572. *Hexamethyl Compounds of Silicon, Germanium, and Tin.*

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Hexamethyldisilane, hexamethyldigermane, and hexamethyldistannane have been prepared, the germanium compound for the first time. The conditions for preparation of hexamethyldisilane from trimethylchlorosilane have been systematically studied. Whereas the hexamethyl compounds of silicon and germanium are not cleaved by solutions of sodium–potassium alloy in ethylene glycol dimethyl ether, hexamethyldistannane gives the potassium salt of trimethyltin.

Carbon, silicon, germanium, tin, and lead form compounds $(R_3M)_2$, where R is alkyl or aryl. Whereas the hexa-aryl compounds have been studied in some detail by Gilman and his co-workers (1953—57),[1] little systematic work has been reported for the hexa-alkyls since the investigations by Kraus *et al.* (1925—34).[2,3,4] As we wished to study the metal–metal bonds through the Raman and infrared spectra of the hexamethyl compounds (to be published), we prepared and examined the silicon, germanium, and tin compounds.

The most important general preparative method, the reduction of the appropriate trialkylhalogeno-compound by an alkali metal, is best carried out in liquid ammonia with tin compounds, and in this solvent we have repeated Kraus and Sessions's [2] preparation of hexamethyldistannane. Since silicon– and germanium–halogen bonds are readily ammonolysed, the hexa-alkyl compounds of these elements cannot be prepared in liquid ammonia, and the trialkylhalogeno-compound is usually reduced by refluxing it with the alkali metal, sometimes in an inert solvent. Hexamethyldigermane was obtained in good yield by the reduction of trimethylbromogermane by molten potassium. As hexamethyldisilane had been made, until recently, only by the reaction of hexahalogenodisilanes with organometallic compounds,[5] we studied the reduction of trimethylchlorosilane. Although the results of a study of the analogous reduction of trimethyliodosilane [6] are now available, in view of the greater availability of the chloro-compound we extended our study in order to find the best method for preparing hexamethyldisilane. Results are shown in the Table.

Reaction of trimethylchlorosilane with alkali metals.

Alkali metal	Solvent	(ml.)	Me_3SiCl (ml.)	Reflux time (hr.)	Yield of Me_6Si_2 (%) *
Li (solid)	None		10	2·5	0
Li (solid)	Di-*n*-butyl ether	(10)	10	2·5	0
Na (liquid)	None		10	24 †	0
Na (solid)	Tetrahydrofuran	(50)	10	12	0
Na (liquid)	Xylene	(200)	30	12	0
K (liquid)	None		10	24	92
K (liquid)	Tetrahydrofuran	(20)	10	3	50
K (liquid)	Ethylene glycol dimethyl ether	(80)	20	3	59
Na/K (liquid)	Ethylene glycol dimethyl ether	(15)	3	2 ‡	43

* 0 = No reaction. † In a sealed tube at 120°. ‡ At room temperature.

Although trimethyliodosilane,[6] trimethylbromosilane,[4] and triethylchlorosilane [7] can be reduced by molten sodium, trimethylchlorosilane did not react even in boiling xylene, yet molten potassium readily reduced it; in the presence of tetrahydrofuran or ethylene glycol dimethyl ether yields were somewhat lower, partly because of the difficulty in

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[1] Gilman and Gerow, *J. Org. Chem.*, 1957, **22**, 334. This paper, which describes triphenylgermyltriphenyltin, is the latest of the series on hexaphenyl compounds.
[2] Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361.
[3] Kraus and Flood, *J. Amer. Chem. Soc.*, 1932, **54**, 1635.
[4] Kraus and Nelson, *J. Amer. Chem. Soc.*, 1934, **56**, 195.
[5] Brockway and Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287.
[6] Voronkov and Khudobin, *Zhur. obshchei Khim.*, 1956, **26**, 584.
[7] Gilman, Ingham, and Smith, *J. Org. Chem.*, 1953, **18**, 1743.

" working up " and possibly owing to solvolysis of the trimethylchlorosilane.[6] Potassium probably forms transient solutions which react immediately with trimethylchlorosilane, since both potassium and sodium–potassium alloy [8] (but not lithium or sodium) form fairly stable, blue, diamagnetic solutions in this ether, analogous to those formed by alkali metals in amines.[9] Trimethylchlorosilane was rapidly reduced by these metal solutions, and although the blue colour disappeared throughout the solvent, reaction continued at the metal surface. Unlike reductions in liquid ammonia, the effects of solvolysis did not appear to be important.

In all successful reductions of trimethylchlorosilane and trimethylbromogermane, the potassium halide was dark blue, presumably because of colloidal particles of excess of alkali metal or F centres in the halide crystals.[10]

Properties of the Hexamethyl Compounds.—The simple physical properties show, as expected, a greater change between germanium and tin than between silicon and germanium: Si_2Me_6: m. p. 12°, b. p. 113°/760 mm., n_D^{20} 1·4224; Ge_2Me_6: m. p. −40°, b. p. 138°/750 mm., n_D^{25} 1·4564; Sn_2Me_6: m. p. 23°, b. p. 182°/756 mm. The silicon and germanium compounds are colourless liquids with pleasant fruity smells, which can be distilled in air and do not react appreciably with cold concentrated sulphuric acid. Kumada [17] *et al.* have, however, shown that prolonged stirring with concentrated sulphuric acid leads to the ionisation of a silicon–carbon bond. Hexamethyldistannane has an unpleasant smell, and reacts slowly with oxygen at room temperature to form bis(trimethyltin) oxide.

Hexa-aryl compounds of all the Group IVB elements [11,12] and hexa-alkyl compounds of tin and lead can be split by alkali metals to give the alkali-metal salts, *e.g.*, $Ph_6Si_2 + 2K = 2Ph_3SiK$. Hexa-alkyl compounds of silicon and germanium are more resistant, however; thus hexaethyldisilane is not split by solutions of sodium in liquid ammonia, by lithium in ethylamine,[4] or by sodium–potassium alloy (either alone or with a number of ethers); hexaethyldigermane is not split by metal–ammonia solutions although some reaction appears to take place with solutions of lithium and potassium in ethylamine.[3]

Since the non-reduction of the hexa-alkyl compounds of silicon and germanium by metal–ammonia solutions might be attributed in part to their insolubility in liquid ammonia, we attempted the reduction with solutions of sodium–potassium alloy in ethylene glycol dimethyl ether (in which the hexamethyl compounds are soluble). Substantial amounts of the hexamethyls could be recovered even after three days, and the yellow colour expected [18] if potassium salts were formed did not appear. Hexamethyldigermane was not, moreover, reduced when refluxed with potassium. It seems, therefore, that the silicon–silicon and germanium–germanium bonds in the hexamethyl compounds are truly resistant to reduction by alkali metals. Gilman [18] has shown that reduction becomes possible when methyl groups are replaced by phenyl groups; thus 1 : 1 : 2 : 2-tetramethyl-1 : 2-diphenyldisilane reacts slowly with lithium in tetrahydrofuran, whereas 1 : 2-dimethyl-1 : 1 : 2 : 2-tetraphenyldisilane reacts immediately.

In contrast to the stability of the silicon–silicon and germanium–germanium bonds, the tin–tin bond is easily cleaved; hexamethyldistannane reacts immediately with alloy solutions in ethylene glycol dimethyl ether to give potassium trimethyltin; this salt with tri-*p*-tolylbromostannane gave 1 : 1 : 1-trimethyl-2 : 2 : 2-tri-*p*-tolyldistannane.

Metal–metal bonds in the hexa-alkyl and hexa-aryl compounds are cleaved both with metal solutions and with the metal in an inert solvent. When the metal is in solution, we can consider it to be dissociated completely into metal ions and (solvated) electrons [9] (single or paired), $M \longrightarrow M^+ + e$, and it seems reasonable to consider the reduction to

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[8] Down, Lewis, Moore, and Wilkinson, *Proc. Chem. Soc.*, 1957, 209.

[9] Fowles, McGregor, and Symons, *J.*, 1957, 3329.

[10] Seitz, *Rev. Mod. Phys.*, 1954, **26**, 7.

[11] Gilman and Dunn, *Chem. Rev.*, 1953, **52**, 94.

[12] Brook and Gilman, *J. Amer. Chem. Soc.*, 1954, **76**, 278.

be caused by these electrons, $R_3M{-}MR_3 + 2e \longrightarrow 2R_3M^-$. From the low ionisation potentials of the alkali metals, we might expect that the first stage of the reduction by the metal in an inert solvent would be the ionisation of the metal atoms, followed by the interaction of the electron with the hexa-alkyl compound.

As the atomic weight of M increases, so the M–M bond in the R_6M_2 compounds gets weaker and longer, and should accordingly break more easily. It is not surprising therefore that hexamethyldistannane is cleaved whereas the analogous germanium and silicon compounds are inert. When the methyl groups are replaced by phenyl groups, the M–M bond should weaken because of the greater electron-withdrawing power of the phenyl groups. The M–M bonds become more vulnerable to attack by the electrons. Moreover, the triarylmetal anions formed in the reaction will be appreciably stabilised by delocalisation of the negative charge on to the three phenyl groups.

EXPERIMENTAL

Analysis.—Silicon, germanium, and tin were estimated by dry combustion.[13]

Materials.—Solvents were fractionated and dried. Germanium(IV) bromide was prepared [14] from bromine vapour and germanium metal at 400°. Tetramethylgermane was obtained in 75% yield from germanium(IV) bromide and methylmagnesium iodide in di-*n*-butyl ether.[15] Trimethylbromogermane was prepared in 85% yield by keeping tetramethylgermane and bromine (*ca.* 0·2 mol. excess) in a sealed tube for a week, followed by fractionation.[16] Trimethylbromostannane was prepared and purified by Kraus's method.[2]

Tri-*p*-tolylchlorostannane, prepared from tin(IV) chloride and tetra-*p*-tolylstannane, was hydrolysed to the hydroxide, and then converted into the bromo-analogue with hydrobromic acid.

Solutions of sodium–potassium alloy in ethylene glycol dimethyl ether were made by melting the metals together *in vacuo* and distilling on the freshly dried ($LiAlH_4$) ether. These blue solutions were shown by paramagnetic resonance measurements [9] to be diamagnetic. Solutions of potassium metal could also be made, but lithium and sodium alone did not dissolve.

1. *Preparation of Hexamethyldisilane.*—(a) *Refluxing of trimethylchlorosilane with potassium and ethylene glycol dimethyl ether.* Trimethylchlorosilane (99%, Messrs. Hopkin and Williams) (0·78 mole) and potassium (0·86 g.-atom) were added, in portions of about 0·2 mole each, to the ether (200 ml.), and the mixture was refluxed under nitrogen for 6 hr. Volatile constituents were condensed *sub vacuo* into another flask and shaken with water, and then with cold concentrated sulphuric acid. The immiscible layer of hexamethyldisilane was washed with water, dried ($CaSO_4$), and fractionated to give a product with b. p. 113·1°/750 mm. and n_D^{20} 1·4224 [6] (Found: Si, 38·35, 38·24. Calc. for $C_6H_{18}Si_2$: Si, 38·38%). Reactions were carried out with other solvents (cf. Table) similarly.

(b) *Reaction of sodium and trimethylchlorosilane in a sealed tube.* Trimethylchlorosilane (1 mol.) and sodium (1 mol.) were heated in a sealed tube at 120° for 24 hr. The surface of the sodium became brown, but no hexamethyldisilane was isolated when the reaction mixture was worked up as in 1(a).

(c) *Reaction of trimethylchlorosilane with a solution of sodium–potassium alloy in ethylene glycol dimethyl ether.* The alloy (0·046 mole) was filtered *in vacuo* through a glass sinter to remove oxide into a tube made from an extended B14 joint, and the ether (15 ml.) and trimethylchlorosilane (0·023 mole) were condensed successively into the lower and upper parts of the tube; this was then sealed off *sub vacuo*. As the ether melted, the alloy dissolved to give a blue solution, but the colour disappeared as the trimethylchlorosilane melted and ran into it. After being shaken for 2 hr., the tube was opened under nitrogen, and the colourless volatile liquid was distilled from the blue-black solid and worked up as in experiment 1(a) to give hexamethyldisilane (43%).

2. *Preparation of Hexamethyldigermane by Refluxing of Trimethylbromogermane with*

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[13] Brown and Fowles, *Analyt. Chem.*, in the press.
[14] Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 299.
[15] Lippincott and Tobin, *J. Amer. Chem. Soc.*, 1953, **75**, 4141.
[16] Dennis and Patnode, *J. Amer. Chem. Soc.*, 1930, **52**, 2779.

Potassium.—This reaction was carried out on the vacuum line. Potassium (0·115 g.-atom) was filtered (sinter) into the reaction flask; trimethylbromogermane (0·092 mole) was condensed in and refluxed with the potassium in nitrogen. The voluminous potassium bromide formed hindered the reaction, and so the volatile material was several times condensed on fresh potassium. Unchanged trimethylbromogermane was removed by bubbling ammonia through the product and filtering off the white complex formed. The filtrate consisted of pure *hexamethyldigermane* (0·034 mole, 74%) distilling at 137°/772 mm., n_D^{25} 1·4564 (Found: Ge, 61·41, 61·37. $C_6H_{18}Ge_2$ requires Ge, 61·67%). It did not react when refluxed with potassium or shaken with cold concentrated sulphuric acid.

3. *Hexamethyldistannane.*—Trimethylbromostannane was reduced by sodium in liquid ammonia by Kraus and Sessions's [2] method; the hexamethyldistannane was recrystallised *in vacuo* from light petroleum (b. p. 60—80°) at −78°. The average yield of once-recrystallised hexamethyldistannane (m. p. 23°) was 71% (Found: Sn, 71·23, 71·48. Calc. for $C_6H_{18}Sn_2$: Sn, 72·46%).

4. *Action of Solutions of Sodium–Potassium Alloy in Ethylene Glycol Dimethyl Ether on the Hexamethyl Compounds.*—These experiments were carried out *in vacuo* in a similar apparatus to that used for experiment 1(c).

(a) *Hexamethyldisilane.* Sodium–potassium alloy, the ether (15 ml.), and hexamethyldisilane (1 ml.) were condensed into the reaction tube, which was then sealed. The blue colour of the alloy–ether solution faded as it touched the melting disilane, but the colour returned immediately when the tube was shaken. After intermittent shaking for three days, the tube was opened, and the volatile materials were removed and worked up as usual to give unchanged hexamethyldisilane (0·75 ml., b. p. 112°). A trace of white solid remained with the alloy, formed probably by the known reaction of the alloy with the ether.

(b) *Hexamethyldigermane.* This (0·9 g.) behaved similarly to hexamethyldisilane, although the blue colour of the alloy solution disappeared more quickly. After intermittent shaking for three days—a blue solution still formed, and was stable for about 5 min.—the tube was opened and the volatile materials were worked up as in (a) to give unchanged hexamethyldigermane (0·4 g.).

(c) *Hexamethyldistannane.* This (0·0094 mole) reacted immediately at room temperature to give a greenish-yellow solution. After being shaken for 10 min. the tube was opened under nitrogen and the contents filtered into tri-*p*-tolylbromostannane (0·0187 mole); the greenish-yellow colour disappeared on shaking. After removal of the volatile materials, extraction of the residue with light petroleum gave crystals of 1 : 1 : 1-*trimethyl*-2 : 2 : 2-*tri*-p-*tolyldistannane* (0·0051 mole, 38%), m. p. 139·5—141° (Found: Sn, 42·74, 43·01. $C_{24}H_{30}Sn_2$ requires Sn, 42·30%). Further extraction of the residue with toluene gave hexa-*p*-tolyldistannane (0·0023 mole, 25%), m. p. 251—252° (Found: Sn, 30·0, 30·2. Calc. for $C_{42}H_{42}Sn_2$: Sn, 30·27%).

(5) *Hexa*-p-*tolyldistannane.*—Tri-*p*-tolylbromostannane (0·0042 mole) was allowed to react with a solution of sodium–potassium alloy in ethylene glycol dimethyl ether; excess of alloy was removed by amalgamation with mercury. The mixture was filtered, and extraction of the residue with benzene gave crystals of hexa-*p*-tolyldistannane (0·00094 mole, 45%) (Found: Sn, 30·1%), m. p. undepressed on admixture with the product formed in reaction 4(c).

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[17] Kumada *et al.*, *J. Org. Chem.*, 1956, **21**, 1264.
[18] Gilman, *J. Amer. Chem. Soc.*, 1958, **80**, 608.