119 g. (5.2 moles) of sodium dispersed in 5 l. of refined tetrahydrofuran. The reaction temperature was maintained at 0 to 5° during the addition and for 1 hr. thereafter. After further stirring at room temperature for 7 hr., the solution was cooled to 0° and 2.5 moles of freshly prepared iron(II) chloride[14] in 2 l. of refined tetrahydrofuran was added in portions with vigorous stirring. The temperature rose to 18° during this addition. The resulting suspension was stirred at ambient temperature for 1 hr., then at 55 to 60° for 12 hr. The solvent was then distilled at reduced pressure, and 5 l. of low boiling petroleum ether was added. The resulting solids were removed by centrifugation, and the petroleum ether and residual tetrahydrofuran were distilled to a flask temperature of 100°/10 mm. The residual concentrate was refined on a DPI molecular still to yield 1684 g. (1.34 moles, 53.5%) of an oil, vapor temperature 290–295°/0.004 mm. Fourteen separate fractions were collected n_D^{20} 1.4916 to 1.4931; the spectra of all 14 fractions were practically identical.

Composite, n_D^{20} 1.4922.

An infrared spectrum of this material indicated that it was free of Si—H and Si—O—Si bonds. There were weak bonds at 9 and 9.95 μ. These bonds also appeared in the spectrum of chlorotri-*n*-dodecylsilane.

Anal. Calcd. for $C_{82}H_{158}FeSi_2$: C, 78.41; H, 12.66; Fe, 4.48; Si, 4.45; mol. wt., 1256. Found: C, 78.32; H, 12.73; Fe, 4.49; Si, 4.15; mol. wt. (Menzies-Wright in benzene), 1234.

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[14] Prepared by the method of G. Wilkinson, *Org. Syntheses*, 36, 31 (1956), using a 40 mole per cent excess of iron powder.

[CONTRIBUTION FROM THE NONMETALLIC MATERIALS LABORATORY, DIRECTORATE OF MATERIALS & PROCESSES, AERONAUTICAL SYSTEMS DIVISION]

Synthesis of Organolithium Compounds of Some Group IV and V Elements

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Triphenylgermyllithium, triphenyltinlithium, triphenylleadlithium and diphenylphosphinolithium have been prepared by the reaction of the various chlorides with lithium in tetrahydrofuran. Hexaphenyldigermane, hexaphenylditin, hexaphenyldilead, and tetraphenylbiphosphine have also been cleaved by lithium in tetrahydrofuran to yield the corresponding $(C_6H_5)_nM^{n+1}Li$ in excellent yields.

The direct method of preparing triphenylsilyllithium from chlorotriphenylsilane and lithium metal in tetrahydrofuran was first reported by Gilman.[1a] This report prompted our investigation to determine whether this was a convenient and general reaction applicable to other elements of Group IV and V of the periodic table to yield organolithium reagents of the general formula $(C_6H_5)_nM^{n+1}Li$. Wittig and later Tomboulian have prepared triphenylmethyllithium[2] from chlorotriphenylmethane and lithium in tetrahydrofuran, while Gilman[3] has reported the preparation of triphenylgermyllithium from bromotriphenylgermane and lithium in tetrahydrofuran.

In the past organolithium compounds have also been prepared by various other means: A. Butyllithium or phenyllithium reacts with $(C_6H_5)_3CH$,[4] $(C_6H_5)_2PH$,[5] and $(C_6H_5)_3GeH$[6] to yield $(C_6H_5)_3CLi$, $(C_6H_5)_2PLi$, and $(C_6H_5)_3GeLi$, respectively.

$$(C_6H_5)_nM^{n+1}H + C_4H_9Li \longrightarrow (C_6H_5)_nM^{n+1}Li + C_4H_{10} \quad (1)$$
$$M = C, P, Ge$$

B. Lithium in tetrahydrofuran has thus far successfully cleaved hexaphenyldisilane[7] and hexaphenyldigermane[8] to yield triphenylsilyllithium and triphenylgermyllithium. Attempts to cleave hexaphenylditin[9] have been reported to produce

$$(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n + 2Li \longrightarrow 2(C_6H_5)_nM^{n+1}Li \quad (2)$$
$$M = Si, Ge, Sn$$

triphenyltinlithium in low yields.

C. Lithium in tetrahydrofuran can also cleave a phenyl group from certain perphenylated elements[10]

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$$(C_6H_5)_nM^n + 2Li \longrightarrow (C_6H_5)_{n-1}M^nLi + C_6H_5Li \quad (3)$$
$$M = Si, Ge, N, P, As, Sb$$

to yield a mixture of organolithium reagents.

D. Preparation of triphenyltinlithium and triphenylleadlithium has also been reported by Gilman and co-workers by the addition of phenyllithium to stannous chloride[11] and plumbous chloride,[12] respectively.

$$MCl_2 + 3C_6H_5Li \longrightarrow (C_6H_5)_3MLi + 2LiCl \quad (4)$$
$$M = Sn, Pb$$

Earlier Wittig[13] reported the preparation of triphenyltinlithium by the addition of phenyllithium to diphenyltin.

$$C_6H_5Li + (C_6H_5)_2Sn \longrightarrow (C_6H_5)_3SnLi \quad (5)$$

From our studies on the preparation of organolithium compounds, $(C_6H_5)_nM^{n+1}Li$ (M = C, Si, Ge, Sn, Pb, P), the direct method of synthesis, that is, the reaction of a metallic chloride with lithium in tetrahydrofuran, was applicable and found to be a general reaction. Besides the use of chlorotriphenylmethane[2] and chlorotriphenylsilane,[1] the direct method of synthesis has now been extended to include chlorotriphenylgermane, triphenyltin chloride, triphenyllead chloride, and diphenylphosphinous chloride. These chlorides readily react with lithium in tetrahydrofuran to yield the desirable organolithium compound in good yields. When subjected to color test I,[14] all the organolithium compounds produced a positive color test which indicated the presence of a M—Li bond.

In the course of preparing the various organolithium compounds *via* the direct method, it appeared that an intermediate compound is formed prior to the formation of the organolithium compound. This assumption is based on the following observations: (1) shortly after the clear tetrahydrofuran solution of the chloride is added to the lithium, a white cloudiness appears[15]; at this stage color test I is negative; however, with further reaction the white cloudiness disappears with the formation of a dark colored solution which gives a positive color test I; (2) by-product of this reaction usually found in small quantities is the coupled product $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$; and (3) the by-product $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$ can readily be cleaved by lithium in tetrahydrofuran to produce excellent yields of $(C_6H_5)^nM^{n+1}Li$. Gilman[10c] and co-workers in the direct preparation of triphenylsilyllithium noted similar observations and proposed the following series of reactions.

$$(C_6H_5)_3SiCl + 2Li \longrightarrow (C_6H_5)_3SiLi + LiCl \quad (6)$$

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiCl \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + LiCl \quad (7)$$

$$(C_6H_5)_3SiSi(C_6H_5)_3 + 2Li \longrightarrow 2(C_6H_5)_3SiLi \quad (8)$$

To verify our observations, hexaphenylditin, hexaphenyldigermane, hexaphenyldilead, and tetraphenylbiphosphine were all subjected to lithium cleavage in tetrahydrofuran and produced excellent yields of the organolithium compound according to Equation 2. No attempts were made to optimize the yields of the organolithium compounds prepared either by the direct method or the cleavage of the $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$ compounds. Each organolithium reagent was treated with benzyl chloride to produce the benzyl derivatives as shown in Table I. The same benzyl derivatives were synthesized by an alternate route so that mixed melting points and comparisons of their infrared spectra could be made.

$$C_6H_5CH_2MgCl + (C_6H_5)_nM^{n+1}Cl \longrightarrow (C_6H_5)_nM^{n+1}CH_2C_6H_5 + MgCl_2 \quad (9)$$

The various benzyl derivatives were characterized by elemental analysis, mixture melting points, and comparison of the infrared curves of each benzyl derivative made by the three synthesis routes.

Of the two methods used for the preparation of the organolithium compounds, the cleavage of $(C_6H_5)_nM^{n+1}M^{n+1}(C_6H_5)_n$ method offers some advantage in that the starting material can be obtained in a higher degree of purity and the yields are somewhat higher (see Table I). For the preparation of the various $(C_6H_5)_nM^{n+1}Li$ compounds, it is felt, however, that either one of these two methods is preferable to those reported in literature under A, C, and D since only one species of organolithium compound is present and this offers a cleaner reaction.

Further studies on the reactions of the individual $(C_6H_5)_nM^{n+1}Li$ compounds prepared above are under investigation and will be published in the near future.

EXPERIMENTAL

Starting materials. Chlorotriphenylmethane, chlorotriphenylsilane, triphenyltin chloride, triphenyllead chloride, diphenylphosphinous chloride, and hexaphenylditin were commercially available and were used without further purification. The chlorotriphenylgermane[22] was prepared by the chlorination of triphenylgermane, while hexaphenyldi-

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TABLE I

$(C_6H_5)_nM^{n+1}Li$	Benzyl Derivative	M.P.[e]	Yield, %	Reference
$(C_6H_5)_3CLi$[a]	$(C_6H_5)_3CCH_2Ph$	143.5–145	67	16
—	$(C_6H_5)_3CCH_2Ph$[c]	141.0–142.0	75	
$(C_6H_5)_3SiLi$[a]	$(C_6H_5)_3SiCH_2Ph$	98.5–99.5	39	17
—	$(C_6H_5)_3SiCH_2Ph$[c]	96.0–97.0	65	
$(C_6H_5)_3GeLi$[a]	$(C_6H_5)_3GeCH_2Ph$	85.0–86.5	60	18
$(C_6H_5)_3GeLi$[b]	$(C_6H_5)_3GeCH_2Ph$	85.0–87.0	75	
$(C_6H_5)_2SnLi$[a]	$(C_6H_5)_3SnCH_2Ph$	90.0–91.0	77	19
$(C_6H_5)_3SnLi$[b]	$(C_6H_5)_3SnCH_2Ph$	91.0–92.0	72	
—	$(C_6H_5)_3SnCH_2Ph$[c]	91.0–92.0	80	
$(C_6H_5)_3PbLi$[a]	$(C_6H_5)_3PbCH_2Ph$	95.0–96.0	76	20
$(C_6H_5)_3PbLi$[b]	$(C_6H_5)_3PbCH_2Ph$	95.0–97.0	87	
—	$(C_6H_5)_3PbCH_2Ph$[c]	94.0–95.0	67	
$(C_6H_5)_2PLi$[a]	$(C_6H_5)_2P(O)CH_2Ph$[d]	193.0–194.0	80	21
$(C_6H_5)_2PLi$[b]	$(C_6H_5)_2P(O)CH_2Ph$	193.0–194.0	83	
—	$(C_6H_5)_2P(O)CH_2Ph$[c]	192.0–193.5	64	

[a] Prepared by the direct method. [b] Prepared by cleavage of $(C_6H_5)_nMMPh_n$. [c] Prepared by the reaction of the benzyl Grignard with the $(C_6H_5)_nM^{n+1}Cl$. [d] Benzyl-substituted phosphine compounds are easily air oxidized to the phosphine oxide. Since the purification of the benzylphosphine derivative was done with no precaution to exclude atmospheric oxygen, the phosphine was readily converted to the phosphine oxide. [e] Melting points are uncorrected.

lead[13] and tetraphenylbiphosphine[23] were synthesized by published procedures.

Because in each method of synthesis, direct method, cleavage method, and benzyl-Grignard method, all the members of the series were subjected to the same experimental procedure, only one representative example will be described for each method. All the reactions were carried out in an atmosphere of dry nitrogen.

A. *Direct method. Reaction of benzyl chloride with triphenylgermyllithium.* A solution of 5.43 g. (0.016 mole) of chlorotriphenylgermane in 17 ml. of tetrahydrofuran was added during 4 min. to a stirred mixture of 0.62 g. (0 08 g.-atom) of lithium clippings in 16 ml. of tetrahydrofuran. The reaction was slightly exothermic and a white precipitate appeared. On further stirring for 3 hr., the white precipitate disappeared with the formation of a deep yellow color giving a positive color test I. After an additional 2.5 hr. of stirring, the mixture was filtered through glass wool under a dry nitrogen atmosphere. To the organolithium solution was added over a period of 2 min. a solution of 2.02 g. (0.016 mole) of benzyl chloride dissolved in 16 ml. of tetrahydrofuran. The reaction mixture was stirred for an additional 0.5 hr. at room temperature; color test I was negative. The mixture was hydrolyzed with 50 ml. of saturated ammonium chloride solution and extracted with ether. The ether layer was dried over sodium sulfate. Evaporation of the solvent left a yellow viscous liquid containing a small amount of solid. The solid was filtered off, and the filtrate was dissolved in isopropyl alcohol. On cooling 3.52 g. (60.0%) of benzyltriphenylgermane, m.p. 85.0–86.5° was obtained.

Anal. Calcd. for $C_{25}H_{22}Ge$: C, 76.00; H, 5.61; mol. wt., 395. Found: C, 75.88, 75.78; H, 5.40, 5.47; mol. wt., 405.

The small amount of solid material which was filtered off was identified as hexaphenyldigermane by a mixed melting point with an authentic sample and infrared analysis.

B. Cleavage method. Reaction of benzyl chloride with triphenyltinlithium. To a rapidly stirred mixture of 8.75 g. (0.0125 mole) of hexaphenylditin and 1.0 g. (0.14 g.-atom) of lithium clippings was added enough anhydrous tetrahydrofuran to form a thick paste. After about 7 min., the mixture started turning yellow-green. A total of 50 ml. of tetrahydrofuran was added dropwise during 15 min. The dark olive-green mixture gave a positive color test I[14] within 5 min. After being stirred for 3 hr., the greenish black mixture was filtered through glass wool under an atmosphere of dry nitrogen. To the filtered organolithium solution was added 3.8 g. (0.030 mole) of benzyl chloride dissolved in 30 ml. of anhydrous tetrahydrofuran over a period of 3 min.; color test I was negative. After 1 hr. of stirring at room temperature, the black mixture was hydrolyzed with saturated ammonium chloride solution and extracted with ether. The combined organic layer was dried over magnesium sulfate. Evaporation of solvents left a white solid which was recrystallized from ethanol to give 7.96 g. (72%) of benzyltriphenyltin, m.p. 91.0–92.0°.

Anal. Calcd. for $C_{25}H_{22}Sn$: C, 68.07; H, 5.02; Sn, 26.91; mol. wt., 441. Found: C, 68.16, 68.08; H, 5.22, 5.23; Sn, 26.76, 26.56; mol. wt., 439.

This product was also identified by a mixed melting point with an authentic sample and infrared analysis.

C. *Benzyl-Grignard method. Reaction of triphenyllead chloride with benzyl-Grignard.* A slurry of 9.57 g. (0.020 mole) of triphenyllead chloride in 60 ml. of anhydrous tetrahydrofuran was added to a stirred tetrahydrofuran solution of (30 ml. of 0.92*N*) benzylmagnesium chloride (0.027 mole) over a period of 10 min. A slight exotherm was noted. Stirring was continued for an additional 2 hr. during which the reaction mixture turned from pale green-yellow to a cloudy gray. The reaction mixture was hydrolyzed by the addition of 75 ml. of a saturated ammonium chloride solution. The mixture was extracted with three 75-ml. portions of diethyl ether. The combined ether extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure to yield 12.0 g. of a crude brown solid. This material was dissolved in a mixture of absolute ethanol–dioxane, treated with charcoal, filtered, and cooled. The yellow-white solid which precipitated was removed by filtration. This material (0.87 g.) melted between 210–225° and its infrared spectrum was identical to that of tetraphenyllead (lit. m.p. 225°).

The filtrate from above was concentrated and water was added until cloudiness appeared. On cooling in the refrigerator there was obtained 7.14 g. (67.3%) of a white crystalline solid, m.p. 94–95°.

Anal. Calcd. for $C_{25}H_{22}Pb$: C, 56.69; H, 4.19; Pb, 39.12. Found: C, 56.30, 56.61; H, 4.04, 3.80; Pb, 39.02, 39.06.

The product triphenylbenzyllead was also identified by a mixed melting point determination and comparison of the infrared spectrum with that of an authentic sample.

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