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The synthesis of triethylsilyllithium and triethylgermyllithium and the investigation of some of their reactions

In recent years, interest has grown in the chemistry of organometallic compounds containing Ge–Hg[1–3], Si–Hg[3–5], Ge–Tl[6], Si–Sb[7] and related linkages. They are thermally stable but very reactive compounds. We have found that bis(triethylgermyl)- and bis(triethylsilyl)-mercury react with metallic lithium under mild conditions according to the equation

$$[(C_2H_5)_3M]_2Hg + 2\,Li \rightarrow Hg + \underset{\text{(I)}}{2\,(C_2H_5)_3MLi} \tag{1}$$

(a) M = Si; (b) M = Ge

Similarly, triethylgermyllithium (Ib) can be prepared from tris(triethylgermyl)-thallium by a metal exchange reaction with lithium. These reactions in tetrahydrofuran (THF) are complete at room temperature in about 24 h. With benzene as solvent, the rate of interaction was slower then with THF.

We have used (Ib) in syntheses of unsymmetrical compounds with Si–Ge bonds. When two equivalents of (Ib) were allowed to react with dichlorodiphenylsilane, bis(triethylgermyl)diphenylsilane (II) was formed

$$2\,(C_2H_5)_3GeLi + (C_6H_5)_2SiCl_2 \rightarrow 2\,LiCl + \underset{\text{(II)}}{[(C_2H_5)_3Ge]_2Si(C_6H_5)_2} \tag{2}$$

Reaction (2) takes place at room temperature but moderate heating is necessary for its completion. The generality of this reaction was demonstrated using dimethylethylchlorosilane and trichlorosilane, both of which gave the corresponding compounds with Si–Ge bonds when reacted with (Ib). The yields in general were about 38–46%

$$(C_2H_5)_3GeLi + (C_2H_5)(CH_3)_2SiCl \rightarrow LiCl + \underset{\text{(III)}}{(C_2H_5)_3GeSi(CH_3)_2C_2H_5} \tag{3}$$

$$3(C_2H_5)_3GeLi + SiHCl_3 \rightarrow 3\,LiCl + \underset{\text{(IV)}}{[(C_2H_5)_3Ge]_3SiH} \tag{4}$$

A small amount of hexaethyldigermane was produced as a by-product of reactions (2), (3) and (4). We have also studied the metal exchange reaction between lithium and unsymmetrical ethyl(triethylsilyl)mercury. This reaction proceeds smoothly at $\sim 20^\circ$ for 3 days when benzene is used as a solvent.

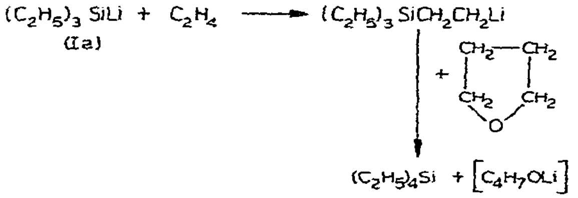
$$C_2H_5HgSi(C_2H_5)_3 + 2\,Li \rightarrow Hg + \underset{\text{(Ia)}}{(C_2H_5)_3SiLi} + C_2H_5Li \tag{5}$$

The yield of metallic mercury is 91.2%. The presence of ethyllithium and of triethylsilyllitium (Ia) was confirmed by the addition of dichlorodiphenylsilane to the reaction mixture. Diethyldiphenylsilane together with bis(triethylsilyl)diphenylsilane (80.0%) and lithium chloride (78.6%) were isolated.

When ethyl(triethylsilyl)mercury was allowed to react with lithium in THF, metallic mercury (80.7%), ethane (54.0%), ethylene (traces), butane, tetraethylsilane

(29.7%) and (Ia)(16–25%) were formed. No ethyllithium was detected. The products formed in this reaction may be accounted for by the following series of equations

$$2\,C_2H_5HgSi(C_2H_5)_3+2\,Li \xrightarrow{THF} 2Hg+C_2H_6+C_2H_4+2\,\underset{(Ia)}{(C_2H_5)_3SiLi} \qquad (6)$$



(7)

The yield of the (Ia) was determined in two ways:

(a) When the reaction mixture was treated with CO_2, triethylsilanecarboxylic acid (V) was obtained in 16.5% yield.

(b) Treatment of the reaction mixture with triethyltin bromide gave a 25.0% yield of triethyl(triethylsilyl)tin (VI).

To verify the reaction path given in eqns. (6) and (7), experiments were carried out with model compounds. When metallic lithium was added to a solution of the diethylmercury in THF, free mercury, ethane, ethylene and butane were produced in 100, 54, 40 and 6% yield, respectively. Diethylmercury reacted with lithium in ether[8] in a similar manner.

The reaction of (Ia) with ethylene in benzene at ~20° yielded, after hydrolysis, tetraethylsilane (43.0%), in agreement with eqn. (7). Similarly, the addition of (Ib) to ethylene at room temperature gave tetraethylgermane (67.8%). Moderate yields of unsymmetrical compounds of the $(C_2H_5)_3MCH_2CH_2R$ type were obtained when (Ia) or (Ib) was added to olefins

$$(C_2H_5)_3MLi+CH_2{=}CHR \rightarrow (C_2H_5)_3MCH_2CHLiR \xrightarrow{H_2O} (C_2H_5)_3MCH_2CH_2R \qquad (8)$$

$$M = Si, Ge, R = CH_3, n\text{-}C_4H_9, C_6H_5$$

The following compounds have been prepared by the method indicated: triethyl-n-propylsilane (36.0%), triethyl-n-hexylsilane (16.3%), triethyl-n-hexylgermane (VII) (8.6%), triethyl-2-phenylethylsilane (23.5%) and triethyl-2-phenylethylgermane (VIII)(42.7%).

Attempts to prepare triethylcyclohexylsilane from (Ia) and cyclohexene were unsuccessful.

Finally, it was found that (Ib) reacts with triethyl-silane, -germane and -stannane, respectively, to give compounds of the $(C_2H_5)_3GeM(C_2H_5)_3$ type.

$$(C_2H_5)_3GeLi+(C_2H_5)_3MH \rightarrow LiH+\underset{(IX)}{(C_2H_5)_3GeM(C_2H_5)_3} \qquad (9)$$

(a) M = Sn, (b) M = Ge, (c) M = Si

Thus, $(C_2H_5)_3GeLi$ reacts with triethylstannane at ~20° for 5–7 h to give triethylstannyltriethylgermane (IXa) (33.8%). The reaction with triethylgermane requires heating at 60–70° for 7 h when hexaethyldigermane (IXb) (42.2%) was obtained. Triethylsilyltriethylgermane (IXc) (48.0%) was prepared by heating the reaction mixture at 80–90° for 13 h.

An attempt to prepare trialkylsilyl-metallic compounds by the cleavage of hexaalkyldisilanes with alkali metals was unsuccessful[9]. Hexaalkyldigermanes also seem to resist this treatment.

In this report we show that the reaction of compounds containing Si–Hg–Si and Ge–Hg–Ge linkages with lithium is a convenient method for the preparation of trialkylsilyl- and trialkylgermyl-lithium. Similar metal exchange reactions between mercury and bis(triethylgermyl)cadmium[10] or tris(triethylgermyl)thallium[6] have already been described.

TABLE 1

NEW COMPOUNDS DESCRIBED IN THIS PAPER

Compound	*Formula*	*B.p. (°C/mm)*	n_D^{20}	d_4^{20}	*Found*		*Calcd.*	
					C	*H*	*C*	*H*
(II)	$[(C_2H_5)_3Ge]_2Si(C_6H_5)_2$	199–200/1.5	1.5853	1.117	58.05	8.16	57.44	8.03
(III)	$(C_2H_5)_3GeSi(CH_3)_2C_2H_5$	65/1	1.4729[a]	0.976	48.02	10.57	48.62	10.61
(IV)	$[(C_2H_5)_3Ge]_3SiH$	160–161/1	1.5425		42.57	9.19	42.52	9.12
(VI)	$(C_2H_5)_3SiSn(C_2H_5)_3$	61–63/1	1.4835		45.13	9.59	44.88	9.41
(VII)	$(C_2H_5)_3GeC_6H_{13}$	117/20	1.4580		58.43	11.56	58.83	11.52
(VIII)	$(C_2H_5)_3GeCH_2CH_2C_6H_5$	107/1.5	1.5078		63.14	9.28	63.52	9.11
(IXa)	$(C_2H_5)_3GeSn(C_2H_5)_3$	109/1.5	1.5130[b]	1.287	39.05	8.69	39.41	8.27

[a] n_D^{23}; [b] n_D^{22}

EXPERIMENTAL

Reactions were carried out under a nitrogen atmosphere in carefully evacuated, sealed ampoules. The composition of the starting mixtures and the separation and identification of the products were arranged without contact of air in the special preliminary evacuated apparatus. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ before use. Typical experiments are described below.

Triethylgermyllithium (Ib). Into a 40 ml ampoule, previously swept out with dry argon, were placed 15 ml of THF, 0.70 g (0.1009 g-atom) of lithium in the form of small pieces of thin foil and 3.78 g (0.0073 mole) of bis(triethylgermyl)mercury[1]. After outgassing, the ampoule was sealed off and the mixture shaken at ~20° for 24 h. The organic layer was decanted from the metallic mercury (1.24 g, 85.1%) and derivatives were prepared as described below.

The interaction of bis(triethylsilyl)mercury (8.60 g, 0.01995 mole) with lithium (1.00 g, 0.1441 g-atom), in 20 ml of THF under the same conditions as described for (Ib) yielded triethylsilyllithium (Ia).

Bis(triethylgermyl)diphenylsilane (II). To a solution of (Ib) prepared as described above from 0.0073 mole of bis(triethylgermyl)mercury, was added 1.83 g (0.0072 mole) of dichlorodiphenylsilane and the mixture heated for 5–7 h at 50°. The mixture gave a negative Color Test I and was filtered. After the THF had been distilled off, the residue was vacuum distilled to give 2.40 g (77.4%) of (II).

Triethylstannyltriethylgermane (IXa). To the (Ib) prepared from 2.75 g (0.0053 mole) of bis(triethylgermyl)mercury in 5 ml of THF, was added 1.90 g (0.0092 mole) of triethyltin hydride and the mixture allowed to stand at room temperature. After standing overnight the mixture was filtered. Fractional distillation of the organic layer gave 1,17 g (33.8%) of (IXa).

Triethylsilyltriethylgermane (IXc). To a solution of (Ib) prepared as described above from 1.65 g (0.0024 mole) of tris(triethylgermyl)thallium[6] and 0.30 g (0.0432 g-atom) of lithium in 4 ml of THF was added 1.20 g (0.0103 mole) of triethylsilane. The mixture was heated for 13 h at 80–90° and filtered. The filtrate was distilled. The yield of (IXc) was 1.02 g (48.1%), b.p. 87° (1 mm), n_D^{20} 1.4879 (literature[4], b.p. 92° (1.5 mm); n_D^{20} 1.4858). (Found: C, 51.81; H, 11.06. $C_{12}H_{30}GeSi$ calcd.: C, 52.40; H, 10.99%).

Reaction of triethylgermyllithium (Ib) with ethylene. A benzene solution of (Ib) was prepared as described above by the reaction of 11.4 g (0.02191 mole) of bis(triethylgermyl)mercury with 1.0 g (0.1441 g-atom) of lithium in 25 ml of benzene at ~20° for 3 days. This solution was placed into a 100-ml evacuated ampoule. The oxygen-free ethylene (300 ml) was condensed, by cooling with liquid nitrogen, into the ampoule before sealing and the ampoule was shaken for 24 h at ~20°. Upon opening the ampoule, no internal pressure was observed.

Condensation of the ethylene into the ampoule and other operations were repeated 3 times; 860 ml (96.6%) of ethylene were absorbed. The mixture was then treated with oxygen-free water and extracted three times with ether. The combined ethereal layers were washed with water, dried ($CaCl_2$) and fractionally distilled to give 5.1 g (67.8%) of tetraethylgermane, b.p. 155–160°; n_D^{20} 1.4430. (literature[11], b.p. 162.5° (760 mm); $n_D^{17.5}$ 1.443).

Reaction of ethyl(triethylsilyl)mercury with lithium in benzene. A mixture of 14.64 g (0.0424 mole) of ethyl(triethylsilyl)mercury 1.47 g (0.2118 g-atom) of lithium, cut into thin slices, and 25 ml of dry benzene was shaken at room temperature for 3 days. There was no formation of gaseous products. The organic layer was decanted from the metallic mercury (7.77 g, 91.2%). Treatment with 11.00 g (0.0434 mole) of dichlorodiphenylsilane at 50° for 5 h gave 1.43 g (16.0%) of diethyldiphenylsilane, b.p. 92–97° (1 mm), n_D^{20} 1.5619 (literature[12], b.p. 134–135° (3 mm); n_D^{20} 1.5603) and 6.40 g (80.0%) of bis(triethylsilyl)diphenylsilane, b.p. 158–161° (1 mm). (Found: C, 70.15; H, 9.54. $C_{24}H_{40}Si_3$ calcd.: C, 69.83; H, 9.77%).

Reaction of ethyl(triethylsilyl)mercury with lithium in THF. A mixture of 12.00 g (0.0348 mole) of ethyl(triethylsilyl)mercury, 1.70 g (0.2449 g-atom) of lithium, cut into thin slices, and 30 ml of THF was shaken at ~20° for 2 days. Metallic mercury (5.63 g, 80.7%) was precipitated and a gaseous mixture (360 ml, 57.3%) containing 94.3% of ethane, 1.4% of ethylene and 2.9% of butane was formed. The organic layer was decanted from the mercury and then added to 10.20 g (0.0707 mole) of triethyltin bromide. The mixture was heated for 1 h at 50° and filtered. Lithium bromide (1.89 g, 72.6%) was isolated. The filtrate was fractionally distilled. The products isolated were tetraethylsilane (1.28 g, 29.7%), b.p. 154°, n_D^{20} 1.4205 and (VI) (2.40 g, 25.0%) b.p. 61–63° (1 mm), n_D^{20} 1.4831.

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Preparation of disulphides from organomercury compounds and sulphur

Current work on aromatic mercuration and transmercuration reactions[1] has led us to study the interaction of organomercury compounds and sulphur. So far, the only investigation in this direction appears to be that of Dreher and Otto[2], who reacted diphenylmercury with sulphur to obtain poor yields of diphenyl sulphide and diphenyl disulphide.

It has now been found that aromatic as well as aliphatic mercury chlorides smoothly react with sulphur in suitable solvents at temperatures of 140–180°. Disulphides (60–75% yield) and mercurous chloride (85–95%) are formed:

$$2\,\mathrm{ArHgCl} + 2\,\mathrm{S} \rightarrow \mathrm{ArSSAr} + \mathrm{Hg_2Cl_2} \qquad (1)$$

Since equilibration of arylmercury salts generally leads to *ortho*-isomers as the main components[1], these isomers are readily available. Reaction with sulphur leads to *ortho*-substituted disulphides which are sometimes difficult to prepare by other routes.

General procedure

About 25 millimoles of the aryl- or alkylmercury chloride and 25 milliatoms of sulphur in 75 ml of purified sulpholan were heated with stirring for 24 h. Mercurous chloride was filtered off and washed with water and acetone. The filtrate was diluted with water and extracted with n-hexane. Column chromatography, using neutral aluminium oxide (Woelm) as the adsorbent and hexane/benzene as the eluent led to pure disulphides. Examples are given in Table 1.

No kinetic measurements were made. Reactivities of the mercury compounds were high for the methoxyphenyl, mesityl and dodecyl derivatives (reaction temperature 140–150°) and lowest for the 2,6-dichlorophenyl compound (reaction