparation of tris(trimethylsilyl)arsine. Bis- and tris(trimethylsilyl)arsines were obtained under the same conditions as bis- and tris(trimethylsilyl)phosphines. On reaction of potassium dihydroarsenide (23.2 g) with trimethylfluorosilane (21.9 g), 4.1 g of tris(trimethylsilyl)arsine was obtained (17.5% of theory), b.p. 82-84° (4 mm); d_4^{20} 0.9939.

$C_9H_{27}Si_3As$.	Found, %:	C 37.0;	H 9.6;	Si + As 53.3
	Calculated, %:	C 36.7;	H 9.2;	Si + As 54.1

Mol. wt.: found 291.8, calculated 294.5. The substance does not ignite spontaneously in air.

In addition to tris(trimethylsilyl)arsine, bis(trimethylsilyl)arsine was isolated in a yield of 7% of theory; its b.p. is 55° (15 mm).

4. Preparation of tris(trimethylstannyl)phosphine. To a solution of sodium hydrophosphide (8.26 g) in liquid ammonia was added dropwise an ethereal solution of trimethyltin bromide (17.5 g). The ammonia was evaporated, and the ethereal solution was decanted from the precipitate. After removal of the ether, the remaining liquid was distilled under reduced pressure. B.p. 136–137° (3 mm). 7.9 g (63.2% of theory) of tris(trimethylstannyl)phosphine was obtained; d_{20}^{20} 1.6769; n_D^{20} 1.5970.

$C_9H_{27}Sn_3P$.	Found, %:	C 21.3; H 5.5; Sn + P 72.7
	Calculated, %:	C 20.7; H 5.2; Sn + P 74.1

Mol. wt.: found 510.0, calculated 522.3. The substance does not ignite spontaneously in air.

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