Anal. Calcd. for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.62; N, 12.84. Found: C, 60.15; H, 4.62; N, 12.69.

The aqueous liquor was acidified to *p*H 3 to precipitate a solid which was collected, dried and extracted with chloroform to furnish 2.5 g. or 58% of recovered 4-hydroxy-1-methyl-2-quinolone.

2-Carbamoyl-4,7,8,9-tetrahydro-4,7-methyleneindane-1,3-dione (XII). A powdered mixture of 4.51 g. (0.0275 mole) of 4,7,8,9-tetrahydro-4,7-methyleneindane-1,3-dione[4] and 3.3 g. (0.055 mole) of urea was heated under nitrogen at 132–135° for 20 min. The melt was cooled and dissolved in 60 ml. of water. The orange solid which separated upon slow cooling was collected and dried. This portion (3.2 g.) did not give a precipitate with methanolic cupric acetate and was discarded. The aqueous liquor was acidified and chilled for 30 hr. to give 1 g. of separated solid, m.p. 132–144°. The product was suspended in 50 ml. of a solution of equal parts of benzene and heptane and the insoluble material removed with Norite activated charcoal. Dilution of the liquor with 100 ml. of *n*-heptane and strong chilling furnished needles which were recrystallized from 25 ml. of 30% aqueous methanol. There was obtained 0.5 g. (9%) of buff needles, m.p. 158–161°. The product gives a precipitate with methanolic cupric acetate. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 256 mμ (ϵ 19,610); $\lambda_{\max}^{0.1N\ \mathrm{HCl\ in\ CH_3OH}}$ 251 mμ (ϵ 11,880).

Anal. Calcd. for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.94; H, 5.52; N, 6.71.

The intermediate cyclopentene-3,5-dione was readily obtained[19] as reported by DePuy[4] except that the crude material was conveniently purified by recrystallization from diisopropyl ether instead of by vacuum sublimation prior to reaction with cyclopentadiene.[21]

Ureido derivative of 2-methyl-1,3,5-cyclopentanetrione. A powdered mixture of 1.43 g. (0.01 mole) of 2-methyl-1,3,5-cyclopentanetrione[5] and 1.2 g. (0.02 mole) of urea was heated at 110–120° for 4 min. to furnish a clear red solution which solidified during the latter stages of heating. The mixture was recrystallized from water and from ethanol to furnish 1 g. (60%), m.p. 215°. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 320 and 228 mμ (ϵ 9850 and 8310); $\lambda_{\max}^{0.1N\ \mathrm{HCl}}$ 290 mμ (ϵ 14,500).

Anal. Calcd. for $C_7H_5N_2O_3$: N, 16.66. Found: N, 16.51.

Cyclohexylidene 2-carbamoylcyclohex-1-enylamine (XIII). A mixture of 9.8 g. (0.1 mole) of cyclohexanone and 12.0 g. (0.2 mole) of urea was heated at 140° for 1 hr. The mixture which completely solidified upon cooling was recrystallized several times from aqueous methanol to furnish 8.9 g. (81%), m.p. 200–202°. Lit.[7]: m.p. 224–225° (evac. capil.). The same product was obtained by heating 8.4 g. (0.05 mole) of 1-(*N*-morpholino)cyclohexene[22] and 6 g. (0.1 mole) of urea in 20 ml. of 1-methyl-2-pyrrolidone at 140° for 30 min. The yield was 4.5 g. (82%).

Anal. Calcd. for $C_{13}H_{20}N_2O$: C, 70.87; H, 9.15; N, 12.72. Found: C, 71.13; H, 9.35; N, 12.97.

The product was characterized by reduction in ethanol containing hydrochloric acid to cyclohexyl-2-carbamoylcyclohexylamine hydrochloride, m.p. 270–273°. Lit.[7]: m.p. 276°. The addition of aqueous sodium hydroxide to a solution of the hydrochloride in water furnished the free base, m.p. 127°. Lit.[7] m.p. 128°.

N-(α-Methylbenzylidene)urea (XIV). This material was obtained from the reaction of 12 g. (0.1 mole) of acetophenone and 12 g. (0.1 mole) of urea as above, m.p. 175–179°. There was no precipitate with methanolic cupric acetate. Lit.[8]: m.p. 176.°

Succinimide-urea addition compound. A mixture of 9.9 g. (0.1 mole) of succinimide and 12 g. (0.2 mole) of urea was heated at 132–138° for 30 min. during which ammonia was evolved and a clear solution was obtained. The reaction product which solidified on cooling was recrystallized from methanol, extracted with cold water and finally recrystallized from methanol to furnish 10 g. (63%), m.p. 124–128°, good depression on admixture with urea.

Anal. Calcd. for $C_4H_5NO_2{\cdot}CH_4NO$: N, 26.41. Found: N, 26.43.

Acknowledgment. The authors are indebted to Dr. Coy W. Waller and to Dr. Rolland F. Feldkamp for their suggestions during the course of this work.

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(21) A generous sample of intermediate dicyclopentadiene was furnished by Enjay Co., Inc.

(22) S. Hunig, E. Benzing, and E. Lücke, *Ber.*, **90**, 2833 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Direct Preparation of Benzyllithium and α-Methylbenzyllithium in Tetrahydrofuran

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Benzyllithium has been prepared by the lithium cleavage of ethers of the type $C_6H_5CH_2OR$, where R is methyl, ethyl, phenyl, and benzyl. Benzyltriphenylsilane has also been cleaved by lithium. Bis(α-methylbenzyl) ether was cleaved to give α-methylbenzyllithium.

Benzyllithium has been prepared by a number of indirect methods.[1] In each instance, the organometallic compound had at least a transitory existence. However, these methods were not satis-

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(1)(a) Fr. Hein, E. Petzchner, K. Wagler, and Fr. A. Segitz, *Z. anorg. allgem. Chem.*, **141**, 161 (1924); (b) K. Ziegler and F. Dersch, *Ber.*, **64**, 448 (1931); (c) T. V. Talalaeva and K. A. Kocheshkov, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, **1953**, 263 (English) [*Chem. Abstr.*, **48**, 12672 (1954)]; (d) H. Gilman, H. A. Pacevitz, and O. Baine, *J. Am. Chem. Soc.*, **62**, 1514 (1940); (e) A. H. Haubein, Doctoral Dissertation, Iowa State College, 1942; (f) G. Wittig and H. Witt, *Ber.*, **74B**, 1474 (1941); (g) H. Gilman, F. W. Moore, and R. G. Jones, *J. Am. Chem. Soc.*, **63**, 2482 (1941); (h) A. Lüttringhaus, G. Wagner-v. Sääf, E. Sucker, and G. Borth, *Ann.*, **557**, 46 (1945); (i) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944); **67**, 1420 (1945); (j) H. Gilman and H. Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951); (k) B. Gaj, private communication; (l) H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

factory enough to make benzyllithium readily available as a synthetic tool.

Benzyllithium was first prepared by Hein *et al.*,[1a] in both benzene and diethylzinc solvents by treating dibenzylmercury with ethyllithium to give solutions having a characteristic lemon yellow color. The reaction of benzyl chloride with lithium[2] as well as with phenyllithium[1f] gave bibenzyl rather than a solution of benzyllithium. Reactions of *n*-butyllithium and ethyllithium with benzyl chloride also led to the formation of bibenzyl.[1i]

Due to the stability of benzyllithium in diethyl ether it was found to be preparable from benzylmagnesium chloride and lithium.[1b] This reaction is seriously limited because it proceeds very slowly, and requires a highly dilute solution, since a 0.1*N* solution of benzyllithium is reported[1b] to be supersaturated. By using phenyllithium in place of lithium metal, the rate of the reaction was increased. Thus a 0.1*N* solution of benzyllithium was prepared from the reaction of phenyllithium with benzylmagnesium chloride in diethyl ether (50% yield based on benzyl chloride). This method of preparation also suffers from several important limitations. The solution of benzyllithium still cannot exceed a 0.1*N* concentration, and, since the reaction between phenyllithium and benzylmagnesium chloride does not go to completion, both the benzyl Grignard reagent and benzyllithium must be present in addition to phenyllithium. From the following reaction scheme it is seen that benzylphenylmagnesium and diphenylmagnesium also may be present:

$$C_6H_5CH_2MgCl + C_6H_5Li \longrightarrow C_6H_5CH_2MgC_6H_5 + LiCl$$

$$C_6H_5CH_2MgC_6H_5 + C_6H_5Li \longrightarrow C_6H_5CH_2Li + (C_6H_5)_2Mg$$

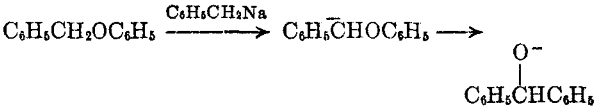
This large mixture of organometallic compounds will lead to serious difficulties when the solution is used for further reactions, and it is necessary to consider the expense and inconvenience of synthesizing benzyllithium from two specially prepared intermediates.

Toluene has been metalated by *tert*-butyllithium[11] and by *n*-butyllithium[1k] to give, after carbonation, 8% and 24% of phenylacetic acid, respectively. Benzyllithium has been prepared by cleaving dibenzylmercury with *n*-butyllithium in a mixed benzene–petroleum ether solvent, as well as with methyllithium in diethyl ether.[1g] Tribenzylantimony was treated with ethyllithium in diethyl ether to give 56% of benzyllithium.[1c]

Though some of the foregoing procedures have been successful in varying degrees for the synthesis of benzyllithium, they entail an indirect preparation, *i.e.*, they do not involve a one-step synthesis from commercially available reagents. The first direct preparation of benzyllithium was achieved using benzyl chloride and lithium in dioxane.[3] Carbonation afforded a 1.5% yield of phenylacetic acid. There have been no further reports concerning the direct preparation of benzyllithium although it has been postulated as a side product from the reaction of lithium with 2-bromobenzyl methyl ether.[4]

The cleavage of alkyl ethers by alkali metals and their alloys is generally very difficult at temperatures below 200°,[5] but the cleavage of aryl ethers is much easier to accomplish. Diphenyl ether is cleaved by sodium[6a] at 180° and by sodium-potassium alloy[6b] at room temperature. When the sodium metal is used in the form of a powder or "sand," cleavage can be obtained in some cases at room temperature.[7] Diphenyl ether was cleaved by lithium in refluxing dioxane to give, on hydrolysis, 64% of phenol.[8]

Ethers containing the benzyl or α-substituted benzyl function also are cleaved readily.[9] Benzyl phenyl ether reacts with bulk sodium slowly at 39° but rapidly at 100° to give cleavage exclusively at the benzyl-oxygen bond.[9a] This is followed by some rearrangement to benzhydrol, possibly by the action of benzylsodium metalating the ether. Benzyl ethyl ether was cleaved by sodium at 140° mainly



$$C_6H_5CH_2OC_6H_5 \xrightarrow{C_6H_5CH_2Na} C_6H_5\bar{C}HOC_6H_5 \longrightarrow C_6H_5\underset{}{\overset{O^-}{\overset{|}{C}}}HC_6H_5$$

at the benzyl-oxygen bond, but a small amount of sodium benzyl oxide was obtained.[8] A secondary reaction between benzylsodium and benzyl ethyl ether produced the sodium salt of α-ethylbenzyl alcohol in a 32% yield.

Dibenzhydryl ether and benzhydryl ethyl ether have been cleaved by potassium to give benzhydrylpotassium.[7c] Phenylisopropyl methyl ether was cleaved by potassium[9d] and by sodium-potassium alloy[9b] to give phenylisopropylpotassium. Similarly, the reaction of potassium with 1,1-diphenylethyl methyl ether and with 1,1-diphenylpropyl methyl ether produced 1,1-diphenylethyl- and 1,1-diphenylpropylpotassium, respectively.[7a] 1,2,3-Triphenylisopropylpotassium is produced from the

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

(3) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **77,** 3134 (1955).

(4) R. C. Fuson and B. Freedman, *J. Org. Chem.*, **23,** 1161 (1958).

(5) R. L. Burwell, *Chem. Revs.*, **54,** 615 (1954).

(6)(a) P. Schorigin, *Ber.*, **56B,** 176 (1923); (b) E. Müller and W. Bunge, *Ber.*, **69B,** 2164 (1936).

(7)(a) K. Ziegler and B. Schnell, *Ann.*, **437,** 227 (1924); (b) R. L. Letsinger and J. G. Traynham, *J. Am. Chem. Soc.*, **70,** 3342 (1948); (c) K. Ziegler and F. Thielmann, *Ber.*, **56B,** 1740 (1923).

(8) Y. Watanabe, *J. Pharm. Soc. Japan*, **75,** 313 (1955) [*Chem. Abstr.*, **50,** 1821 (1956)].

(9)(a) P. Schorigin, *Ber.*, **57B,** 1634 (1927); (b) K. Ziegler and H. Dislich, *Ber.*, **90,** 1107 (1957); (c) R. V. Young, Doctoral Dissertation, Iowa State College, 1936; (d) K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, *Ann.*, **473,** 1 (1928).

corresponding methyl ether and potassium[7a] or with sodium-potassium alloy.[9c]

Lithium also is effective in cleaving some ether linkages.[10] The metal reacts with benzophenone dimethylacetal to give lithium benzhydryl methyl ether which rearranges to give 1,1-diphenylethyl alcohol upon hydrolysis.[10a] However, within six days at room temperature, lithium reacts completely with benzophenone dimethyl-acetal in dioxane, whereas sodium and potassium are less effective.[10b] Benzhydryl methyl ether is metalated by lithium after several hours to give lithium benzhydryl methyl ether which then rearranges to the lithium salt of 1,1-diphenylethyl alcohol.[10b]

The cleavages of silanes have been less widely studied than ether cleavages. Some instances have been reported in which tetrasubstituted silanes were cleaved by organometallic reagents,[6b,7b] but these are not cleaved so readily as are siloxanes.[11] Sodium-potassium alloy reacts[12] with some compounds of the type R_3SiR', as well as with triphenylsilane[13a] and tetraphenylsilane.[13b] An attempt to cleave benzyltriphenylsilane using sodium dispersed in tetrahydronaphthalene was unsuccessful.[13b] However, a solution of potassium in liquid ammonia cleaves benzyl-, benzhydryl-, and trityltrimethylsilane to give on hydrolysis, toluene, diphenylmethane, and triphenylmethane, respectively.[14] Tetraphenylsilane in liquid ammonia reacts with potassium to form benzene in a 62% yield.[14]

Though a large amount of work has been done on cleavages of sulfides,[15] very little of this has been concerned with alkali metals or their organic derivatives. Dibenzyl sulfide and the benzhydryl and trityl analogs undergo a variety of cleavage reactions. The ease of the cleavages increases with increasing phenylation of the α-carbon of the benzyl group. The reactions of sulfides with alkali metals and their alloys often give rearrangement products,[16] although some cleavages have met with success.[16,9a,7c]

The direct preparation of benzyllithium and related compounds by the lithium cleavage of benzyl ethers now provides an alkyllithium type which has not been accessible hitherto on a preparative scale. In the early stages of this investigation, several factors were found to influence the yield of the organolithium reagent. The effect of some essential variations are given in Tables I and II. If the temperature is too low, the cleavage reaction is slowed significantly. If a temperature range of −5° to −15° is used, the cleavage proceeds at a satisfactory rate. Higher temperatures tend toward decreased yields of benzyllithium, probably due to increased side reactions. If the solution of the compound to be cleaved is added too rapidly, the reaction mixture contains an excess of the reactant, and side reactions are thereby increased. An excess of benzyl ether in the presence of benzyllithium gives rise to the formation of bibenzyl. The most satisfactory rate of addition was found to be about sixty drops per minute. The most important variable in these cleavage reactions, the theoretical concentration of the benzyllithium to be formed, appeared to be the most limiting factor.

Some attempts to prepare benzyllithium in concentrations higher than $0.3N$ resulted in seriously decreased yields and the formation of a gelatinous precipitate. The preparation of a solution of benzyllithium having a normality of 0.2 as a theoretical maximum appeared to be the optimum concentration for small runs (0.023 mole). However, larger runs (0.069 mole) have given good yields when the concentration of benzyllithium was $0.3N$. The largest preparation (0.10 mole) carried out in these laboratories, using a $0.3N$ solution of benzyl methyl ether, indicated a 90% yield of benzyllithium by a double titration.[17] Derivatization with chlorotriphenylsilane gave 60% of benzyltriphenylsilane.

Bis(α-methylbenzyl) ether was cleaved by lithium in tetrahydrofuran to give 68% yield of α-methylbenzyllithium. Derivatization with chlorotriphenylsilane afforded 38.4% of α-methylbenzyltriphenylsilane (Table II).

Benzyltriphenylsilane was cleaved by lithium in tetrahydrofuran to give on carbonation, 18.5% of phenylacetic acid (Table III). Dibenzyl sulfide was cleaved in tetrahydrofuran, but the only products found were intractable tars. When diethyl ether was used as the solvent, 90% of unchanged dibenzyl sulfide was recovered.

Since it was found in these laboratories[18] that triphenylsilyllithium, formed by the cleavage of hexaphenyldisiloxane with lithium in tetrahydrofuran, accelerated the cleavage of hexaphenyldisilane, this compound was investigated as a possible

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(18) M. V. George, private communication.

TABLE I

BENZYLLITHIUM BY CLEAVAGE OF BENZYL ETHERS

					Titer		
Run	Solvent	$C_6H_5CH_2OR$, R = G. (Mole), Solv. Ml.	Lithium, G. (G.-Atom), Solv. Ml.	Reaction Temp.	Time[a]	Yield $C_6H_5CH_2Li$, %	$(C_6H_5)_3SiCH_2C_6H_5$[b] (Yield, %)
1	THF	$C_6H_5CH_2$—, 19.8 (0.1), 150 ml.	2.6 (0.36), 50 ml.	−30° to −40°	30 min.	[c]	
2	THF	$C_6H_5CH_2$— 4.55 (0.023), 50 ml.	2.6 (0.36), 60 ml.	−30° to −40°	1.2 hr.	68	31.5
3	THF	$C_6H_5CH_2$—, 4.55 (0.023), 50 ml.	2.6 (0.36), 60 ml.	−5° to 5°	1.2 hr.	74	49.6
4	THF	$C_6H_5CH_2$—, 4.55 (0.023), 50 ml.	2.6 (0.36), 60 ml.	−5° to −15°	40 min.	81	61
5	THF	CH_3—, 2.8 (0.023), 52 ml.	2.6 (0.36), 60 ml.	Rm. temp., −5° to −15°	30 min.	80	54
6	THF	CH_3—, 2.8 (0.023), 74 ml.	2.6 (0.36)	Rm. temp., −5° to −15°	30 min.	87	
7	THF	CH_3—, 2.8 (0.023), 74 ml.	2.6 (0.36)	Rm. temp., −5° to −15°	30 min.	50	28.5
8	THF	CH_3—, 2.8 (0.023), 74 ml.	2.6 (0.36)	Rm. temp., −5° to −15°	30 min.	55	35.4
9	THF	CH_3—, 2.8 (0.023), 321 ml.	11.3 (1.6)	Rm. temp., −5° to −15°	30 min.	90	54
10	THF	CH_3—, 8.42 (0.069), 222 ml.	7.8 (1.08)	Rm. temp., −5° to −15°	20 min.	71	53
11[d]	THF	CH_3—, 2.8 (0.023), 110 ml.	2.6 (0.36), 5 ml.	0° to −10°	20 min.	60	41.6
12	THF	CH_3CH_2—, 3.13 (0.023), 55 ml.	2.6 (0.36), 60 ml.	−5° to −15°	20 min.	74	59.6
13	THF	C_6H_5—, 4.23 (0.023), 50 ml.	2.6 (0.36), 60 ml.	−5° to −15°	50 min.	61	37.2
14	THP	$C_6H_5CH_2$—, 6.53 (0.033), 75 ml.	3.82 (0.55), 90 ml.	−5° to −15°	1 hr.	64	
15	DEE	$C_6H_5CH_2$—, 4.55 (0.023), 55 ml.	2.6 (0.36), 60 ml.	Rm. temp.	45 min.	40	16

[a] Stirring time after complete addition of the ether solution. [b] Benzyllithium formed a derivative after adding the reaction mixture to chlorotriphenylsilane to give benzyltriphenylsilane. See Experimental. [c] Gelatinous suspension. [d] Hexaphenyldisiloxane (0.1 g.) was cleaved with lithium at room temperature, followed by the addition of the ether solution to the silylmetallic compound at 0° to 10°.

means of catalyzing cleavages of ethers, silanes, and sulfides. However, the extent of cleavage of benzyl methyl ether, benzyltriphenylsilane, and dibenzyl sulfide was not enhanced by the presence of triphenylsilyllithium even though the induction period was eliminated.

The solvent used for these cleavage reactions is important. When diethyl ether was used in the cleavage of dibenzyl ether, the yield of benzyllithium was only 40%. Tetrahydropyran is better than diethyl ether, but less satisfactory than tetrahydrofuran as a solvent for these reactions. Dibenzyl ether gave 64% of benzyllithium in tetrahydropyran, whereas bis(α-methylbenzyl) ether afforded only 33% of α-methylbenzyllithium. It also was found that these organolithium reagents are less stable in tetrahydropyran.

Some preliminary attempts to cleave diallyl, allyl ethyl, and allyl phenyl ethers were unsuccessful. Although positive Color Tests I[19] were obtained, they might have been due to finely divided lithium

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[19] H. Gilman and F. Schultz, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

TABLE II

α-METHYLBENZYLLITHIUM AND OTHER SUBSTITUTED BENZYLLITHIUM DERIVATIVES BY CLEAVAGE OF VARIOUS ETHERS

Run	Solvent	Ether, G. (Mole), Solv. Ml.	Lithium G. (G.-Atom), Solv. Ml.	Reaction Temp.	Titer		$(C_6H_5)_3SiR$ R (Yield, %)
					Time[a]	% Yield, RLi	
			α-METHYLBENZYLLITHIUM				
1	THF	Bis(α-methylbenzyl), 4.97 (0.022), 55 ml.	2.4 (0.35), 60 ml.	−5° to −15°	55 min.	68	α-Methylbenzyl (38.4)
2	THP	Bis(α-methylbenzyl), 5.2 (0.023), 50 ml.	2.6 (0.36), 60 ml.	0°,[b] rm. temp.	Overnight	23	
3	THP	Bis(α-methylbenzyl), 5.2 (0.023), 50 ml.	2.6 (0.36), 60 ml.		9.5 hr.	[c]	
			CHLOROBENZYLLITHIUM DERIVATIVES				
4	THF	4-Chlorobenzyl methyl, 3.61 (0.023), 55 ml.	2.6 (0.36), 60 ml.	−5° to −13°	3.2 hr.	51	
5	THF	4-Chlorobenzyl methyl, 3.61 (0.023), 55 ml.	2.6 (0.36), 60 ml.	−5° to −13°	3.2 hr.	42	[d]
6	THF	4-Chlorobenzyl methyl, 3.61 (0.023), 55 ml.	2.6 (0.36), 60 ml.	−5° to −13°	3.2 hr.	32	[e]
7	THF	2-Chlorobenzyl methyl, 3.61 (0.023), 55 ml.	2.6 (0.36), 60 ml.	−5° to −13°	3.2 hr.	43	[f]

[a] Stirring time after complete addition. [b] Stirred 3.5 hr. at 0°, then overnight at room temperature. [c] Insufficient to titrate. [d] An unidentifiable solid (0.6 g.) was isolated, m.p. 144–146°. [e] Reaction mixture was carbonated; no acidic products. [f] Oils were obtained which could not be purified.

TABLE III

BENZYLLITHIUM BY CLEAVAGE OF BENZYLTRIPHENYLSILANE IN TETRAHYDROFURAN FOLLOWED BY CARBONATION

Run	$(C_6H_5)_3SiCH_2C_6H_5$, G. (Mole), THF, Ml.	Lithium G. (G.-Atom) THF, Ml.	Reaction Conditions		Yield $C_6H_5CH_2CO_2H$, %	Other Products (% Yield) $R = C_6H_5$
			Temp.	Time[a]		
1	8.05 (0.023), 55 ml.	2.6 (0.36) 60 ml.	Rm. temp.,[b] 0° to −10°	1 hr.	9.6	R_3SiOH (11), R_3SiSiR_3 (4.2), R_3SiCH_2R (13.2)
2	12.08 (0.0345), 8 ml.	3.9 (0.54), 90 ml.	−5° to −13°,[c] rm. temp.	1 hr.	18.5	R_4Si (0.5), R_3SiSiR_3 (0.6)
3	8.05 (0.023), 55 ml.	2.6 (0.36), 60 ml.	−5° to −13°	5 min.	Trace	Tars

[a] Stirring time after complete addition. [b] Cleavage initiated at room temperature. [c] No cleavage at this temperature. Reaction was allowed to warm to room temperature and after 3.5 hr., the cleavage began. [d] Hexaphenyldisiloxane (0.1 g.) was cleaved with the lithium in a small amount of tetrahydrofuran prior to the addition of the benzyltriphenylsilane solution.

TABLE IV

SUBSTITUTED BENZYL METHYL ETHERS

$ROCH_3$ R =	B.P. (Mm.)	n_D^{20}	d_{20}^{20}	Yield, %	Calcd.		Found	
					C	H	C	H
2-Chlorobenzyl	46–49° (1.6–1.8)	1.5280	1.1366	71	61.34	5.79	61.08	5.72
4-Chlorobenzyl	49–54° (1.7–1.8)	1.5248	1.1256	80	61.34	5.79	61.02	6.01
							61.19	6.08
2,4-Dichlorobenzyl	72–73° (1.7)	1.5462	1.2730	81	50.28	4.22	50.03	4.39
							50.16	4.23
3,4-Dichlorobenzyl	82–85° (1.7–1.8)	1.5463	1.2710	84	50.28	4.22	50.40	4.39
							50.56	4.38

metal.[20] However, a colored reaction mixture was obtained in some instances, which indicates that the general procedure may be useful for the preparation of allylithium types.

4-Chloro- and 2-chlorobenzyl methyl ether were prepared by the Williamson synthesis[21] (Table IV). When these ethers were treated with lithium in the manner employed to prepare benzyllithium, organolithium compounds were produced, but attempts to identify them by derivatization have so

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[20] M. B. Hughes, doctoral dissertation, Iowa State College, 1958.

[21] W. Theilheimer, *Synthetic Methods of Organic Chemistry*, Interscience Publishers, Inc., New York, N. Y., Vol. VII, pp. 112–113.

far been unsuccessful. The results of these cleavages are summarized in Table II.

2,4-Dichloro- and 3,4-dichlorobenzyl methyl ether also were prepared, but they have not yet been examined for cleavage. 4-Chloro- and 3,4-dichlorobenzyltriphenylsilane were prepared from chlorotriphenylsilane and the corresponding benzyl Grignard reagents.

EXPERIMENTAL[22]

Directions follow of two selected, representative procedures for the preparation of benzyllithium.

Benzyllithium from dibenzyl ether. Run 4 (Table I). To a mixture of 2.6 g. (0.36 g.-atom) of lithium and 60 ml. of tetrahydrofuran there was added dropwise (40 to 60 drops per min.) with vigorous stirring, at −5° to −15°, 55 ml. of a solution of 4.55 g. (0.023 mole) of dibenzyl ether in tetrahydrofuran. The cleavage was in progress within 20 min. after the addition was begun, as evidenced by a red-brown solution and positive Color Tests I and IIa.[23] The cleavage was complete after 40 min. of stirring. Using the double titration method[11] the titer for benzyllithium indicated an 81% yield. The benzyllithium formed a derivative after filtering the reaction mixture under nitrogen through a glass wool plug into a stirred solution of the theoretical amount of chlorotriphenylsilane in 25 ml. of tetrahydrofuran at the temperature of a Dry Ice–acetone bath. The resulting solution was hydrolyzed and extracted with diethyl ether. After drying over anhydrous sodium sulfate, the combined organic layer was evaporated. The residue was taken up in petroleum ether (b.p. 60–70°), and this solution was poured onto a column of dry alumina. Elution with the same solvent gave white solid which was recrystallized from petroleum ether to give 61% of benzyltriphenylsilane, m.p. 98–100° (mixed melting point).

When the yield of an organolithium reagent of the benzyl type is determined by the double titration method, care must be exercised to obtain a representative sample. Since the solution contains some suspended matter (possibly a complex of benzyllithium and the solvent), the solid material settles toward the bottom of the container upon standing. The most satisfactory procedure is to take the aliquot seconds after the solution has been vigorously stirred.

Benzyllithium from benzyl methyl ether. Run 9 (Table I). A 0.3*N* solution of benzyl methyl ether in tetrahydrofuran was prepared by dissolving 12.2 g. (0.10 mole) of the ether in 321 ml. of tetrahydrofuran. A 30-ml. portion of this solution was added to 11.3 g. (1.63 g.-atoms) of lithium, and the mixture was stirred at room temperature. The cleavage began after 2 min. The remainder of the solution was added at the rate of *ca.* 60 drops per min. at −5° to −15°. After 30 min. of stirring, the yield of benzyllithium was 90%. Derivatization with chlorotriphenylsilane gave 54% of benzyltriphenylsilane, m.p. 99–101° (mixed melting point).

The yields of benzyllithium under varying conditions and in various solvents are listed in Tables I and III.

α-Methylbenzyllithium from bis (α-methylbenzyl) ether. Run 1 (Table II). To a mixture of 2.4 g. (0.35 g.-atom) of lithium and 60 ml. of tetrahydrofuran there was added dropwise (20 to 40 drops per min.) with vigorous stirring, at −5° to −15°, 55 ml. of a solution of 4.97 g. (0.022 mole) of bis (α-methylbenzyl) ether in tetrahydrofuran. After 20 ml. of the solution had been added, the reaction mixture became cherry red. Following completion of the addition, stirring was continued for 55 min. The titer for α-methylbenzyllithium represented a 68% yield. Derivatization was accomplished by filtering the reaction mixture under nitrogen through a glass wool plug into a stirred solution of the theoretical amount of chlorotriphenylsilane in 25 ml. of tetrahydrofuran at the temperature of a Dry Ice–acetone bath. The resulting solution was worked up using the procedure for the isolation of benzyltriphenylsilane. Two recrystallizations of the crude material from absolute ethanol afforded 38.4% of α-methylbenzyltriphenylsilane, m.p. 124.5–126.5°.

Anal. Calcd. for $C_{26}H_{24}Si$: C, 84.66; H, 6.64; Si, 7.71. Found: C, 85.58, 85.69; H, 6.30, 6.26; Si, 7.58, 7.65.

The results of the cleavage of bis (α-methylbenzyl) ether in tetrahydropyran are given in Table II.

Preparation of 4-chlorobenzyl methyl ether. To a warm solution of sodium methoxide prepared from 22.1 g. (0.96 g.-atom) of sodium and 450 ml. of absolute methanol there was added rapidly a solution of 30.8 g. (0.19 mole) of 4-chlorobenzyl chloride in 30 ml. of absolute methanol. After stirring for 2.5 hr. under reflux, the mixture was reduced to *ca.* 250 ml. by distillation. A white solid precipitated. The concentrated solution was refluxed for 24 hr. before being cooled and hydrolyzed by cautiously adding distilled water. The remaining organic solvent was then distilled. The aqueous residue was extracted with diethyl ether which was subsequently dried over sodium sulfate and evaporated. The product was distilled under reduced pressure to give 24.2 g. (79.5%) of 4-chlorobenzyl methyl ether, b.p. 49–54° at 1.7 to 1.8 mm., n_D^{20} 1.5248, d_{20}^{20} 1.1256.

Anal. Calcd. for C_8H_9ClO: C, 61.34; H, 5.79; MR_D, 42.39. Found: C, 61.02, 61.19; H, 6.01, 6.08; MR_D, 42.33.

The methyl ethers of 2-chlorobenzyl, 2,4-dichlorobenzyl, and 3,4-dichlorobenzyl were prepared in an analogous manner. Their physical properties and analyses are given in Table IV.

Cleavage of 4-chlorobenzyl methyl ether. Run 5 (Table II). To 2.6 g. (0.36 g.-atom) of lithium and 60 ml. of tetrahydrofuran there was added dropwise (40 to 60 drops per min.) at −5° to −13°, 55 ml. of a solution of 3.61 g. (0.023 mole) of 4-chlorobenzyl methyl ether in tetrahydrofuran. The reaction mixture had a pale golden color after the addition of 20 ml. of the reacting ether solution. The color became intensely red-brown when the addition was complete. The yield of the organolithium reagent was 51% after 3 hr. and 10 min. of stirring.

In a second experiment the titer for the organolithium reagent indicated a 42% yield. Derivatization with chlor-. triphenylsilane gave 0.85 g. of a white solid, m.p. 136–143°. Two recrystallizations from petroleum ether (b.p. 60–70°) afforded 0.60 g. of product, m.p. 144–146°. Qualitative analysis revealed the absence of chlorine. A mixture melting point determination with an authentic sample[24] of *p*-tolyltriphenylsilane (m.p. 144–146°) was depressed to 124–138°. This product was not identified.

Anal. Found: C, 82.06, 82.11; H, 6.34, 6.26; Si, 7.39, 7.35.

The analyses indicate an empirical formula of $C_{26}H_{24}Si$, thus making the compound an isomer of a silane containing two phenyl and two benzyl or tolyl groups. However, none of the known isomeric compounds in this category agrees in melting point with this unknown compound.

The organolithium reagent prepared in 23% yield in a third experiment was carbonated, but no identified acidic material was obtained.

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[22] All solvents used in these experiments were anhydrous. Diethyl ether (DEE) was dried over sodium wire, and tetrahydropyran (THP) was distilled from lithium aluminum hydride immediately before use. The tetrahydrofuran (THF) was dried and purified by refluxing over sodium wire for at least 24 hr. and finally distilling from lithium aluminum hydride shortly before it was used. The lithium used in these experiments was in the form of finely cut wire. All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. All melting points are uncorrected.

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

[24] H. N. Benedict, master's dissertation, Iowa State College, 1950.

Preparation of 3,4-dichlorobenzyltriphenylsilane. To 1.0 g. (0.042 g.-atom) of magnesium and 10 ml. of diethyl ether there was added dropwise with vigorous stirring a solution of 7.49 g. (0.038 mole) of 3,4-dichlorobenzyl chloride in 28 ml. of diethyl ether at a rate sufficient to maintain gentle refluxing. After 1 hr. of stirring, following completion of addition, acid titration[25] indicated a 90% yield of the Grignard reagent. The mixture was filtered under nitrogen into a stirred suspension of 10.90 g. (0.034 mole) of chlorotriphenylsilane in 25 ml. of diethyl ether. The resulting solution was stirred under reflux for 19 hr. before it was cooled and hydrolyzed. The aqueous layer was extracted with diethyl ether, and the combined organic solution was dried and evaporated. The residue was dissolved in boiling cyclohexane. Crystallization gave 3.95 g. (24.7%) of triphenylsilanol, m.p. 153–156° (mixed melting point). The filtrate was poured onto a column of dry alumina and eluted with cyclohexane to liberate a white solid, m.p. 107–110°. Recrystallization from cyclohexane gave 2.52 g. (15.7%) of 3,4-dichlorobenzyltriphenylsilane, m.p. 107–109°.

Anal. Calcd. for $C_{25}H_{20}Cl_2Si$: C, 71.58; H, 4.81; Si, 6.69. Found: C, 71.69, 71.53; H, 4.79, 4.68; Si, 6.78, 6.65.

Preparation of 4-chlorobenzyltriphenylsilane. To 1.0 g. (0.042 g.-atom) of magnesium and 10 ml. of diethyl ether there was added dropwise a solution of 6.70 g. (0.042 mole) of 4-chlorobenzyl chloride in 32 ml. of diethyl ether. The mixture was stirred for 3. 5 hr. and then filtered into a solution of 12.2 g. (0.042 mole) of chlorotriphenylsilane in 40 ml. of tetrahydrofuran to give a semisolid mass. The addition of 50 ml. of tetrahydrofuran gave a suspension. After 1 hr. of stirring at room temperature, the suspension was hydrolyzed. The water layer was extracted with diethyl ether, and the combined organic solution was dried before being evaporated. The residue was dissolved in petroleum ether (b.p. 60–70°), and the solution was poured onto a column of dry alumina. Elution with the same solvent afforded 9.95 g. (62.5%) of 4-chlorobenzyltriphenylsilane, m.p. 116–118°. Recrystallization from petroleum ether (b.p. 60–70°) raised the melting point to 117–119°.

Anal. Calcd. for $C_{25}H_{21}ClSi$: C, 77.99; H, 5.49; Si, 7.29. Found: C, 78.24, 78.18; H, 5.36, 5.52; Si, 7.20, 6.98.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Synthesis of $\Delta^{8,9}$- and $\Delta^{9,10}$-Octal-1-one[1]

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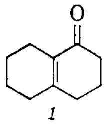
Dehydrochlorination of the chloro ketone *6*, the predominant product obtained by chlorination of 1-decalone, afforded primarily $\Delta^{9,10}$-octal-1-one (*1*). Reaction of 1-decalone with mercuric acetate afforded a mixture of compounds *1*, *2*, *8*, *9*, *10*, and *11*, the predominant products resulting from attack at position 2. The enol acetates *14* and *15* were prepared. Reaction of *14* with peracetic acid followed by pyrolysis of the resulting acetoxy ketone *8* afforded a mixture of the octalones *1* and *2* in which the $\Delta^{8,9}$-isomer *2* predominated.

The chemical literature describes[2–12] a variety of reactions leading to a 1-octalone usually assigned the structure *1*. Although the chemical properties of this substance were in accord with structure *1*, the observation[5] that this substance exhibited an ultraviolet absorption maximum at 243 mμ led Campbell and Harris to assign structure *2* to this ketone. The question was resolved by the subsequent synthesis[12] of both ketones *1* and *2*. The $\Delta^{9,10}$-isomer *1*, obtained by the dehydrohalogenation of one of the 9-chloro-1-decalones *3*[12] (*cf.* ref. 10), was found to be identical with the octalone previously described.[2–11] The $\Delta^{8,9}$-isomer



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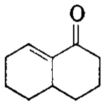

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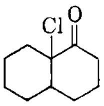

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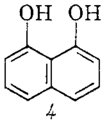

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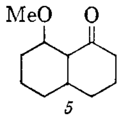

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[1] This research has been supported by National Science Foundation Grant, No. G5107.

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