894 cm.$^{-1}$ (m) (Beckman IR-7); the C=O stretching frequency had been shifted from 5.84 to 5.92 μ. Otherwise the infrared spectra of the protium and deuterium aldehydes were identical. The absence of any absorption around 2.8 μ indicated that less than 2% of the corresponding alcohol could be present. The absence of any absorption around 7.9 μ indicated that less than 1% of the corresponding Tischenko ester could be present. A 17% yield of *p*-nitrobenzyl alcohol-α-d_2, m.p. 91–92°, was obtained from the last chromatography fractions (elution with 10:1 benzene–ether).

Reaction of Sodium Hydride with *p*-Nitrobenzaldehyde-α-*d*.—Two experiments were performed using the same procedure as given above for the protium aldehyde. The reaction time in each case was 30 min. The *p*-nitrobenzyl alcohol, m.p. 91–92°, isolated by column chromatography (10% yield in both cases) possessed an infrared spectrum identical with that of the completely deuterated alcohol described above. The absence of any methylene proton signal around τ 5.17 indicated that the alcohol in each case was better than 95% deuterated. The n.m.r. spectrum of the recovered *p*-nitrobenzaldehyde showed the amount of deuteration was still better than 97%.

Preparation of *p*-Nitrobenzyl *p*-Nitrobenzoate.—This compound was prepared from *p*-nitrobenzoyl chloride and *p*-nitrobenzyl alcohol in pyridine, m.p. 168–170° (lit.[22] m.p. 169–170°).

Reaction of Sodium Hydride with *p*-Nitrobenzyl *p*-Nitrobenzoate. A. Protic Work-Up.—The procedure given above for *p*-nitrobenzaldehyde was used with a reaction time of 50 min. The isolated yields of *p*-nitrobenzoic acid and *p*-nitrobenzyl alcohol were 96 and 90%, respectively.

B. Aprotic Work-Up.—After a 15-min. reaction time the reaction mixture was filtered several times through glass wool plugs until clear. The filtrate was evaporated and the residue was washed several times with petroleum ether to remove mineral oil leaving 169 mg. (69% recovery) of ester, m.p. 168–170°. In a similar experiment with *p*-nitrobenzaldehyde, comparison of the infrared spectrum of the evaporated filtrate with synthetic spectra showed the presence of a 25% yield of *p*-nitrobenzaldehyde and an 8% yield of *p*-nitrobenzyl *p*-nitrobenzoate.

Reaction of Other Nucleophiles with *p*-Nitrobenzaldehyde.—Sodium peroxide was taken directly from a previously unopened container. Reagent grade sodium hydroxide pellets were finely ground and dried at 130° for 1 hr. The same procedure as described for *p*-nitrobenzaldehyde was used. The yields of *p*-nitrobenzoic acid obtained after a 1-hr. reaction time were 37% for sodium peroxide and 64% for sodium hydroxide.

Reactions in an Evacuated System.—Sodium hydride and *p*-nitrobenzaldehyde (or *p*-nitrobenzyl alcohol) were placed in the receiver of a small distillation apparatus. Tetrahydrofuran and sodium hydride were placed in the distilling flask which was immersed in a Dry Ice–acetone bath. The system was evacuated at 0.1 mm. for 1 hr. At the end of this time the Dry Ice–acetone bath was switched to the receiver resulting in a rapid condensation of tetrahydrofuran there. After approximately 20 min. the stopcock to the vacuum pump was closed and the cooling bath was replaced with a magnetic stirrer. Within 5 min. (for both *p*-nitrobenzaldehyde and *p*-nitrobenzyl alcohol) a blue color appeared which gradually intensified. After another 20 min., the reaction was quenched by either admitting air and pouring onto ice or by injecting water with a hypodermic syringe through a rubber septum. The admission of air resulted in a gradual change of color to either a green or a dirty brown; both instantly changed to a pale yellow on ice. The injection of water resulted in a vigorous reaction and an instantaneous color change to yellow. The product yields were quite variable: the yield of *p*-nitrobenzoic acid ranged from 3 to 31%.

Experiments in which heavy water was injected into the blue solution led to no deuterium incorporation in either *p*-nitrobenzaldehyde or *p*-nitrobenzyl alcohol. The infrared spectra of the reaction mixtures showed no bands in the 4.7–5.0-μ region at concentrations which would have allowed 2% of either deuterated aldehyde or alcohol to be detected. An experiment in which *p*-nitrobenzaldehyde-α-*d* which had been combined with sodium hydride in an evacuated system and injected with ordinary water showed no loss of deuterium in the recovered aldehyde by either infrared (examination of the 2121-, 2067-, and 894-cm.$^{-1}$ bands with a Beckman IR-7; precision ±3%) or n.m.r. (examination of the τ -0.13 region; sensitivity 3%) spectroscopy.

Experiments with *p*-nitrobenzophenone resulted in only a slight yellow color after several hours. Substitution of sodium for sodium hydride resulted in a dark blue-green color within 10 min.

Acknowledgment. — Grateful acknowledgment is made to the donors of the Petroleum Research Fund for support of this work; to Joseph J. Creely, Armand Pepperman, and Ray O'Neil for technical assistance with the preliminary experiments; and to Professor H. M. Walborsky and J. L. Webb for the n.m.r. data.

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[22] M. Davis, *J. Chem. Soc.*, 3981 (1956).

The Competition of Trimethylhalosilanes and Styrene for Organolithium Reagents[1]

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The addition of an organolithium reagent, RLi, to a mixture of trimethylhalosilane and styrene in tetrahydrofuran gives the organotrimethylsilane, RSiMe$_3$ (I), and a silane, Me$_3$SiCHPhCH$_2$R (II), in which one styrene unit has been inserted between the silicon and organo group. The ratios of I–II with trimethylchlorosilane and alkyllithium reagents (3, 3, 0, and 0 with R $\equiv$ *n*-butyl, isobutyl, *sec*-butyl, and *t*-butyl, respectively) and the complete absence of structures containing more than one styrene unit show that (a) primary alkyllithium reagents react at comparable rates with the chlorosilane and styrene; (b) secondary and tertiary alkyllithium reagents react exclusively with styrene; and (c) all intermediate benzylic organolithium reagents, formed *via* the addition of the alkyllithium to styrene, react exclusively with the chlorosilanes. These data and previous estimates of the relative rates of initiation and propagation in the *n*-butyllithium-catalyzed polymerization of styrene show that the intermediate benzylic organolithium reagents are at least 250 times as reactive as *n*-butyllithium toward trimethylchlorosilane in tetrahydrofuran. Phenyl- and vinyllithium gave only I. The preparation of 2,2-dimethyl-4-phenylpentane by substitution of dimethyl sulfate for chlorosilane in this competitive scheme (R $\equiv$ *t*-butyl) provides an alternative method of trapping the intermediate benzylic organolithium reagent. The lithium reagent from the addition of *t*-butyllithium to α-methylstyrene reacts with trimethylchlorosilane to yield *p*-silyl rather than α-silyl derivatives.

Among the facile reactions of organolithium reagents are the coupling with chlorosilanes[2] (see eq. 1) and

$$\mathrm{RLi + R'_3SiCl \longrightarrow R'_3SiR + LiCl} \qquad (1)$$

the addition across the double bond of aryl olefins. This latter reaction is one example of the widely useful anionic polymerization of monoaryl olefins.[3]

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[1] Presented before the Organic Section at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1964.

[2] C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, Chapter 2.

[3] M. Szwarc, *Macromol. Chem.*, **35**, 132 (1960).

TABLE I

THE REACTION OF STYRENE, TRIMETHYLCHLOROSILANE, AND ORGANOLITHIUM REAGENTS IN TETRAHYDROFURAN[a]

Organolithium reagent[b]	Molar ratio of products I	II	III[c]	Yield of II, %[d]
n-Butyllithium	75	25	0	23
Isobutyllithium	75	25	0	18
sec-Butyllithium	0	100	0	50
t-Butyllithium	0	100	0	85
Vinyllithium[e]	100	0	0	
Phenyllithium[f]	100	0	0	

[a] Procedure given in Experimental section. [b] Organolithium reagents in hydrocarbon solvents. [c] Less than 2.5% of the initial amount of styrene. [d] Yield is based on organolithium reagent. [e] Vinyllithium in THF. [f] Phenyllithium in diethyl ether.

TABLE II

NEW COMPOUNDS

Compd.	Formula	B.p., °C. (mm.)	$n^{25}D$	% C Calcd.	% C Found	% H Calcd.	% H Found	% Si Calcd.	% Si Found
Isobutyltrimethylsilane (Ib)	$C_7H_{18}Si$	106–107 (atm.)	1.3987	66.1	64.5	14.4	13.9	21.0	21.6
Sec-butyltrimethylsilane (Ic)	$C_7H_{18}Si$	114 (atm.)	1.4064	65.4	64.5	13.7	13.9	19.2	21.6
1-Phenylhexyltrimethylsilane[a] (IIa)	$C_{15}H_{26}Si$	120–124 (7)	1.4888	77.3	76.8	11.5	11.2	11.7	12.0
1-Phenyl-4-methylpentyltrimethylsilane (IIb)	$C_{15}H_{26}Si$	125 (13)	1.4873	76.8	76.8	11.6	11.2	12.1	12.0
1-Phenyl-3-methylpentyltrimethylsilane (IIc)	$C_{15}H_{26}Si$	138–143 (18–19)	1.4889	76.1	76.8	10.8	11.2	12.0	12.0
1-Phenyl-3,3-dimethylbutyltrimethylsilane (IId)	$C_{15}H_{26}Si$	239 (737)	1.4887	76.7	76.8	11.1	11.2	12.0	12.0
1-Phenyl-3,3-dimethylbutane	$C_{12}H_{18}$	125–127 (74)	1.4805	90.1	88.3	11.5	11.7	...	...
2-Phenyl-4,4-dimethylpentane (IV)	$C_{13}H_{20}$	124 (38)	1.4824	88.8	88.6	11.0	11.4	...	...
[4-(1,3,3-Trimethylbutyl)phenyl]trimethylsilane (V)	$C_{16}H_{28}Si$	116 (3)	1.4862	76.8	77.3	13.3	13.4	11.3	11.3

[a] H¹ n.m.r. and infrared spectra identical with sample from Dr. M. C. Musolf [M. C. Musolf and J. Speier, *J. Org. Chem.*, **29**, 2519 (1964)].

$$\text{initiation: } RLi + CH_2{=}CHPh \longrightarrow \underset{A}{RCH_2CHPhLi}$$

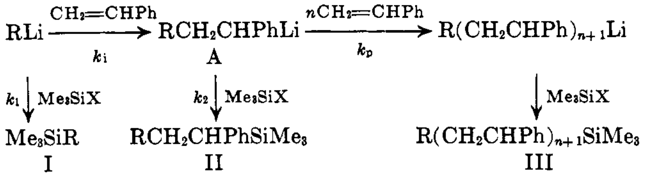
$$\text{propagation: } A + nCH_2{=}CHPh \longrightarrow R(CH_2CHPh)_{n+1}Li$$

Our use of trimethylchlorosilane to trap the intermediates from styrene and lithium[4] suggested that benzylic lithium reagents, such as A, react more rapidly with chlorosilanes than with styrene. To determine whether this specificity for chlorosilane was general, the study of the competition of styrene and halosilanes for a variety of organolithium reagents was undertaken.

Discussion

The combination of reactions 1 and 2 by adding an organolithium reagent to an excess of styrene and halosilane leads to the competitive scheme shown in Chart I, where each step involves the competition of styrene and halosilane for an organolithium reagent. The possible products from this scheme are the organotrimethylsilane (I), a silane (II) in which one styrene unit has been inserted between the organo group from the organolithium reagent and the trimethylsilyl group, and silanes (III) containing more than one styrene unit. The ratios of these three products are determined by the relative reactivities of the initial and intermediate organolithium reagents toward the chlorosilane and styrene.

CHART I



Ia and IIa, R ≡ *n*-butyl
b, R ≡ isobutyl
c, R ≡ *sec*-butyl
d, R ≡ *t*-butyl

Table I gives the ratios of I, II, and III from the slow addition of various organolithium reagents to trimethylchlorosilane and styrene in tetrahydrofuran (THF). These ratios were determined by a combination of v.p.c. and distillation analyses. All new compounds, Table II, were characterized by elemental, infrared, and H¹ n.m.r. analyses. The position of the trimethylsilyl group in II was further confirmed by the facile desilylation on treatment with alcoholic alkali.[5]

The varying amounts of I and II and complete absence of III show the large effect of structural variations in the organolithium reagent on its relative reactivity toward a chlorosilane and styrene. Although *n*-butyllithium and isobutyllithium react rather indiscriminately with trimethylchlorosilane and styrene, the intermediate benzylic organolithium reagent (A) reacts exclusively with the chlorosilane. This effect is shown more dramatically with *sec*-butyllithium and *t*-butyllithium which react exclusively with styrene in the first step to give an intermediate reagent which reacts exclusively with the chlorosilane in the subsequent step. An 85% yield of IId was obtained from this reaction. Vinyllithium and phenyllithium gave only I.

The approximate relative reactivities of styrene and trimethylchlorosilane toward the various organolithium reagents are summarized in Table III. The preference of *sec*- and *t*-butyllithium for styrene over chlorosilane probably reflects the greater sensitivity of the latter reaction to steric factors.[2] The preference of vinyl- and phenyllithium for the chlorosilane is consistent with the lower reactivity of these reagents toward styrene.[6]

The preference of the intermediate benzylic organolithium reagent for the chlorosilane is a synthetically useful and mechanistically interesting phenomenon. The data of Cubbon and Morgerison[7] and Waack and

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[4] D. R. Weyenberg, L. H. Toporcer, and M. J. Napoli, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 31-Q.

[5] The α-arylalkyl group is cleaved from silicon by alcoholic alkali, whereas other alkyl and aryl groups are unaffected by this reagent. Aryl groups, but not alkyl groups, are cleaved from silicon by acidic reagents: ref. 2, Chapter 4.

[6] R. Waack and M. A. Doran, *Polymer*, **2**, 365 (1961).

[7] R. C. P. Cubbon and D. Morgerison, *Proc. Chem. Soc.*, 146 (1960).

TABLE III

RELATIVE REACTIVITIES OF STYRENE AND TRIMETHYLCHLOROSILANE TOWARD ORGANOLITHIUM REAGENTS IN TETRAHYDROFURAN

Organolithium reagent	$k_{\mathrm{Me_3SiCl}}/k_{\mathrm{PhCH{=}CH_2}}$[a]
$RCH_2CH(Ph)Li$	>20[b]
n-Butyllithium	3.9[c]
Isobutyllithium	3.9[c]
sec-Butyllithium	<0.05[b]
t-Butyllithium	<0.05[b]
Vinyllithium	>20[b]
Phenyllithium	>20[b]

[a] k_1/k_i and k_2/k_p in Chart I. [b] Represents estimated detection limits when compounds were not observed. [c] Calculated from the integrated equation expressing the formation of I and II assuming the reactions to be first order in silane and styrene, and each pair of competitive reactions to be of the same order in organolithium reagent

$$\log\left(1 - \frac{\mathrm{II}}{C_0}\right) = \frac{1}{K}\log\left(1 - \frac{\mathrm{I}(1-K) - K\mathrm{II}}{B_0(1-K) - C_0}\right)$$

where $K = k_1/k_i$, B_0 = initial concentration of trimethylchlorosilane, and C_0 = initial concentration of styrene. The organolithium-catalyzed polymerization of styrene in THF has been shown to be first order in styrene [C. Geacintov, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 1253 (1961)], and the reaction of organometallic reagents (methylmagnesium halides) with trimethylhalosilanes has been shown to be first order in the silane [A. F. Reid and C. J. Wilkins, *J. Chem. Soc.*, 4029 (1955)].

Doran[6] show that the rate of propagation (k_p) is much greater than the rate of initiation (k_i) in the polymerization of styrene with *n*-butyllithium in ether and THF. A minimum value of k_p/k_i of 50 is estimated from the latter work. Thus, the preference of the benzylic reagent for the chlorosilane represents a *greatly enhanced rate of reaction* of these reagents with the chlorosilane. Substitution of the appropriate values from Table III in the simple identity relating k_1 and k_2

$$k_2/k_1 = (k_2/k_p)(k_i/k_1)(k_p/k_i)$$

shows that the intermediate benzylic reagent is at least 250 times as reactive as *n*-butyllithium toward trimethylchlorosilane. This higher reactivity of the benzylic lithium reagent toward a chlorosilane is consistent with other studies bearing on the mechanism of this reaction. The invertive displacement of chlorine from silicon by organolithium reagents, which was reported recently by Brook and Warner[8] and by Sommer, Rodewald, and Parker,[9] suggests a reaction path involving primarily nucleophilic attack at the silicon. In the absence of electrophilic assistance from the lithium, the more ionic benzylic organolithium reagent should be the more effective nucleophile.

This greater nucleophilicity of the more ionic organolithium reagents was demonstrated by Ziegler in a competitive scheme quite analogous to the current study.[10] The addition of styrene to a mixture of alkyllithium reagent and alkyl bromide in ether gave the hydrocarbon from the reaction of the benzylic reagent and alkyl bromide.

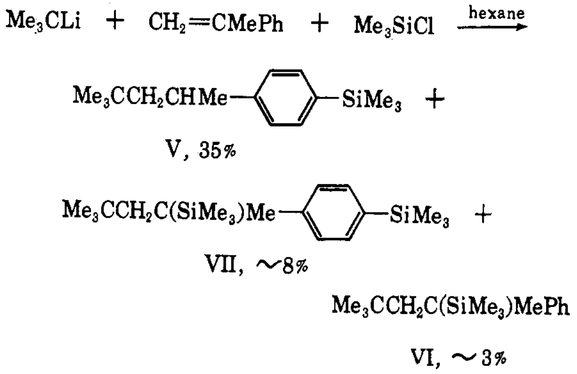
$$RLi + CH_2{=}CHPh + R'Br \longrightarrow RCH_2CHPhR' + LiBr$$

We have shown by the following synthesis that dimethyl sulfate serves in a similar manner to intercept the intermediate benzylic reagent.

$$(CH_3)_3CLi + CH_2{=}CHPh + (CH_3O)_2SO_2 \xrightarrow{\text{THF}} \underset{\text{IV}}{(CH_3)_3CCH_2CH(CH_3)Ph}$$

Trimethylfluorosilane with *n*-butyllithium and styrene in THF gave an 8:1:0 ratio of I-II-III which shows a larger k_1/k_i for trimethylfluorosilane than for trimethylchlorosilane. Unfortunately, these competitive experiments must be carried out in the presence of different lithium salts (LiF or LiCl). Owing to the known effects of lithium halides on the reactivities of organolithium reagents,[11,12] no conclusions can be drawn from these data concerning the relative reactivities of the chlorosilane and fluorosilane toward *n*-butyllithium. Trimethylmethoxysilane with *n*-butyllithium gave only I and III, suggesting that the relative reactivities of benzylic and alkyllithium reagents are reversed on changing from the chloro- to methoxysilane. Substitution of ether or hexane for THF in the addition of *n*-butyllithium to trimethylchlorosilane and styrene had little effect on the relative amounts of I and II but increased the amount of polymeric residues.

The substitution of α-methylstyrene for styrene gave a quite different series of reactions. Only Ia was obtained with *n*-butyllithium and trimethylchlorosilane in THF which is consistent with the lower reactivity of α-methylstyrene toward organoalkali reagents.[13] The use of *t*-butyllithium in hexane gave a 35% yield of V and an approximately 8% yield of VII along with several other unidentified by-products in lesser amounts.

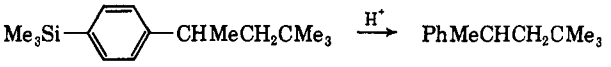


V, 35%

VII, ~8%

VI, ~3%

The expected product VI was formed in less than 5% yield. Structures V, VI, and VII could be assigned quite unequivocally from their H^1 n.m.r. spectra shown in Table IV. The structural assignment for V was confirmed by its facile desilylation under acidic conditions[5] to IV. The compound was recovered unchanged upon treatment with alkali.



V IV

The preparation of V involves an "abnormal" reaction of a benzylic anion where reaction occurs at the *para* position of the aromatic ring as shown in Chart II. Benzylic organometallic reagents owe many of their unusual properties to delocalization of the charge into the aromatic ring which increases the electron density at the *ortho* and *para* positions of the ring. Many abnor-

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(8) A. G. Brook and C. M. Warner, *Tetrahedron Letters*, **No. 18**, 815 (1962).

(9) L. H. Sommer, P. G. Rodewald, and G. A. Parker, *ibid.*, **No. 18**, 821 (1962).

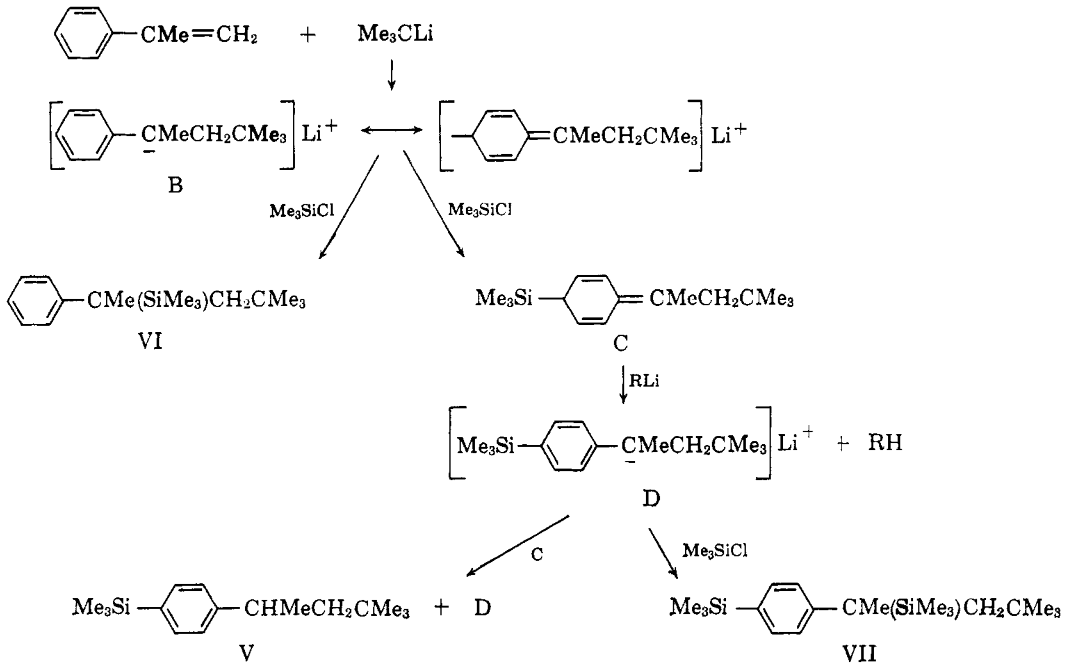
(10) K. Ziegler, E. Eimers, W. Hechelhammer, and H. Wilms, *Ann.*; **567**, 43 (1950).

(11) W. Glaze and R. West, *J. Am. Chem. Soc.*, **82**, 4437 (1960).

(12) R. Waack and M. A. Doran, *Chem. Ind.* (London), 496 (1964).

(13) J. Smid and M. Szwarc, *J. Polymer Sci.*, **61**, 31 (1962).

CHART II



mal reactions of benzylic Grignard reagents are known.[14] Although abnormal reactions of benzylic organoalkali reagents are less common, several examples have been reported. Gilman and Breuer[15] obtained *o*-methylbenzyl alcohol from benzyllithium and formaldehyde, and Brook, Gilman, and Miller[16] obtained *p*-triphenylsilylphenyldiphenylmethane, in low yield, from the reaction of triphenylmethylsodium or -lithium with triphenylhalosilanes. Russell[17] obtained cumene-*d* and cumene-d_2 with deuterium in the *α*, *ortho*, and *para* positions from the neutralization of cumylpotassium with deuterium chloride. The current example of abnormal coupling is undoubtedly aided by steric inhibition of the normal reaction at the *α* position.

The conversion of the intermediate alkylidenecyclohexadiene (C) to the aromatic structure V could proceed *via* a sequence of transmetalation reactions involving abstraction of the allylic hydrogen from the cyclohexadiene ring in C. Interruption of this sequence by coupling with chlorosilane would lead to the disilyl derivative VII. A similar sequence was proposed by Russell[17] to explain the formation of cumene-d_2 from cumylpotassium and deuterium chloride.

The greater reactivity of the more ionic organolithium reagents with chlorosilanes allows the trapping of a specific short-lived organolithium intermediate in a reaction sequence involving the conversion of one organolithium reagent to another. The syntheses of IIa–d and the corresponding hydrocarbons by removal of the silyl groups exemplify the synthetic utility of this reaction. Also, this ability to perform organolithium transformations in the presence of specific trapping agents should find utility in the structural elucidation of shortlived organolithium intermediates.

Experimental

Starting Materials and Standards.—Organolithium reagents were obtained from the Lithium Corp. of America and Foote Mineral Co. and used in the solvent in which they were supplied.

Authentic samples of *sec*-butyltrimethylsilane and isobutyltrimethylsilane were prepared in 30 and 60% yields from the corresponding organolithium reagents and trimethylchlorosilane.

Competition of Styrene and Trimethylchlorosilane for Organolithium Reagents.—In the experiments summarized in Table I, 0.20 mole of organolithium reagent in hydrocarbon solvent was added to a stirred solution of 0.40 mole of styrene and 0.40 mole of trimethylchlorosilane in 200 ml. of tetrahydrofuran. The temperature was maintained at 5–15° during the 1–2-hr. addition. The ratios of I–II were determined by v.p.c. on a silicone gum column. A five-point calibration gave the following relationship between area and mole per cent for Ia and IIa (thermal con-

$$\text{area of IIa–Ia} = 1.5 \pm 0.05 \text{ moles of IIa–Ia}$$

ductivity detectors). The yield of II was determined by fractional distillation. These distillations afforded little or no polymeric residue when an inhibitor (sulfur) was added to prevent polymerization of the recovered styrene.

The substitution of diethyl ether for THF in the above procedure with *n*-butyllithium gave a 1.3:1 molar ratio of IIa–Ia and a 48.5% yield of IIa. The distillation gave 9.6 g. of residual polymer. This same experiment with hexane as the solvent gave a 1.5:1 molar ratio of IIa–Ia, a 41% yield of IIa, and 18.1 g. of polymeric residue.

The physical properties and analyses for IIa–d are given in Table II. Their infrared spectra contained the absorptions characteristic of monosubstituted benzene (5–6 μ)[18] and the expected absorptions for the alkyl and trimethylsilyl groups. The H^1 n.m.r. spectra contained singlets for Me_3Si (τ 10.07–10.09), multiplets for the remaining alkyl hydrogens (τ 7.7–9.4), and multiplets for aromatic hydrogen (τ 2.7–3.2). The integrated intensities were in accord with the assigned structures.

Competition of Styrene and Trimethylfluorosilane for *n*-Butyllithium.—A solution of *n*-butyllithium in hexane (129 ml., 0.20 mole) was added during 2.5 hr. to 33.6 g. (0.36 mole) of trimethylfluorosilane and 41.7 g. (0.40 mole) of styrene in 200 ml. of THF at 5–15°. Analysis by v.p.c. showed an 8:1 molar ratio of Ia–IIa. Distillation gave 4.88 g. (0.021 mole, 10% yield) of IIa and no residual polymer.

Competition of Styrene and Trimethylmethoxysilane for *n*-Butyllithium.—A solution of *n*-butyllithium in hexane (129 ml.,

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[14] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, Inc., New York, N. Y., 1954, p. 1133.

[15] H. Gilman and F. Breuer, *J. Am. Chem. Soc.*, **56**, 1127 (1934).

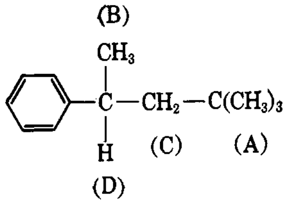
[16] A. G. Brook, H. Gilman, and L. S. Miller, *ibid.*, **75**, 4759 (1953).

[17] G. A. Russell, *ibid.*, **81**, 2017 (1959).

[18] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day Inc., San Francisco, Calif., 1962, Chapter 2.

Table IV

H^1 N.m.r. Spectra



	τ values for various protons[a]					
Compd.	Si(CH$_3$)$_3$	C(CH$_3$)$_3$ (A)	CCH$_3$ (B)	CH$_2$ (C)	CH (D)	Aromatic
IV		9.20 s	8.80 d (7)	8.1–8.6 m	6.9–7.5 m	2.92 n m
V	9.77 s	9.19 s	8.80 d (7)	8.1–8.5 m	7.4–7.7 m	(a) 2.85[b] (b) 2.72
VI	10.15 s	9.22 s	8.51 s	(a) 8.46[b] (b) 7.71	...	2.92 n m
VII	(a) 10.15 s (b) 9.76 s	9.22 s	8.52 s	(a) 8.46[b] (b) 7.71	...	(a) 2.89[b] (b) 2.74

[a] Obtained on Varian A-60 n.m.r. spectrometer in CCl$_4$ with tetramethylsilane as internal standard; s = singlet, d = doublet, m = multiplet, n = narrow; *J* values are in cycles per second in parentheses. [b] Symmetrical four-line AB pattern.

0.20 mole) was added to 41.7 g. (0.40 mole) of styrene and 41.7 g. (0.40 mole) of trimethylmethoxysilane in 200 ml. of THF. The temperature was maintained at 5–15° during the 2.25-hr. addition. Analysis by v.p.c. showed *n*-butyltrimethylsilane (Ia) but no styrene or IIa. Styrene added at this point in a separate experiment did not polymerize. Distillation gave 19.1 g. (0.15 mole, 73% yield) of Ia and 45 g. of residual polymer. The infrared and H^1 n.m.r. spectra of the polymer were nearly identical with those of polystyrene with only weak absorptions due to the trimethylsilyl group.

Reaction of *t*-Butyllithium, Styrene, and Dimethyl Sulfate.—A solution of *t*-butyllithium in heptane (55.5 ml., 0.10 mole) was added to 20.8 g. (0.20 mole) of styrene and 25.2 g. (0.20 mole) of dimethyl sulfate in 100 ml. of THF. The temperature was maintained at 5–15° during the 1-hr. addition. After adding 100 ml. of 15% aqueous ammonium hydroxide, the organic layer was washed with 50 ml. of water. Distillation afforded 7.86 g. (0.045 mole, 45% yield) of 2,2-dimethyl-4-phenylpentane (IV). The n.m.r. spectrum of IV is summarized in Table IV.

Reaction of *t*-Butyllithium, α-Methylstyrene, and Trimethylchlorosilane.—A solution of *t*-butyllithium in pentane (70.5 ml., 0.10 mole) was added during 1.25 hr. to 21.8 g. (0.20 mole) of trimethylchlorosilane and 23.7 g. (0.20 mole) of α-methylstyrene in 100 ml. of hexane at 20 to 30°. Analysis by v.p.c. showed nine compounds with retention times greater than α-methylstyrene. Distillation gave 8.7 g. (0.035 mole, 35% yield) of the major product V. The infrared spectrum of V showed the characteristic absorptions at 5–6 μ for 1,4-disubstituted benzenes.[18]

Only two other components were collected (impure) in any significant quantities during the distillation which was carried to a flask temperature of 190° at 8 mm. These compounds, VI and VII, were isolated in *ca.* 20-mg. quantities by v.p.c. from the distillation fractions prior to and after V, respectively. The v.p.c. analyses of the various distillation fractions indicated that V, VI, and VII were produced in a ratio of approximately 10:1:3. The H^1 n.m.r. spectra of V, VI, and VII are summarized in Table IV.

Desilylation of [4-(1,3,3-Trimethylbutyl)phenyl]trimethylsilane (V).—A mixture of 1.50 g. of V, 0.80 g. of *p*-toluenesulfonic acid, 2.3 g. of water, and 14.0 g. of diglyme was heated at 150–160° for 16 hr. Analysis by v.p.c. revealed no V and a single lower boiling product. Preparative v.p.c. after dissolving the mixture in ether, extracting with water, and concentrating to 2 ml. gave 0.45 g. (2.6 × 10^{-3} mole, 43% yield) of 2,2-dimethyl-4-phenylpentane (IV).

Heating 1.5 g. of V, 1.0 g. of potassium hydroxide, 1.0 g. of water, and 6.0 g. of ethanol at 150° for 24 hr. in a Parr bomb gave only recovered V.

Desilylation of (1-Phenyl-3,3-dimethylbutyl)trimethylsilane (IId).—A mixture of 8.0 g. (0.034 mole) of IId, 20 g. of ethanol, 5 g. of water, and 20 g. potassium hydroxide was heated at reflux for 64 hr. The mixture was added to 300 ml. of water and extracted with ether, and the ether extract was dried over anhydrous sodium sulfate. Distillation gave 4.20 g. (0.026 m.), 76% yield, of 1-phenyl-3,3-dimethylbutane (see Table II). The H^1 n.m.r. spectrum showed a singlet for (CH$_3$)$_3$C (τ 9.05), an A_2B_2 pattern for the Ph*CH$_2$* and Me$_3$*CCH$_2$* protons (multiplets centering at τ 7.45 and 8.45), and a multiplet for aromatic protons (τ 2.88). The integrated intensities for these absorptions are in the ratio of 9.0:4.1:5.0.

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