220°, under reduced pressure (10–20 mm), gave 0.32 g of colorless fine crystals, mp 360° dec.

The infrared and ultraviolet absorption spectra of the compound were identical with those of adenine.

Anal. Calcd for $C_5H_5N_5$: C, 44.45; H, 3.73; N, 51.82. Found: C, 44.31; H, 3.79; N, 51.70.

Another ultraviolet-absorbing substance, 4,5-dicyanoimidazole, was extracted with ethyl acetate from the hot water extract of the dark brown solid. After the extract was evaporated to dryness, the residue was recrystallized from a small amount of water to give colorless pure crystals, mp 174–175°.

The ultraviolet spectra of the compound showed absorption maximum at 247 $m\mu$ in 0.1 N hydrochloric acid and 263 $m\mu$ in 0.1 N sodium hydroxide solution. The infrared absorption spectrum of the compound exhibited characteristic bands due to the -CN group at 2259 and 2243 cm^{-1}.

Anal. Calcd for $C_5H_2N_4$: C, 50.85; H, 1.70; N, 47.45. Found: C, 50.70; H, 1.85; N, 47.58.

An authentic sample of 4,5-dicyanoimidazole was prepared from 4,5-imidazoledicarboxylic acid according to the method of Tamamushi.[3] The ultraviolet and infrared absorption spectra, the paper chromatographic behavior, and the melting point of the isolated crystals were identical with those of the authentic sample.

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[3] Y. Tamamushi, *Yakugaku Zasshi*, **55**, 1053 (1935).

The Competition of Fluorene or Bromobenzene with Trimethylchlorosilane for *n*-Butyllithium

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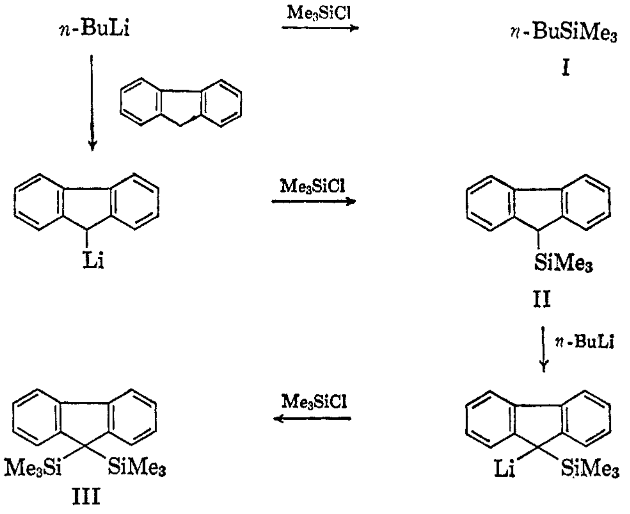
Our recent studies[1,2] on the competition of halosilanes and aryl olefins for organolithium reagents revealed that primary alkyllithium reagents (*e.g.*, *n*-butyllithium) react at comparable rates with styrene and trimethylchlorosilane in tetrahydrofuran (THF). This somewhat surprising result and the common use of chlorosilanes to derivatize organolithium reagents prompted an investigation of the rates of other organometallic transformations (specifically, the transmetalation[3] and halogen–metal exchange[4]) relative to the rate of reaction with trimethylchlorosilane. We now wish to report that, in certain cases with *n*-butyllithium, both transformations are considerably faster than the coupling of the *n*-butyllithium with trimethylchlorosilane.

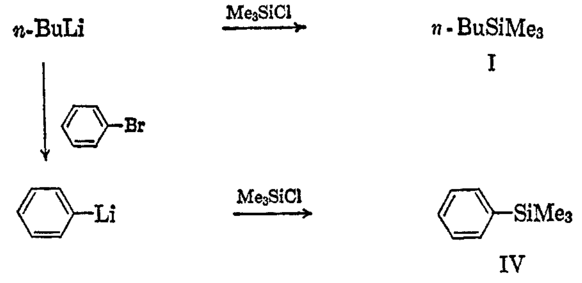
Competitive reactions were used to examine these organometallic reagent transformations. The slow addition of *n*-butyllithium to a fivefold excess of fluorene ($pK = 25$)[5,6] and of trimethylchlorosilane in THF gave a 1:3:1 molar ratio of *n*-butyltrimethylsilane (I), 9-trimethylsilylfluorene (II), and 9,9-bis(trimethylsilyl)fluorene (III) which indicates that *n*-butyllithium reacts somewhat faster with fluorene and 9-trimethylsilylfluorene than with trimethylchlorosilane. In a similar preparative experiment a high yield of III was obtained at a ratio of 3 equiv of *n*-butyllithium per mole of fluorene. The addition of *n*-butyllithium to fluorene in THF and the addition of this slurry to trimethylchlorosilane gave a high yield of II. Compounds II and III in the former reaction must arise *via* the series of transmetalation and coupling reactions shown in Scheme I. The substantial amount of III in these experiments, even when employing a large excess of fluorene, shows that 9-trimethylsilylfluorene is more readily metalated than is fluorene. As the rate of proton abstraction usually parallels the hydrocarbon acidity,[6] this result suggests an enhanced acidity for this hydrocarbon (II) relative to fluorene, which would be consistent with the stabilization of the 9-trimethylsilylfluorenyl anion *via* $d\pi$–$p\pi$ bonding with the silicon.[7] Substitution of the less acidic hydrocarbon, triphenylmethane ($pK = 33$),[5,6] for fluorene in the above reaction gave only I.

SCHEME I



The addition of *n*-butyllithium to an excess of bromobenzene and trimethylchlorosilane in THF gave a 2:1 ratio of phenyltrimethylsilane (IV) to I (Scheme II).

SCHEME II



The formation of IV must involve a halogen–metal exchange to give phenyllithium followed by coupling with the chlorosilane. Thus, *n*-butyllithium reacts more rapidly with the bromobenzene than with the trimethylchlorosilane under these conditions. Substitution of chlorobenzene for bromobenzene in the above reaction gave only I, which is consistent with the lower reactivity of the organic chlorides relative to the bromides in the halogen–metal exchange.[4]

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[1] A. E. Bey and D. R. Weyenberg, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1964, p 2-S.

[2] A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, **30**, 2436 (1965).

[3] H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954).

[4] R. G. Jones and H. Gilman, *ibid.*, **6**, 339 (1951).

[5] A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 14.

[6] A. Streitweiser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965).

[7] C. Eaborn, "Organosilicon Compounds," Butterworths and Co. (Publishers) Ltd., London, 1960, Chapter 3.

We would anticipate, by analogy to our previous work,[1,2] that secondary and tertiary organolithium reagents would show a greater preference for reaction with acidic hydrocarbons and halobenzenes in these competitive reactions because of the greater sensitivity of the reaction with chlorosilane to steric factors.[8]

These data again show the utility of trimethylchlorosilane in the trapping of specific organolithium reagents in a reaction sequence. It should also be noted that extreme caution must be exercised in assigning the structure of an organolithium reagent *via* derivative formation, since the rate of such a reaction may well be slower than the interconversions among several organolithium reagents.

Experimental Section

All experiments were carried out under dry nitrogen in a flask fitted with stirrer and reflux condenser. Boiling points and melting points are uncorrected.

9-Trimethylsilylfluorene (II).—A solution of *n*-butyllithium in hexane (96 ml, 0.15 mole) was added during 3 hr at 25–32° to 8.31 g (0.05 mole) of fluorene in 125 ml of THF. The resulting orange-brown solution was added *via* a capillary tube to 97.4 g (0.90 mole) of rapidly stirred trimethylchlorosilane. The temperature was maintained at 10–20° during the 1.25-hr addition. Analysis by vpc showed the absence of fluorene and the presence of two compounds (*ca.* 20:1 ratio) with retention times greater than fluorene. After solvent removal by distillation, the residue was dissolved in 200 ml of chloroform and filtered, giving 5.98 g (0.14 mole) of lithium chloride. The filtrate was concentrated on a rotary evaporator to afford 13.2 g of solid. Crystallization from 150 ml of ethanol gave 5.82 g (0.0244 mole) of II, mp 96–97° (lit.[9] mp 97.5°). Further concentration of the ethanol solution gave an additional 3.01 g (0.0126 mole) of II, mp 95–97°; the total yield was 74%. The H^1 nmr spectrum of II showed singlets for trimethylsilyl (τ 10.11) and methine protons (6.29), and a multiplet for aromatic protons (2.2–2.9). The integrated intensities were in accord with the proposed structure. The infrared spectrum showed the characteristic absorptions for aromatic structures (5–6, 13.5 μ) and for the trimethylsilyl group (8.0, 11.9 μ).

Anal. Calcd for $SiC_{15}H_{18}$: Si, 11.8; C, 80.6; H, 7.6. Found: Si, 12.4, 12.06; C, 80.3, 80.7; H, 7.84, 7.85.

9,9-Bis(trimethylsilyl)fluorene (III).—A solution of *n*-butyllithium in hexane (36 ml, 0.06 mole) was added during 45 min at 10–20° to 10.8 g (0.10 mole) of trimethylchlorosilane and 16.6 g (0.10 mole) of fluorene in 100 ml of THF. After stirring 16 hr at room temperature, 32.6 g (0.30 mole) of trimethylchlorosilane and 50 ml of THF were added to the mixture. An additional 155 ml (0.25 mole) of *n*-butyllithium solution was then added at 10–20° over a period of 3 hr. Analysis by vpc showed solvents, *n*-butyltrimethylsilane (I), and a single peak with a retention time greater than that of fluorene. Distillation and crystallization from ethanol afforded 25.2 g (0.084 mole) of III, mp 109–110° (lit.[9] mp 110°), 84% yield. The H^1 nmr spectrum showed a singlet for trimethylsilyl (τ 9.91) and a multiplet for the aromatic protons (1.9–2.8) in a ratio of 18:8. The infrared spectrum showed the characteristic absorptions noted for II.

Anal. Calcd for $Si_2C_{19}H_{26}$: Si, 18.1; C, 73.5; H, 8.4. Found: Si, 18.0, 18.1; C, 74.3, 74.8; H, 8.68, 8.87.

Competition of Fluorene and Trimethylchlorosilane for *n*-Butyllithium.—A solution of *n*-butyllithium in hexane (31.5 ml, 0.05 mole) was added during 45 min at 30–40° to 27.2 g (0.25 mole) of trimethylchlorosilane and 41.6 g (0.25 mole) of fluorene. Analysis by vpc showed a 1:3:1 molar ratio of I:II:III. Calibration of the vpc (thermal conductivity detectors) gave the following relationship: area I to area II to area III = 1.50 mole of I to 1.05 mole of II to 0.75 mole of III.

Competititon of Triphenylmethane and Trimethylchlorosilane for *n*-Butyllithium.—A solution of *n*-butyllithium in hexane (25.1 ml, 0.04 mole) was added during 2.5 hr at 5–25° to 21.7 g (0.20 mole) of trimethylchlorosilane and 48.9 g (0.20 mole) of triphenylmethane in 80 ml of THF. No color change was observed during the addition. Analysis by vpc revealed the presence of starting materials and I. No compounds with retention times greater than triphenylmethane could be detected.

When *n*-butyllithium was added to a solution of triphenylmethane in THF, the characteristic red color of triphenylmethyllithium was immediately evident. The red color rapidly disappeared when the organolithium solution was mixed with trimethylchlorosilane. Analysis by vpc showed that the major component present had a retention time greater than that of triphenylmethane.

Competition of Bromobenzene and Trimethylchlorosilane for *n*-Butyllithium.—A solution of *n*-butyllithium in hexane (126 ml, 0.20 mole) was added to 157.0 g (1.0 mole) of bromobenzene and 108.6 g (1.0 mole) of trimethylchlorosilane in 200 ml of THF. The temperature was maintained at 5–15° during the 2-hr addition. Fractional distillation of the mixture afforded 4.0 g (0.0306 mole) of I and 10.7 g (0.071 mole) of phenyltrimethylsilane (IV) in addition to solvent starting materials and *n*-butyl bromide. Compounds I and IV were identified by vpc retention times and by comparison of their infrared spectra with those of authentic samples.

Competition of Chlorobenzene and Trimethylchlorosilane for *n*-Butyllithium.—A solution of *n*-butyllithium in hexane (62.9 ml, 0.10 mole) was added to 56.1 g (0.50 mole) of chlorobenzene and 54.3 g (0.50 mole) of trimethylchlorosilane in 100 ml of THF. The temperature was maintained at 5–15° during the 1.5-hr addition. Analysis by vpc showed starting materials and I. Distillation afforded 11.1 g (0.085 mole) of I.

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(8) See ref 7, Chapter 2.

(9) C. Eaborn and R. A. Shaw, *J. Chem. Soc.*, 1420 (1955).

Alkoxide-Initiated Eliminations on Substrates Bearing Poor Leaving Groups. I. Diglyme as Substrate in Potassium *t*-Butoxide Initiated Elimination

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Acid- and base-catalyzed elimination reactions have been very extensively studied.[1-3] However, the alkoxide- and hydroxide-initiated elimination reactions on substrates carrying poor leaving groups such as alkoxyl and hydroxyl have received little attention. In most of the examples of this type of elimination reaction reported in the literature, the hydrogen β to the leaving group is activated by a substituent which allows formation of a relatively stable carbanion.[4-6] It was therefore of interest to investigate substrates which contain poor carbanion-stabilizing groups, *i.e.*, alkoxyl. Snyder[7] in a preliminary investigation demonstrated that diglyme (the dimethyl ether of diethylene glycol) undergoes elimination in the presence of potassium *t*-butoxide at 160°. We have examined this elimination in more detail.

(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 420–472.

(2) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, Chapter 12.

(3) D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 6, p 304.

(4) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p 180.

(5) P. Schorigin, *Ber.*, **43**, 1931 (1910).

(6) R. L. Letsinger and E. Bobko, *J. Am. Chem. Soc.*, **75**, 2649 (1953).

(7) W. H. Snyder, unpublished research done as a graduate student at the University of Pennsylvania, Philadelphia, Pa.