

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Chemistry of the Tris-(triphenylgermany)-silyl Group¹BY JOHN G. MILLIGAN² AND CHARLES A. KRAUS**I. Introduction**

The reaction of sodium triphenylgermanide with organic polyhalides is, in general, complex and depends upon the nature of the halide as well as upon that of the solvent. With chloroform, complete substitution of the chlorine atoms does not occur. As shown by Nutting,³ in liquid ammonia, two chlorine atoms are largely substituted by triphenylgermany groups, while a third is completely replaced by hydrogen. Hydrogen is derived from the solvent, whereupon the residual NH₂ group combines with the remaining triphenylgermany group to form the amine. Reactions with chloroform in ether⁴ and benzene⁵ have not been characterized as completely as have those in liquid ammonia. It appears that not more than two chlorine atoms are substituted by triphenylgermany groups; aside from small amounts of bis-(triphenylgermany)-methane, no substitution products were isolated. Here, residual triphenylgermany groups dimerize to hexaphenyldigermane rather than react with the solvent.

It seemed of interest to extend the study to the polyhalides of silicon. It was found that, with silicochloroform in ether solution, the chlorine atoms are replaced quantitatively by triphenylgermany groups to form the compound tris-(triphenylgermany)-silane. The Ge-Si bonds in this compound are considerably more stable than in (triphenylgermany)-triethylsilane. For example, Kraus and Nelson⁶ have shown that the Ge-Si bond in the latter compound may be broken readily by strong oxidizing agents, such as bromine, or by strong reducing agents, such as lithium in ethylamine. In contrast, on treating tris-(triphenylgermany)-silane with these agents, it was found that the H-Si bond is preferentially broken, yielding the bromide and the lithium salt, respectively.

Normally, the hydrogen atom attached to silicon in trialkyl- or triarylsilanes is not replaced by alkali metals in liquid ammonia or the amines. Instead the reaction is more complicated; hydrogen is evolved and an amino derivative is invariably formed. Thus, Kraus and Nelson⁶ found that, on treating triethylsilane with lithium in

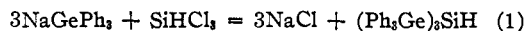
ethylamine, the metal acts as a catalyst for a reaction in which hydrogen and (triethylsilyl)-ethylamine are produced. Likewise, Reynolds, Bigelow and Kraus⁷ found that triphenylsilane reacts with sodium in liquid ammonia to form hydrogen and bis-(triphenylsilyl)-imine.

In view of the stability of the Ge-Si bond in tris-(triphenylgermany)-silane and the ease with which hydrogen may be replaced by other elements, it has been found possible to investigate the chemistry of the tris-(triphenylgermany)-silyl group in some detail. In addition to the silane and its lithium salt, the bromide, chloride, amine and silol have been prepared and their properties investigated. A characteristic property of these substances is their tendency to form surprisingly stable molecular addition compounds with essentially non-polar solvent molecules. For example, the bromide crystallizes with one-half molecule of ethylene dichloride and with three molecules of benzene. The dissociation pressure of several of these solvates has been measured. Ethyltris-(triphenylgermany)-silane has also been prepared.

An exploratory investigation was made of the reaction between sodium triphenylgermanide and silicon tetrachloride in ether solution. Approximately one-half of the germanium was recovered as hexaphenyldigermane. The remaining product, an amorphous solid, could not be crystallized but, from molecular weight determinations and other evidence, it seems likely that the material was tetrakis-(triphenylgermany)-silicoethylene.

II. Tris-(triphenylgermany)-silane

Sodium triphenylgermanide, prepared according to the method of Kraus and Foster,⁸ and silicochloroform react in ether solution to form tris-(triphenylgermany)-silane, according to the equation



The apparatus and procedure were essentially the same as those employed by Smith⁴ for carrying out reactions between sodium triphenylgermanide and halogenated organic compounds in ether solution. Starting materials were on hand in the laboratory.

After removing ether from the product, the residue was extracted alternately with water and benzene, to separate out the sodium chloride and the organic constituents, respectively. The silane was purified by recrystallizing from ethyl acetate and petroleum ether (95-112°).

(7) Reynolds, Bigelow and Kraus, *ibid.*, **51**, 3067 (1929).(8) Kraus and Foster, *ibid.*, **49**, 457 (1927).

(1) This paper is based on a portion of a thesis presented by John G. Milligan in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1934.

(2) (a) George R. Chamberlin Fellow from Dartmouth College, 1931-1932; Jesse Metcalf Fellow, 1932-1933. (b) Jefferson Chemical Company, Austin, Texas.

(3) Kraus and Nutting, *THIS JOURNAL*, **54**, 1622 (1932).

(4) F. B. Smith, Thesis, Brown University, June, 1934.

(5) L. S. Foster, Thesis, Brown University, 1927.

(6) Kraus and Nelson, *THIS JOURNAL*, **56**, 195 (1934).

Analyses.—Analyses were made for carbon and hydrogen and for mixed oxides of germanium and silicon. The latter were determined by a method commonly employed in this laboratory, which consists of oxidizing weighed samples of material with fuming nitric and sulfuric acids in weighed silica tubes.

Carbon and hydrogen were determined by the semi-micro combustion method of Lauer and Dobrovolny.⁹ The same difficulty was met with in obtaining complete combustion as was encountered by Simon, Wagner and Müller¹⁰ in the combustion of polygermanium compounds. It was found necessary to mix the sample with cupric oxide powder, as they suggested, and to heat the combustion tube to the softening point of Pyrex glass. *Anal.* Calcd. for $C_{54}H_{48}Ge_3Si$: C, 68.90; H, 4.93; mixed oxides, 0.06514, 0.05977. Found: C, 68.3, 68.6; H, 4.99, 5.17; mixed oxides for 0.16381 and 0.15032 g., 0.06512 and 0.05972.

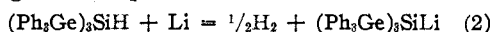
Molecular Weight.—Molecular weights, as ordinarily determined cryoscopically in benzene, were found to be low, not only for this compound, but for all other compounds of high molecular weight which were studied. In view of this, a molecular weight determination was made by Dr. D. A. Rothrock, using a precision method¹¹ developed in the course of investigations relating to dilute solutions of electrolytes. The result by this method was in much better agreement with the calculated value. It would seem that the low results ordinarily obtained are due to the method, rather than to impurities. *Mol. wt.* Ordinary method: sample, 0.2125, 0.4630; benzene, 11.39, 11.39; Δt , 0.115°, 0.245°; mol. wt., 815, 843. Calcd. for $C_{54}H_{48}Ge_3Si$, 940.2. Precision method: 0.002630 g. subs./g. of benzene; Δt , 0.01353°; mol. wt., 986.

Properties.—The silane is extremely soluble in benzene and in most other organic solvents, but only slightly soluble in alcohol. It remains unaffected by heating to 110° for extended periods of time and does not react with hydrogen chloride in ether solution.

The silane crystallizes from solution in two modifications. The more stable, α -form, melts at 187.5–188.5°, and the less stable, β -form, at 170–171°. Either form may be obtained by seeding a supersaturated solution with the proper crystals.

III. Lithium Tris-(triphenylgermanyl)-silide

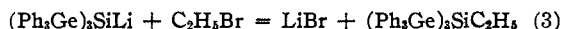
The lithium salt was prepared from the hydride in ethylamine solution by treating with lithium according to the equation



The lithium salt is not completely stable in solution. It reacts slowly with the ethylamine to evolve hydrogen. For example, after standing for a period of twelve hours, the total amount of hydrogen collected was some 59% greater than that calculated according to equation (2). The lithium salt was not isolated as such, but its formation was demonstrated through reaction with ethyl bromide which resulted in the formation of ethyltris-(triphenylgermanyl)-silane.

Ethyltris-(triphenylgermanyl)-silane.—1.782 mmoles. of tris-(triphenylgermanyl)-silide reacted with 1.772 mmoles. of lithium. Although the silane is not appreciably soluble in ethylamine, the lithium reacted as quickly as it dissolved, with the production of minute bubbles of gas. As reaction proceeded, the solution became yellow, and a yellow solid, doubtless the lithium salt, was precipitated. After standing for five hours, during which time more gas was collected, the ethylamine was distilled from the reaction vessel. After standing overnight, the

reaction tube contained a small amount of additional gas; this was combined with that collected previously. Apparently, the lithium salt is stable in the solid state. The salt was put into solution in ammonia and an excess of ethyl bromide was added. This dispelled the yellow color of the solution. Lithium bromide, hexaphenyldigermene and ethyltris(triphenylgermanyl)silane, together with an unidentified oil, were isolated from the product. Yield: H_2 , 26.0 cc. (S.T.P.), 2.321 mmoles., calcd. for equation (2), 19.85 cc., 1.772 mmoles.; H_2 in excess, 6.15 cc., 0.549 mmole.; Ph_3Ge_2 , 0.1665 g., 0.273 mmole.; $(Ph_3Ge)_3SiC_2H_5$, 1.0869 g., 1.123 mmoles.: 63% of the germanium was recovered as the silane and 31% as hexaphenyldigermene. These data indicate that roughly 31% of the lithium salt had reacted with solvent to form hydrogen and hexaphenyldigermene before the ethyl bromide was added. The remaining 69% then reacted with ethyl bromide according to the equation

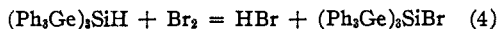


Properties.—Ethyltris-(triphenylgermanyl)-silane is soluble in all common organic solvents. It appears somewhat unstable when heated to melting. The m. p. is lowered several degrees if the bath is heated slowly. However, as ordinarily determined in the Thiele apparatus, the m. p. is reproducible at 283–284.5°. After once being melted, the m. p. was depressed as much as 90°.

Anal. Calcd. for $C_{54}H_{50}Ge_3Si$: mixed oxides, 0.04869, 0.04509; C, 69.4; H, 5.21; mol. wt., 986.3. Found: mixed oxides for 0.1263 and 0.1170, 0.04875 and 0.04516; C, 69.1, 69.1; H, 5.19, 5.21; mol. wt., cryoscopic in benzene, 822, 872.

V. Tris-(triphenylgermanyl)-silyl Bromide

The bromide may be prepared conveniently by treating the silane with bromine in ethyl bromide solution, according to the equation



Color due to free bromine disappeared in approximately one hour. The product was purified by recrystallizing from ethylene dichloride, from which the bromide separated with one-half molecule of solvent of crystallization. Ethylene dichloride was removed by dissolving the material in benzene and boiling off the solvent. The crystals so obtained contain three molecules of benzene of crystallization. The benzene was pumped off at room temperature. The pure bromide melts at 241.5–242.5°.

The bromide may also be prepared in carbon tetrachloride, but reaction in this solvent is very slow and heating is required. The products proved difficult to purify; two preparations gave melting points of 234.5–235.5° and 239.5–240.5°. Further recrystallizations from several solvents failed to raise the melting point. Accordingly the material prepared in ethyl bromide was employed exclusively in further studies.

Analyses.—Mixed oxides were determined in the usual way. Bromine was determined by treating a wet solution of the bromide in benzene with gaseous ammonia. This treatment converts the bromide quantitatively to the silol (Section VI) and ammonium bromide is precipitated. The bromine was determined gravimetrically as silver bromide. Calcd. for $C_{54}H_{48}Ge_3SiBr$: mixed oxides, 0.03625, 0.03045; Br, 7.84; mol. wt., 1019. Found: mixed oxides for 0.09881 and 0.08300; 0.03621, 0.03037; Br, 7.83, 7.83; mol. wt. (cryoscopic in benzene), 948, 941.

Chemical Properties.—The bromide reacts rapidly with lithium in ethylamine to evolve an amount of hydrogen

(9) Lauer and Dobrovolny, *Mikrochemie, Pregl. Festschrift*, 243 (1929).

(10) Simon, Wagner and Müller, *This Journal*, 55, 3705 (1933).

(11) Rothrock and Kraus, *ibid.*, 59, 1899 (1937).

approximately equivalent to the bromide. Roughly 75% of the germanium was recovered as hexaphenyldigermane; the remaining product was an unidentified oil. The bromide doubtless undergoes solvolysis and the hydrogen is liberated from the ammonium salt so formed.

Attempts were made to prepare the free silyl group by two methods, neither of which produced the desired product. The first was to reduce the bromide with sodium in boiling xylene. A 70% yield of bromine was recovered as sodium bromide and 42% of the germanium as hexaphenyldigermane. Extensive rupture of the Ge-Si bond is indicated. The remaining product was a colorless oil which was not investigated further. In the second method, the bromide was treated with an equivalent amount of the lithium salt in anhydrous ether. Two substances, in about equal amounts, were isolated from the reaction mixture. Both compounds were purified by recrystallizing from ethyl acetate and petroleum ether. One compound melted at 189–191°. The second melted at 239.5–241.5°; its molecular weight determined cryoscopically in benzene was 870. These substances were obtained in very small amounts and were not investigated further.

The bromide is not hydrolyzed by water, but ammonia in moist benzene converts it to the silol. Cold sodium hydroxide, dissolved in a mixture of alcohol and benzene, reacts in the same manner as ammonia, but at higher temperatures the Ge-Si bond is broken. A quantitative yield of hexaphenyldigermane was obtained when the bromide was boiled for several hours with a caustic solution. It ammonolyzes in liquid ammonia at -33° yielding the amine. Solutions in benzene and ethylene dichloride were virtually non-conducting.

Molecular Compound with Ethylene Dichloride.—The bromide forms a hemi-solvate with ethylene dichloride. The crystals do not lose a measurable amount of ethylene dichloride if kept in a vacuum desiccator or in an oven at 110° for long periods. In part, the high stability is due to the slow rate at which the solvent escapes from well formed crystals; if solvent is once removed *in vacuo* at 170° and then is reabsorbed by the porous residue, it can be removed more readily. In determining the composition of the solvate, a weighed amount of the compound, dried at room temperature, was heated *in vacuo* to 170° and the weight loss was determined. As a check, the ethylene chloride was caught in a trap, weighed and identified by its melting point, -34.7°. Wt. subst., g., 1.3103, 1.3103; wt. loss, 0.06118, 0.06131; wt. solvent in trap, 0.06112; ratio moles C₂H₄Cl₂/mole bromide, 0.503, 0.504.

The dissociation pressure was determined by approaching the equilibrium value from above and below. In the first method, the system containing the compound was evacuated and the pressure was allowed to build up to the equilibrium value. In the second, most of the ethylene dichloride was removed by exhausting the system, ethylene chloride vapor was introduced to exceed the equilibrium value and the pressure was recorded when it had fallen to a constant value. Pressure was read on a mercury manometer. Results obtained at three temperatures are given in Table I.

TABLE I

t, °C.	VAPOR PRESSURE OF [(Ph ₃ Ge) ₃ SiBr] ₂ ·C ₂ H ₄ Cl ₂		Aver.
	Equil. press., mm.		
	From above	From below	
77	18.9	..	18.9
85	27.2	26.4	26.8
107.5	77.5	76.5	77.0

From the slope of a plot of log *p* vs. 1/*T*, the heat of dissociation is calculated to be 11.0 kcal./mole of ethylene chloride.

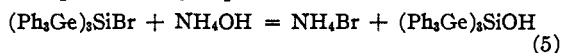
Molecular Compound with Benzene.—The bromide crystallizes from benzene solution with three molecules of benzene of crystallization. The composition of the solvate was determined much as in the case of ethylene

chloride. Because the dissociation pressure was higher, the pressure of benzene vapor in the tube containing the material was maintained at a value somewhat above the dissociation pressure of the compound. The volume of the containing tube was known, and the amount of benzene in the vapor phase could be calculated; this was subtracted from the total amount of benzene collected. Results with two experiments are: wt. subst., g., 1.2494, 1.2494; benzene, total, 0.2905, 0.2986; vol. tube cc., 19.32; press., 71.2, 71.2; temp., 27.0°, 24.4°; benzene combined, 0.2848, 0.2928; ratio moles benzene/mole bromide, 2.985, 3.065.

Vapor pressure measurements were made as described above; average values found were: 53.8 mm. at 25.0°; 48.8 mm. at 23.2°.

VI. Tris-(triphenylgermanyl)-silol

As was mentioned above, the silol may be prepared conveniently by treating the bromide with gaseous ammonia in wet benzene solution. Reaction proceeds by replacement as

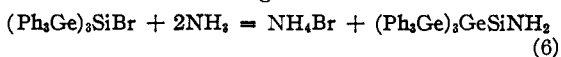


Properties.—The silol melts at 196.5–197.5°. It is very soluble in most organic solvents, alcohol excepted, and may be purified conveniently by recrystallizing from ethyl acetate-alcohol mixtures. When the silol in benzene solution was treated with glacial acetic acid or with a few drops of concentrated hydrochloric acid, a crystalline compound melting at 201–202.5° was sometimes obtained although in insufficient amount for identification.

Anal. Calcd. for C₃₄H₄₈Ge₃OH: mixed oxides, 0.02688, 0.03174; C, 67.8; H, 4.85; mol. wt., 956.2. Found: for 0.06889 and 0.08119, 0.02687 and 0.03178; C, 67.8, 68.1; H, 4.87, 4.80; mol. wt. (cryoscopic in benzene), 876, 904.

VII. Tris-(triphenylgermanyl)-silylamine

Tris-(triphenylgermanyl)-silylamine was prepared by the ammonolysis of the bromide in liquid ammonia according to the reaction



Ammonolysis occurs very slowly, probably because the bromide is virtually insoluble in liquid ammonia at -33°. In a typical experiment, 93% of the amount of ammonia demanded by equation (6) had reacted over a period of 20 hours; 92.8% of the bromide was recovered as ammonium bromide.

The amine may be recrystallized conveniently from benzene. It is obtained from solution with one molecule of benzene of crystallization; the benzene may be removed by heating *in vacuo* to 160°. The melting point of the amine is 206–206.5°.

Molecular Compound with Benzene.—Crystals of the monosolvate do not lose an appreciable amount of benzene when exposed to the atmosphere for days. Judging from the rate at which the benzene comes off at 125°, it appears that this compound has the same order of stability as that formed between the bromide and ethylene dichloride.

The composition of the solvate was determined in two ways. The air-dried material was heated *in vacuo* to 160° and the benzene was collected in a trap, weighed and identified by its melting point. Benzene was then condensed on the solvent-free amine; after two hours, the excess was pumped off and the benzene which combined with the amine was determined as above. Wt.

amine, g., 0.6180, 0.6180; benzene, 0.0545, 0.0522; ratio moles benzene/mole amine, 1.08, 1.03.

Analyses.—The molecular compound was analyzed for its nitrogen content and for mixed oxides. The nitrogen was found indirectly by treating the amine with hydrogen chloride gas in ether solution. Ammonium chloride precipitated; the chlorine was determined gravimetrically as silver chloride. *Anal.* Calcd. for $C_{34}H_{47}Ge_3Si \cdot C_6H_6$: mixed oxides, 0.00928, 0.01180; N, 1.36; mol. wt., 1033. Found: mixed oxides for 0.02565 and 0.03262, 0.00911 and 0.01176; N, 1.30, 1.32; mol. wt. (cryoscopic in benzene), 778, 825.

Tris-(triphenylgermanyl)-silyl Chloride.—The chloride is formed when the amine is treated with hydrogen chloride gas in ether solution. Well-shaped prisms are formed on crystallizing from ethyl acetate; m. p., 230–231°. The chloride resembles the bromide in its stability toward hydrolysis by water and in its reaction with ammonia in moist benzene solution to form the silol.

Analyses.—The chloride was analyzed for mixed oxides and for chlorine. The latter was determined indirectly by treating the chloride with ammonia gas in benzene and determining the chlorine in the ammonium chloride which precipitated. Calcd. for $C_{64}H_{46}Ge_3SiCl$: mixed oxides, 0.01264, 0.01427; Cl, 3.64. Found: mixed oxides for 0.03296 and 0.03720, 0.01239 and 0.01383; Cl, 3.64, 3.57.

VIII. Reaction of Sodium Triphenylgermanide with Silicon Tetrachloride

In view of the ease with which tris-(triphenylgermanyl)-silane was prepared from silicochloroform, it was hoped to prepare the tetrasubstituted silane by treating silicon tetrachloride with sodium triphenylgermanide. Glarum¹² carried out the reaction in ether and in benzene. He found that the products in either case were sodium chloride, hexaphenyldigermane and an amorphous material. But he did not determine the yield of products, nor identify the amorphous material.

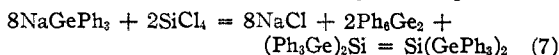
We have repeated the reaction, employing the procedure outlined above for the reaction with silicochloroform. When the reactants were mixed, sodium chloride was precipitated and the solution acquired an orange color. On standing, the color of the solution faded and a small quantity of red crystals separated. Sodium chloride was separated from the organic material by extracting alternately with water and benzene. The organic product was treated with petroleum ether; hexaphenyldigermane remained undissolved and an amorphous substance was obtained on evaporating the solvent. Reactants: meq. $NaGePh_3$, 18.50; $SiCl_4$, 18.84. Products: Ph_6Ge_2 , 8.56; 46.27% of the germanium was recovered as the digermane.

The Amorphous Material.—All efforts to obtain crystals from the amorphous residue proved futile. It was purified by the partial evaporation of an alcohol solution at room temperature. The material which separated was

obtained in the form of a coarse powder. It became tacky on warming to 80°. **Molecular weight (cryoscopic in benzene):** wt. subst., g., 0.0637, 0.0989; benzene, 11.29, 11.29; Δt , 0.033°, 0.051°. Found: mol. wt., 867, 872. These values are in excellent agreement with those obtained by Glarum, namely, 878, 872. This suggests that we may be dealing with a comparatively pure compound.

Glarum made two determinations of the per cent. of mixed oxides of Ge and Si and found the values 42.51 and 42.30.

Tetrakis-(triphenylgermanyl)-silicoethylene satisfies the above analyses; the calculated per cent. of mixed oxides is 42.37. The calculated molecular weight, however, is 1271; but, as was indicated above, molecular weight measurements with these high molecular weight compounds have been uniformly low. In the present reaction, approximately 50% of the germanium was recovered as hexaphenyldigermane. This value is in accord with reaction taking place according to the equation



It appears that the reaction of sodium triphenylgermanide with silicon tetrachloride is much less complicated than that with carbon tetrachloride.^{3,4} The amorphous product obtained in this reaction appears to be essentially a pure substance. A somewhat more extensive study should enable one to establish the course of the reaction with certainty.

IX. Summary

1. Tris-(triphenylgermanyl)-silane has been prepared by the reaction of sodium triphenylgermanide with silicochloroform in ether solution. The yield was substantially quantitative.
2. The hydrogen of the silane is replaceable by lithium in ethylamine and by bromine in ethyl bromide.
3. Tris-(triphenylgermanyl)-silyl bromide, chloride, silol and amine have been prepared and their properties investigated. These compounds form stable complexes with ethylene chloride and benzene. Dissociation pressures have been determined for several of these compounds. The bromide combines with one-half molecule of ethylene chloride and three molecules of benzene; the silol combines with one molecule of benzene.
4. Ethyltris-(triphenylgermanyl)-silane has been prepared by treating the lithium salt of the silane with ethyl bromide in liquid ammonia.
5. The lithium salt reacts with silicon tetrachloride in ether solution to form two compounds. One-half the germanium is recovered as hexaphenyldigermane, the other half appears combined with silicon. The latter compound, which is amorphous, could not be recrystallized but its analysis corresponds quite closely to that of tetrakis-(triphenylgermanyl)-silicoethylene.

(12) Unpublished observations, this Laboratory.