Improved Method for the Preparation of Benzyllithium

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Using an ether–tetrahydrofuran solvent mixture, benzyllithium has been prepared in concentrated solutions in good yields with little formation of bibenzyl. Such solutions were found to cleave hexaphenyldisilane completely and rapidly. Triphenylsilyllithium has been shown possibly to metalate toluene to a small extent.

The direct preparation of benzyllithium as a useful intermediate is beset with difficulties which require special techniques. The organolithium compound can not be prepared in substantial quantities by the general procedure of reaction of an organic halide with lithium metal in a suitable solvent such as ether. With dioxane as solvent, only 1.4% of phenylacetic acid was obtained from the carbonation of a reaction mixture from benzyl chloride and lithium ribbon.[1a] Due to the reactivity of benzyllithium, coupled with the ease with which benzyl halides undergo displacement of the halide ion by organometallic compounds,[1b,c,19] the preparation leads mainly to the coupling product, bibenzyl.[1a,2] Halogen–metal interconversion is also to no avail for the same reasons.[3] Benzyllithium has been prepared in the past in sizable quantities by reaction of either lithium metal or organolithium compounds with other organometallic or organometalloidal compounds such as dibenzylmercury,[4] benzylmagnesium chloride,[5] and tribenzylantimony.[6] More recently a procedure for the direct preparation of benzyllithium in good yields in tetrahydrofuran from lithium metal and alkyl benzyl ethers was reported.[7,8]

A difficulty still present in these preparations is one of solubility. A 0.1 *N* solution of benzyllithium in diethyl ether is supersaturated.[5] In the case of tetrahydrofuran, attempts to prepare benzyllithium solutions of greater than 0.3 *N* resulted in the formation of gelatinous precipitates.[8] The use of such solutions for large scale preparations requires a large volume of solvent.

In the work reported here a method for the preparation of benzyllithium in solutions of high concentrations has been developed. Because of the ease of formation of benzyllithium from alkyl benzyl ethers and lithium metal in tetrahydrofuran[7,8] and because of its high stability in diethyl ether,[5,9] it was decided to employ both of these solvents in such a way that at the beginning of the preparation the reaction solution would have a high tetrahydrofuran concentration, and at the end when the benzyllithium concentration was high the reaction solution would be diluted with diethyl ether. This was accomplished by adding to a suspension of small pieces of lithium metal in tetrahydrofuran, a solution of the alkyl benzyl ether in diethyl ether. By this method solutions of benzyllithium of concentrations as high as 1.16 *N* were obtained in yields up to 83%. No limiting concentration was determined. The solutions were dark brown in color and were homogeneous. Although all preparations were carried out and the resulting solutions kept at *ca.* −10° prior to reaction, this may not have been entirely necessary, due to the fact that benzyllithium is relatively stable in tetrahydrofuran alone, even more so than methyllithium.[8,10]

An interesting observation is noted in the fact that benzyllithium in tetrahydrofuran, concurrent with its stability toward the solvent, is a less efficient agent for metalation than methyllithium, phenyllithium, or butyllithium. However, it is an extremely reactive species in displacement reactions with organic halides[1a,2] and in the cleavage of hexaphenyldisilane.

The cleavage of hexaphenyldisilane with phenyllithium in an ether–tetrahydrofuran mixed solvent system has been reported.[11] When a mixture of two volumes of ether to one of tetrahydrofuran, with phenyllithium in tenfold excess was employed, the cleavage of hexaphenyldisilane was 90% complete after two days of refluxing. In this study it was found that when a mixture of about one volume of ether to four of tetrahydrofuran and a 9.3-fold excess of benzyllithium was used, hexaphenyldisilane was completely cleaved within an hour at temperatures between −10° and room temperature to give an essentially quantitative yield of benzyltriphenylsilane based on equation 1.

$$PhCH_2Li + Ph_3SiSiPh_3 \longrightarrow PhCH_2SiPh_3 + Ph_3SiLi \quad (1)$$

When a 2.1-fold excess of benzyllithium was employed the cleavage was complete within ninety minutes as evidenced by the disappearance of hexa-

(1) (a) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **77**, 3134 (1955); (b) E. Späth, *Monatsh.*, **34**, 1965 (1913); (c) R. C. Fuson, *J. Am. Chem. Soc.*, **48**, 2681 (1926).

(2) K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930).

(3) G. Wittig and H. Witt, *Ber.*, **74B**, 1474 (1941); see G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **24**, 26 (1960) for a different interpretation of the reaction between benzyl chloride and *n*-butyllithium.

(4) Fr. Hein, E. Petzchner, K. Wagler, and Fr. A. Segitz, *Z. anorg. allgem. Chem.*, **141**, 161 (1924).

(5) K. Ziegler and F. Dersch, *Ber.*, **64**, 448 (1931).

(6) T. V. Talalaeva and K. A. Kocheshkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 263 (1953); [*Chem. Abstr.*, **48**, 12672 (1954)].

(7) H. Gilman, H. A. McNinch, and D. Wittenberg, *J. Org. Chem.*, **23**, 2044 (1958).

(8) H. Gilman and H. A. McNinch, *ibid.*, **26**, 3723 (1961).

(9) K. Ziegler and O. Schäfer, *Ann.*, **479**, 150 (1930).

(10) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

(11) B. J. Gaj and H. Gilman, *Chem. Ind.* (London), 493 (1960).

phenyldisilane to give 66% of benzyltriphenylsilane.

Although reactive organolithium compounds such as isopropyllithium and *tert*-butyllithium, which are also unstable in diethyl ether solution, add readily to olefins such as ethylene and propylene at low temperatures to give polymeric products,[12] it was found that benzyllithium was essentially unreactive towards hexadecene-1 and tetradecene-1 under corresponding conditions.

Formation of derivatives of the benzyllithium solutions with benzophenone and chlorotriphenylsilane gave good yields of benzyldiphenylcarbinol and benzyltriphenylsilane, respectively. A significant fact in these experiments is that no identifiable amounts of bibenzyl have as yet been found in the chromatographic work-up as was the case when benzyllithium prepared in tetrahydrofuran alone was treated with benzophenone.[10]

Employing the fact that benzyllithium readily cleaves hexaphenyldisilane, a reaction was carried out which may indicate that triphenylsilyllithium can metalate toluene to a small extent. It is known that *tert*-butyl-[13] and *n*-butyllithium[14] can metalate toluene to the extent of 8 and 24%, respectively. The 1:1 adduct of lithium metal and biphenyl metalates toluene to the extent of 1%.[15] By stirring a mixture of triphenylsilyllithium[16] prepared in tetrahydrofuran, ether,

$$PhCH_3 + Ph_3SiLi \longrightarrow PhCH_2Li + Ph_3SiH$$

$$PhCH_2Li + Ph_3SiSiPh_3 \longrightarrow PhCH_2SiPh_3 + Ph_3SiLi$$

toluene, and hexaphenyldisilane at reflux for six days, a 0.74% yield of benzyltriphenylsilane was realized. However, because the amount of product is small, the possibility that the benzyllithium was formed through the metalation of toluene by species other than triphenylsilyllithium (*e.g.* lithium metal) has not been excluded. This possibility is strengthened by the observation that in the reaction of benzyllithium solutions with benzophenone, blue and purple colors were observed, which is reminiscent of ketyl formation.[17]

Experimental[18]

Benzyllithium from Benzyl Methyl Ether (Run 3, Table I).—To a stirred mixture of 10.4 g. (1.50 g.-atoms) of finely cut lithium wire in 60 ml. of tetrahydrofuran cooled to −10° was added 12.2 g. (0.10 mole) of benzyl methyl ether (Eastman White Label) dissolved in 30 ml. of diethyl ether at a rate of 30 drops per min. Ten minutes after the addition was begun, the solution became green, slowly turning to dark brown as the addition was continued. The internal temperature of the reaction mixture was maintained between −5 and −15° by manipulation of a Dry Ice–acetone bath used for cooling, while the rate of addition was kept constant. Subsequent to the addition, the mixture was stirred for another hour at −10°.

The resulting benzyllithium solution was filtered through glass wool into an addition funnel provided with an outer glass shell into which a cooling mixture of Dry Ice and acetone at −10° was placed. Aliquots were taken and the yield, determined by double titration,[19] was 0.0672 mole (67.0%) of organometallic compound in 88 ml. of solution, corresponding to a 0.76 M solution. The benzyllithium formed a derivative by adding it to 29.5 g. (0.10 mole) of chlorotriphenylsilane dissolved in 50 ml. of tetrahydrofuran cooled to Dry Ice–acetone temperature. The stirred reaction mixture was allowed to warm to room temperature and then was hydrolyzed by pouring into distilled water. The organic and ether extraction layers were combined, dried over anhydrous sodium sulfate, and the solvents removed, leaving a white solid which when recrystallized from methanol gave 16.5 g. (75.0%) of benzyltriphenylsilane, m.p. and mixed m.p. 95–96°.

Benzyllithium from Benzyl Ethyl Ether (Run 8, Table I).—To 6.94 g. (1.0 g.-atom) of finely cut lithium wire suspended in 60 ml. of tetrahydrofuran cooled to −10° was added 20.4 g. (0.15 mole) of benzyl ethyl ether dissolved in 30 ml. of diethyl ether at a rate of 20 drops per min. The reaction started 15 min. after the beginning of the addition as evidenced by coloration of the solution. On two occasions the lithium clumped into a single ball which dispersed on continued stirring. Upon completion of the addition the mixture was stirred for 1 hr. at −10°. The benzyllithium solution was filtered through glass wool into an addition funnel, cooled to −10° as previously described. The yield, determined by double titration, was 0.124 mole (83.0%) of benzyllithium in 107 ml., corresponding to a 1.16 M solution.

The benzyllithium solution (0.117 mole) was added to 22.7 g. (0.124 mole) of benzophenone dissolved in 50 ml. of diethyl ether at ice bath temperature. Throughout the addition the reaction mixture remained dark green until the final milliliter had been added, at which time the solution became purple in color. The mixture was allowed to stir for 45 min. and then was hydrolyzed by pouring onto crushed ice. The subsequent work-up gave a pale yellow oily solid after the solvents had been removed. Recrystallization of the solid from petroleum ether (b.p. 60–70°) afforded 27.2 g. (85.0%) of benzyldiphenylcarbinol, m.p. and mixed m.p. 87–88° (lit.,[20] 87–88°).

Cleavage of Hexaphenyldisilane with Benzyllithium.—Ninety-six milliliters of a tetrahydrofuran–ether solution of 0.0934 mole of benzyllithium was added to 5.18 g. (0.01 mole) of hexaphenyldisilane suspended in 50 ml. of tetrahydrofuran at −10°. The stirred mixture was allowed to warm to room temperature over a period of 60 min., at which time no hexaphenyldisilane was present. The mixture was hydrolyzed by addition of 150 ml. of distilled water. The layers were separated and the organic layer washed several times with water and dried over anhydrous sodium sulfate. Removal of the solvent left an oily solid which was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60–70°) gave in the first fractions a small amount of oil whose infrared spectrum indicated the presence of Si—H linkages; however, no pure compounds were isolated. Further elution with the same solvent afforded 3.73 g. (106%) of benzyltriphenylsilane, m.p. 95–

(12) P. Bartlett, S. Friedman, and R. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953).

(13) H. Gilman, F. W. Moore, and O. Baine, *ibid.*, **63**, 2479 (1941).

(14) B. J. Gaj, unpublished studies.

(15) J. Eisch and W. Kaska, *Chem. Ind.* (London), 470 (1961).

(16) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

(17) W. E. Bachmann, *ibid.*, **55**, 1179 (1933).

(18) All melting points are uncorrected. Reactions involving organometallic compounds were carried out under dry, oxygen-free nitrogen. Tetrahydrofuran was purified before use by refluxing over sodium followed by distillation from lithium aluminum hydride. The diethyl ether was stored over sodium wire. All other reactants were commercially available and were used as supplied with no further purification.

(19) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(20) H. Gilman, H. A. Pacevitz, and O. Baine, *ibid.*, **62**, 1514 (1940).

TABLE I

PREPARATION OF BENZYLLITHIUM FROM BENZYL ALKYL ETHERS IN TETRAHYDROFURAN–ETHER SOLVENT SYSTEM

Run[a,b]	Moles of the benzyl ether	Excess of lithium	Solvent tetrahydrofuran/ether ml./ml.	Rate of addition	% Yield of organometallic[c]	Molarity	Reaction with	Product and yield,[d] %
1	0.046	7.8	Tetrahydrofuran only	40 drops per min.	67	0.27	Ph_3SiCl	Ph_3SiCH_2Ph 66
2	.10	7.5	58/48	40	45	.39	Ph_3SiCl	Ph_3SiCH_2Ph 91
3	.10	7.5	58/30	30	67	.76	Ph_3SiCl	Ph_3SiCH_2Ph 75
4	.15	5.0	60/30	20	68	1.05	$Ph_3SiSiPh_3$	See Table II
5	.15	3.3	60/30	20	83	1.16	PhCOPh	$Ph_2C(CH_2Ph)OH$ 85

[a] In run 5 benzyl ethyl ether was used; in all others benzyl methyl ether was used. [b] All preparations of benzyllithium were carried out at $-10 \pm 5°$. [c] Yield of benzyllithium determined by the method of double titration, see ref. 19. [d] Based on benzyllithium.

96°, based on equation 1. The excess benzyltriphenylsilane possibly arose from a secondary reaction, such as the cleavage of unreacted benzyl methyl ether by triphenylsilyllithium. Elution with benzene and with ethyl acetate gave only small amounts of intractable tars.

An attempt to duplicate the above reaction resulted in a 108% yield of crude benzyltriphenylsilane, m.p. 65–90°. However, recrystallization afforded only 90% of the compound (m.p. 94–96°), of similar purity as that of the previous reaction.

Two other cleavages of hexaphenyldisilane with benzyllithium were carried out. The results are indicated in Table II.

TABLE II

CLEAVAGE OF HEXAPHENYLDISILANE WITH BENZYLLITHIUM

Run	Moles of benzyllithium	Moles of Ph_3Si-$SiPh_3$	Ratio of RLi to $Ph_3SiSiPh_3$	Reaction time (min.)	Yield,[a] % Crude	Yield,[a] % Pure
1	0.0957	0.01	9.6:1	150	85	54
2	.0934	.01	9.3:1	60		106
3	.0210[b]	.01	2.1:1	90	77	66

[a] Based on the reaction $Ph_3SiSiPh_3 + PhCH_2Li \rightarrow Ph_3Si-CH_2Ph + Ph_3SiLi$. [b] Treatment of a portion of this benzyllithium solution with benzophenone provided a 78% yield of benzyldiphenylcarbinol.

Benzyllithium with Hexadecene-1.—To 0.0466 mole of benzyllithium in 50 ml. of tetrahydrofuran–ether solution cooled to −10° was added 10.45 g. (0.0465 mole) of hexadecene-1 dissolved in 50 ml. of tetrahydrofuran. During the addition the stirred mixture was allowed to warm to room temperature. No indication of reaction was evident. The mixture was stirred at room temperature over a period of 5 hr. with Color Test II[21] remaining positive throughout. The reaction mixture was hydrolyzed by pouring onto crushed ice and, subsequent to the usual work-up, the solvents were distilled leaving an oil which was distilled at reduced pressure. The first fraction consisted of 0.47 g. of an oil, b.p. 40–55° (0.3 mm.), whose infrared spectrum indicated an associated hydroxyl group. Its phenyl urethane derivative melted at 76–77° with no depression when admixed with the phenylurethane of benzyl alcohol. The remaining material was 8.59 g. (82.0%) of recovered hexadecene-1, b.p. 79–89° (0.2 mm.). The infrared spectrum was superimposable with that of the starting material. No other products have as yet been isolated.

Benzyllithium with Tetradecene-1.—This reaction was carried out under identical conditions as the previous reaction to give an 85% recovery of tetradecene-1 and a trace of benzyl alcohol, identified as its phenylurethane derivative.

Metalation of Toluene with Triphenylsilyllithium with Subsequent Cleavage of Hexaphenyldisilane.—Five hundredths of a mole of triphenylsilyllithium, prepared by the cleavage of 13.0 g. (0.025 mole) of hexaphenyldisilane by 2.60 g. (0.375 g.-atom) of lithium in 100 ml. of tetrahydrofuran, was added to a mixture of 13.0 g. (0.141 mole) of toluene, 13.0 g. (0.025 mole) of hexaphenyldisilane, and 20 ml. of diethyl ether. The stirred mixture was heated to gentle reflux and after 2 hr., had changed from dark brown to dark red in color. The mixture was allowed to stir at reflux for 6 days. At this time the hexaphenyldisilane was allowed to settle and about 30 ml. of the supernatant liquid was withdrawn and run into a Dry Ice–ether slurry. Work-up of the carbonation reaction yielded a small amount of material having the distinct odor of phenylacetic acid; however, this material was lost due to its small quantity.

The rest of the reaction mixture was hydrolyzed with distilled water, some ether added, and the mixture filtered to give 10.22 g. (78.7%) of recovered hexaphenyldisilane, m.p. and mixed m.p. 365–369°. The combined organic layers from the hydrolysis and carbonation mixtures was dried over anhydrous sodium sulfate and the solvents removed. The resulting oily solid was taken up in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with the same solvent first gave an oil which solidified to give 1.19 g. (9.1%) of triphenylsilane, m.p. and mixed m.p. 42–44°. Further elution with petroleum ether gave small amounts of solids which, when recrystallized from the same solvent gave solids of high melting range (205–215°). These were not investigated further. Evaporation of the mother liquor left a low-melting material which, when recrystallized once from petroleum ether and once from methanol, afforded 0.13 g. (0.74%) of benzyltriphenylsilane as evidenced by comparison of infrared spectra and by a mixture melting point determination with an authentic sample. Further elution of the column with benzene and ethyl acetate gave 5.34 g. of crude 4-hydroxybutyltriphenylsilane, the normal decomposition product of triphenylsilyllithium in tetrahydrofuran.[22]

A re-run of this reaction using 44.3 g. (0.481 mole) of toluene and 50 ml. of diethyl ether under the same conditions, resulted in a 98.5% recovery of the hexaphenyldisilane.

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(21) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

(22) D. Wittenberg and H. Gilman, *ibid.*, **80**, 2677 (1958).