TABLE I

ANALYSES OF SALTS OF THE $[(C_6H_5)_3M\text{-}B(C_6H_5)_3]^-$ ANIONS (M = Si OR Ge)

		Carbon		Hydrogen		M		Nitrogen	
M	Cation	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Si	$(CH_3)_4N$	83.45	82.98	7.36	7.30	4.88	4.60	2.43	2.41
Si	$(C_6H_5)_3PCH_3$	84.81	84.42	6.21	6.24				
Si	K	79.98	79.76	5.59	5.78				
Ge	$(CH_3)_4N$	77.46	77.16	6.83	6.75	11.71	11.63	2.26	2.13
Ge	$(C_6H_5)_3PCH_3$	80.33	80.24	5.88	5.91				

atom) of lithium wire cut into small pieces in 170 ml. of tetrahydrofuran (THF). One hundred-fifty milliliters of this solution was added to 11.3 g. (0.045 mole) of triphenylborane dissolved in 50 ml. of tetrahydrofuran, in a three-necked flask equipped with a mechanical stirrer, reflux condenser, addition funnel, and nitrogen inlet tube. A mildly exothermic reaction resulted in immediate decolorization of the silyllithium reagent as it was added. After the reaction mixture had been stirred at room temperature for 2 hr., fine, white crystals began to deposit. The mixture was allowed to stand overnight, during which time more white solid precipitated. Concentration of the solution gave additional product. The crude lithium triphenylsilyltriphenylborate thus obtained was dissolved in tetrahydrofuran; addition of hexane to this solution precipitated fine white needles (13.6 g.). This product was insoluble in hexane and carbon tetrachloride; moderately soluble in ether; and very soluble in methanol. The lithium salt itself was not obtained in analytical purity. However, three pure derivatives could be prepared by adding to a methanol solution of the crude lithium salt methanolic solutions of methyltriphenylphosphonium bromide and tetramethylammonium bromide, as well as a solution of potassium fluoride in aqueous methanol. All three salts precipitated in the form of white crystals; the phosphonium salt rapidly became yellow in color after its precipitation. None had a sharp melting point; all turned brown on heating and decomposed over a variable temperature range. Such decomposition began at *ca.* 100° with the crude lithium salt, above 200° with the methyltriphenylphosphonium salt. Analyses are given in Table I.

Lithium triphenylgermyltriphenylborate and its derivatives. A solution of triphenylgermyllithium, prepared in ethylene glycol dimethyl ether by the cleavage of hexaphenyldigermane with metallic lithium,[4] was added to 5 g. (0.0207 mole) of triphenylborane in 50 ml. of ethylene glycol dimethyl ether in the same manner as described above, until the triphenylgermyllithium reagent was no longer decolorized. A white crystalline precipitate was formed during this addition. The reaction mixture was stirred at room temperature overnight. The solid was filtered; here also the lithium salt was not isolated in a pure state. The tetramethylammonium and methyltriphenylphosphonium derivatives, however, were isolated in analytical purity by treatment of the crude lithium salt with the respective bromides in methanol solution. Analyses are given in Table I. Both salts showed behavior on heating similar to that observed with their silicon analogs, and the phosphonium salt also rapidly became yellow after its preparation.

A separate experiment in which the crude lithium salt was converted to the methanol-insoluble tetramethylammonium derivative showed that the triphenylgermyltriphenylborate anion had been formed in *ca.* 65% yield.

The reaction of phenyllithium with lithium triphenylsilyltriphenylborate. Three grams of crude lithium triphenylsilyltriphenylborate was suspended in ether, and 9.7 ml. of 0.81*M* phenyllithium solution was added with vigorous stirring. No color changes were apparent while the mixture was stirred for 2 hr. at room temperature and for 2 hr. at reflux. The solid was filtered and identified as starting material by conversion to the methyltriphenylphosphonium salt. Addition of bromobenzene to the filtrate produced no tetraphenylsilane. Similar results were obtained when the mixture was heated at reflux for 20 hr.

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Metalation of Triphenylgermane by Grignard Reagents

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Triphenylgermane was found to react with organolithium reagents in diethyl ether to give triphenylgermyllithium in good yields, together with some of the corresponding tetrasubstituted products.[1] Under comparable conditions, no reaction was observed with Grignard reagents such as allylmagnesium bromide and *n*-butylmagnesium bromide.

A somewhat similar reactivity had been noted with organosilicon hydrides, that is, organolithium reagents gave the respective substitution products,[2] but Grignard reagents were unreactive in the various solvents tried.[2b,3] Recent work, however, has shown that Grignard reagents do alkylate and/or arylate organosilicon hydrides in tetrahydrofuran.[4]

We have found that certain Grignard reagents will metalate triphenylgermane in refluxing tetrahydrofuran (THF). Reaction of triphenylgermane with allylmagnesium chloride in refluxing tetrahydrofuran gave triphenylgermylmagnesium chloride. The presence and structure of the Grignard reagent were confirmed by carbonation, which af-

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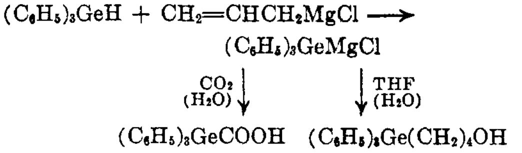
(1) H. Gilman and C. W. Gerow, *J. Am. Chem. Soc.*, **78**, 5435 (1956).

(2) (a) H. Gilman and S. P. Massie, Jr., *J. Am. Chem. Soc.*, **68**, 1128 (1946); R. N. Meals, *J. Am. Chem. Soc.*, **68**, 1880 (1946); (b) H. Gilman and H. W. Melvin, Jr., *J. Am. Chem. Soc.*, **71**, 4050 (1949).

(3) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 303 (1953).

(4) H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **79**, 4560 (1957); **81**, 5925 (1959).

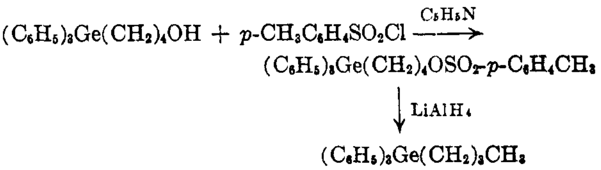
forded the known triphenylgermanecarboxylic acid,[1] and by identification of the tetrahydrofuran cleavage product, 4-hydroxybutyltriphenylgermane. When the reaction was allowed to proceed for two days at reflux before carbonation, triphenylgermanecarboxylic acid and 4-hydroxybutyltriphenylgermane were obtained in yields of 10.4% and 49.8%, respectively, together with allyltriphenylgermane in 3.9% yield. In a run similar to that above, but in which the reaction mixture was refluxed for four days prior to carbonation, none of the acid was isolated. However, the yield of 4-hydroxybutyltriphenylgermane was increased to 83.4%. When the reaction was carried out at room temperature, no products ascribable to metalation could be isolated.



$$\begin{tikzcd}[column sep=small] (C_6H_5)_3GeH + CH_2{=}CHCH_2MgCl \arrow[r] & {} \\ & (C_6H_5)_3GeMgCl \arrow[dl, "CO_2\ (H_2O)"'] \arrow[d, "THF\ (H_2O)"] \\ (C_6H_5)_3GeCOOH & (C_6H_5)_3Ge(CH_2)_4OH \end{tikzcd}$$

Allylmagnesium bromide was also found to metalate triphenylgermane, as did phenylmagnesium bromide. The yields of 4-hydroxybutyltriphenylgermane, however, were lower than from the corresponding allylmagnesium chloride run, particularly in the case of the phenyl Grignard reagent. Also, none of the acid could be isolated from either run. n-Butylmagnesium bromide, on the other hand, appeared to be completely unreactive.

In substantiation of the structure of the tetrahydrofuran cleavage product, 4-hydroxybutyltriphenylgermane, the material was converted to the known compound, n-butyltriphenylgermane. This was accomplished by treating the alcohol with p-toluenesulfonyl chloride in pyridine to form the sulfonate ester, which then was reduced to the alkyl compound by lithium aluminum hydride.



$$\begin{tikzcd} (C_6H_5)_3Ge(CH_2)_4OH + p\text{-}CH_3C_6H_4SO_2Cl \arrow[r, "C_5H_5N"] & {} \\ & (C_6H_5)_3Ge(CH_2)_4OSO_2\text{-}p\text{-}C_6H_4CH_3 \arrow[d, "LiAlH_4"] \\ & (C_6H_5)_3Ge(CH_2)_3CH_3 \end{tikzcd}$$

Jensen and Bedard[5] have recently demonstrated that triphenylmethylmagnesium bromide readily cleaves tetrahydrofuran to produce 5,5,5-triphenylpentanol-1 in excellent yield. In contrast, triphenylmethylsodium is ineffective in cleaving tetrahydrofuran, unless either triphenylaluminum or triphenylboron is present.[6] It appears that the lower complexing ability of sodium accounts for the fact that no cleavage occurred in the absence of the aluminum or boron compounds. For comparison, triphenylgermyllithium was allowed to react with tetrahydrofuran. After refluxing for five days, Color Test I[7] was still positive and subsequent work-up afforded only a 22.8% yield of 4-hydroxybutyltriphenylgermane, which is considerably lower than the 83.4% yield obtained from refluxing a tetrahydrofuran solution of allylmagnesium chloride and triphenylgermane for four days.

EXPERIMENTAL[8]

Reaction of allylmagnesium chloride and triphenylgermane. A solution of 6.10 g. (0.02 mole) of triphenylgermane in 25 ml. of tetrahydrofuran was treated with a tetrahydrofuran solution containing 0.04 mole of allylmagnesium chloride, and heated at slight reflux for 2 days. Color Test I[7] was positive, and the reaction mixture was then carbonated by pouring upon a slurry of Dry Ice and ether. After allowing the mixture to warm to room temperature, water was added and the organic layer separated. The aqueous layer was extracted with ether and the combined organic solutions were dried with anhydrous sodium sulfate. The solvent was removed by distillation and the residue chromatographed over alumina. Elution with petroleum ether (b.p. 60–70°) gave first a trace of impure triphenylgermane, which was identified by infrared spectrum; and then a colorless solid, which was subsequently recrystallized from absolute ethanol to give 0.27 g. (3.9%) of colorless crystals, m.p. 89–91°, identified as allyltriphenylgermane by mixed melting point. Elution with cyclohexane, followed by recrystallization from ethyl acetate, gave 0.03 g. of hexaphenyldigermane, m.p. 343–345°. Using benzene and then ethyl acetate as the eluants, there was obtained a colorless solid, m.p. 99–103°. This material was recrystallized from petroleum ether (b.p. 60–70°) to give 3.74 g. (49.8%) of colorless crystals, m.p. 101–103°, which was shown to be 4-hydroxybutyltriphenylgermane. The analytical sample melted at 103–104.5°. The compound as a carbon disulfide solution exhibited strong absorption bands at 2.76, 3.27, 3.43, and 9.2 μ, which are characteristic of the OH group, C—H aromatic and aliphatic groups, and the germanium-phenyl linkage, respectively.

Anal. Calcd. for $C_{22}H_{24}GeO$: C, 70.27; H, 6.34. Found: C, 69.80; H, 6.48.

The basic aqueous solution was acidified with dilute hydrochloric acid, and extracted with ether. The ethereal solution was dried and evaporated, and the resulting material recrystallized from absolute ethanol to give 0.72 g. (10.4%) of colorless solid, m.p. 183–187° dec., identified as triphenylgermanecarboxylic acid by mixed melting point and by comparison of the infrared spectra.

In a run employing the same quantities of reactants as described above, but heated at reflux for 4 days, there were obtained a 4.5% yield of allyltriphenylgermane and an 83.4% yield of 4-hydroxybutyltriphenylgermane. However, no discernible reaction occurred when triphenylgermane was allowed to react with allylmagnesium chloride at room temperature.

Reaction of other Grignard reagents with triphenylgermane. A tetrahydrofuran solution containing 6.10 g. (0.02 mole) of triphenylgermane in 25 ml. of tetrahydrofuran was allowed to react with 0.04 mole of a tetrahydrofuran solution of allylmagnesium bromide. The reaction mixture was heated at reflux for 2 days, and worked up in the usual manner to give 2.31 g. (30.7%) of 4-hydroxybutyltriphenylgermane, m.p. 101–104°.

Under the conditions described for the allyl Grignard

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(5) F. R. Jensen and R. L. Bedard, *J. Org. Chem.*, **24**, 874 (1959).

(6) G. Wittig and A. Rückert, *Ann.*, **566**, 104 (1950).

(7) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(8) Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. All melting and boiling points are uncorrected.

reagents, phenylmagnesium bromide reacted with triphenylgermane to afford a 7.3% yield of 4-hydroxybutyltriphenylgermane; but *n*-butylmagnesium bromide did not appear to react, as no products attributable to metalation could be isolated.

Structure proof of 4-hydroxybutyltriphenylgermane. p-Toluenesulfonyl chloride (2.5 g., 0.013 mole) was added in three portions over a period of 5 min. to 4.0 g. (0.0106 mole) of 4-hydroxybutyltriphenylgermane dissolved in 10 ml. of dry pyridine, maintained at *ca.* 20°. The reaction mixture was stirred for 1 hr., cooled to 10-15°, and then poured upon crushed ice containing 20 ml. of concd. hydrochloric acid. Ether was added and the organic layer was separated. After drying with anhydrous sodium sulfate, the solvent was evaporated. The resulting white solid was treated with 100 ml. of dry ether and added as a suspension to 1.25 g. (0.033 mole) of lithium aluminum hydride in 30 ml. of ether. This mixture was heated at reflux for 20 hr. and subsequently poured upon crushed ice. The reaction products were worked up in the usual manner and chromatographed over alumina to give 2.99 g. (78.3%) of *n*-butyltriphenylgermane, m.p. 84–86°, identified by mixed melting point and by comparison of the infrared spectra; and 0.52 g. (13%) of recovered 4-hydroxybutyltriphenylgermane.

Reaction of triphenylgermyllithium with refluxing tetrahydrofuran. A tetrahydrofuran solution of triphenylgermyllithium, prepared from 9.12 g. (0.015 mole) of hexaphenyldigermane and 1 g. of lithium in 100 ml. of tetrahydrofuran, was freed of excess lithium by filtration and heated at gentle reflux for 5 days. Color Test I[7] remained positive. Hydrolysis was effected by pouring upon crushed ice, and the solid subsequently filtered. This material was recrystallized from benzene to give 0.96 g. (10.5%) of hexaphenyldigermane, m.p. 344–347°.

The organic layer was worked up and the products chromatographed. Employing the usual techniques, there were obtained 1.03 g. (11.3%) of triphenylgermane, m.p. 45–47°; an additional 0.13 g. (1.4%) of hexaphenyldigermane, m.p. 342–345°; 2.58 g. (22.8%) of 4-hydroxybutyltriphenylgermane, m.p. 101–104°; and 0.97 g. (10.1%) of triphenylgermanol, m.p. 131–134°.

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Preparation and Reactions of Some *n*-Amylated Boranes[1]

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In the course of investigating certain boron-nitrogen bonded materials some *n*-amylated boranes have been prepared. Di-*n*-amylchloroborane was obtained by the reaction of trichloroborane with the commercially available tri-*n*-amylborane[2] according to the method of McCusker and coworkers[3] in 87% yield. The interaction of stoichiometric amounts of di-*n*-amylchloroborane and di-*n*-amylamine afforded the amineborane, which was thermally decomposed to release hydrogen chloride and to form tetra-*n*-amylaminoborane. On treatment of the aminoborane with trichloroborane, di-*n*-amylchloroborane was reconstituted along with lesser amount of di-*n*-amylamino dichloroborane. However, as dialkylchloroboranes tend to disproportionate, the resultant yields were not satisfactory. Di-*n*-amylaminodichloroborane has also been obtained by treating trichloroborane with di-*n*-amylamine.

Alcoholysis of di-*n*-amylchloroborane with methanol afforded di-*n*-amylmethoxyborane. Careful hydrolysis of the methoxyborane or the chloroborane in a nitrogen atmosphere did not yield pure di-*n*-amylhydroxyborane but instead gave disproportionation products contaminated with that material; hydrolysis in open air afforded mainly *n*-amyldihydroxyborane, which was isolated in a high state of purity and in good yield. The latter compound easily eliminates the elements of water to yield B-tri-*n*-amylboroxine. The boroxine reacts with trichloroborane in the usual manner[4] to reconstitute *n*-amyldichloroborane.

EXPERIMENTAL[5]

Di-n-amylchloroborane. One hundred grams (0.445 mole) of tri-*n*-amylborane and 26.1 g. (0.224 mole) of trichloroborane were mixed with vigorous stirring. The mixture was distilled rapidly and the fraction boiling from 180–220° collected. The major portion of the product distilled at 204–216°. Redistillation *in vacuo* through a column afforded 107 g. (87%) of di-*n*-amylchloroborane, b.p. 79–81°/10mm.

Anal. Calcd.: B, 5.7. Found B, 5.8.

Tetra-n-amylaminoborane. A solution of 22.1 g. (0.114 mole) of di-*n*-amylchloroborane in 100 cc. of dry benzene was added with stirring to a solution of 18.5 g (0.117 mole) of di-*n*-amylamine in 500 cc. of benzene. The resultant exothermic reaction produced a white precipitate, which dissolved on refluxing with the release of hydrogen chloride. The mixture was refluxed for several hours until the evolution of hydrogen chloride had almost ceased; the resultant solution was filtered and the solvent removed by evaporation. The residue was distilled *in vacuo* affording 24 g. (69%) of tetra-*n*-amylaminoborane, b.p. 124°/8 mm.

Anal. Calcd. for $(C_5H_{11})_2N—B(C_5H_{11})$: C, 77.6; H, 14.3; B, 3.5; N, 4.5; mol. wt. 309.4. Found: C, 75.4; H, 14.1; B, 4.1; N, 4.3; mol. wt. 317.

Di-n-amylamino-dichloroborane. A solution of 15.7 g. (0.1 mole) of di-*n*-amylamine in 100 cc. of toluene was added with stirring to a solution of 12.9 g. (0.11 mole) trichloroborane in 300 cc. of toluene. The mixture was refluxed for 10 hr. and the solvent stripped. Distillation of the residue

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(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) Anderson Chemical Company, Weston, Mich.

(3) P. A. McCusker, G. F. Hennion, and E. C. Ashby, *J. Am. Chem. Soc.*, **79**, 5192 (1957).

(4) P. A. McCusker, E. C. Ashby, and H. S. Makowski, *J. Am. Chem. Soc.*, **79**, 5182 (1957).

(5) Analyses by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.