mixed m. p. 198°. A sample of the compound obtained by acid-treatment of the Bunte salt, warmed with alcohol and hydrochloric acid, gave 84% of the theory of the thiol, only little contaminated with disulfide.

Summary

1. The α-carbamylmercaptoacetyl derivatives of 5-aminoresorcinol and 6- and 8-aminoquinoline have been prepared.

2. β-Mercaptopropionanilide and ω-mercaptohendecanilide, the corresponding disulfides and auro-mercaptides have been prepared. The two thiols were obtained from the corresponding thiosulfates (Bunte salts) with a mixture of ethanol and concd. hydrochloric acid; treatment of sodium propionanilide β-thiosulfate with dilute aqueous hydrochloric acid unexpectedly led to the aniline salt of propionanilide-β-thiosulfuric acid.

RICHMOND HILL, N. Y. RECEIVED OCTOBER 28, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE AND PURDUE UNIVERSITY]

The Reaction of *n*-Butyllithium with Some Organosilicon Compounds

BY H. GILMAN, R. A. BENKESER[1] AND G. E. DUNN

It has been shown that when triphenylcarbinol,[2a] triphenylamine,[2b] triphenylphosphorus[2c] or triphenylarsenic[2d] is refluxed with *n*-butyllithium in ether, metalation of the aromatic nucleus occurs; whereas, in triphenylbismuth[3a] and tetraphenyltin[3b] the carbon-to-metal bond is cleaved by *n*-butyllithium. The present investigation was undertaken in order to ascertain the effect of *n*-butyllithium on some organosilicon compounds of related structure.

Accordingly, triphenylsilanol was treated with two equivalents of *n*-butyllithium by the method used for triphenylcarbinol.[2a] Upon carbonation of the reaction mixture, benzoic acid and diphenyl-*n*-butylsilanol were isolated. It is apparent, therefore, that *n*-butyllithium attacks the carbon-to-silicon bond in triphenylsilanol rather than the carbon-to-hydrogen bond as is the case with the analogous triphenylcarbinol. Results with some other silanols are shown in Table I. The over-all reaction may be represented by the general equations

$$R_3SiOH + R'Li \longrightarrow R_3SiOLi + R'H \tag{1}$$

$$R_3SiOLi + R'Li \longrightarrow R_2R'SiOLi + RLi \tag{2}$$

where R is an aryl and R′ an alkyl group. In the case of symmetrical silanols, the R_3SiOLi formed in reaction (1) is precipitated immediately upon the addition of the R′Li, and slowly redissolves as reaction (2) proceeds. If R and R′ are both aryl groups, or if alkyl Grignard reagents are used instead of alkyllithium compounds, reaction (2) does not take place to a detectable extent. Neither the nature of the products nor the yields is appreciably altered if the amount of R′Li is increased to as much as four moles to one of silanol.

TABLE I

CLEAVAGE OF SILANOLS BY ORGANOMETALLIC COMPOUNDS

Silanol	Cleaving agent	Acid formed	Yield, %
Triphenyl	*n*-BuLi	Benzoic	76
Triphenyl	*n*-BuMgBr	None	0
Triphenyl	*p*-$CH_3C_6H_4Li$	None	0
Tri-*p*-tolyl	*n*-BuLi	*p*-Toluic	61
Tri-*p*-tolyl	C_6H_5Li	None	0
Diphenyl-*p*-tolyl	*n*-BuLi	*p*-Toluic	18
		Benzoic	6
Tri-1-naphthyl[a]	*n*-BuLi	None	0

[a] This compound was first prepared by Mr. C. G. Brannen, and the procedure will be reported in a forthcoming paper.

When hexaphenyldisiloxane was treated with *n*-butyllithium both the carbon-to-silicon and silicon-to-oxygen bonds were attacked, since triphenyl-*n*-butylsilane and benzoic acid were obtained on carbonation and hydrolysis. It is known that phenyllithium reacts with hexaphenyldisiloxane according to the equation[4]

$$(C_6H_5)_3SiOSi(C_6H_5)_3 + C_6H_5Li \longrightarrow (C_6H_5)_4Si + (C_6H_5)_3SiOLi$$

in which the group $-OSi(C_6H_5)_3$ behaves like the ethoxy group in triphenylethoxysilane. This suggests that the reaction between hexaphenyldisiloxane and *n*-butyllithium should be formulated as follows

$$(C_6H_5)_3SiOSi(C_6H_5)_3 + C_4H_9Li \longrightarrow (C_6H_5)_3SiC_4H_9 + (C_6H_5)_3SiOLi$$

$$(C_6H_5)_3SiOLi + C_4H_9Li \longrightarrow (C_6H_5)_2C_4H_9SiOLi + C_6H_5Li$$

The fact that no diphenyldi-*n*-butylsilane was isolated, as might be expected if the carbon-to-silicon bond were attacked prior to the silicon-to-oxygen bond, tends to support the assumption that the reaction takes place in the manner shown.

Attempts were made to extend the reaction to compounds in which all four valences of silicon are attached to carbon. Table II shows the results obtained when a number of silanes were treated with *n*-butyllithium under the conditions used with the silanols. It is seen that only in the case of trimethyl-9-fluorenylsilane was an acid

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(2) (a) Gilman, Brown, Webb and Spatz, THIS JOURNAL, **62**, 977 (1940); (b) Gilman and Brown, *ibid.*, **62**, 3208 (1940); (c) Gilman and Brown, *ibid.*, **67**, 824 (1945); (d) Gilman and Stuckwisch, *ibid.*, **63**, 3532 (1941).

(3) (a) Gilman, Yablunky and Svigoon, *ibid.*, **61**, 1170 (1939); (b) Gilman, Moore and Jones, *ibid.*, **63**, 2482 (1941).

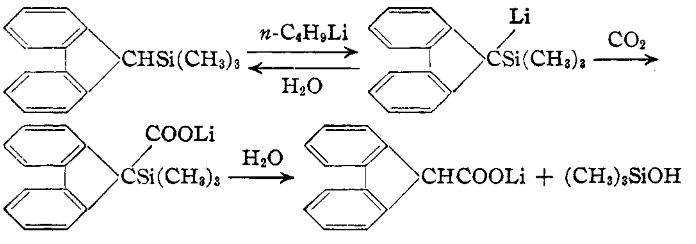
(4) Unpublished studies by H. N. Benedict.

TABLE II

REACTION OF *n*-BUTYLLITHIUM WITH SILANES

Silane	Acid isolated	Yield, %
Tetraphenyl	None	
Triphenyl-*n*-butyl	None	
Trimethylphenyl	None	
Triethylphenyl	None	
Tetra-*p*-tolyl	None	
Trimethyl-1-naphthyl	None	
Triphenyl-2-thienyl	Triphenyl-2-thienyl-5-carboxysilane	45
Triethyl-*p*-anisyl	Triethyl-3-carboxy-4-methoxyphenylsilane	58
Trimethyl-9-fluorenyl	Fluorene-9-carboxylic	82

obtained which resulted from the cleavage of a silicon-to-carbon bond. It was shown, however, that if, after treating trimethyl-9-fluorenylsilane with *n*-butyllithium, the reaction mixture is hydrolyzed instead of carbonated, the starting material is recovered in good yield. This indicates that the initial reaction is a metalation in the 9-position of trimethyl-9-fluorenylsilane, and that the acid formed on carbonation undergoes cleavage of the carboxy-alkyl group from silicon.[5] In no case, then, was a compound of the type R_4Si[6] cleaved by *n*-butyllithium under the conditions of this study. Furthermore, metalation of the aromatic nucleus does not occur under these conditions unless there is attached to that nucleus a strongly activating group other than the central silicon atom.



Experimental

Triphenyl-*n*-butylsilane.—To a solution of 6 g. (0.02 mole) of triphenylchlorosilane in 50 ml. of dry ether was added an ether solution of *n*-butyllithium under dry nitrogen until a positive Color Test I[7] was obtained. After stirring for one hour the solution was hydrolyzed, and the ether was separated, dried and evaporated. The residue was crystallized from absolute methanol to yield 6 g. (85%) of material melting at 87.5–88°.

Anal. Calcd. for $C_{22}H_{24}Si$: Si, 8.88. Found: Si, 8.76.

Triethyl-*p*-anisylsilane.—Triethylchlorosilane and *p*-anisyllithium gave triethyl-*p*-anisylsilane in 64% yield by the above procedure; b. p. 103° at 0.2 mm., n^{20}_{D} 1.5130; d^{20}_{4} 0.9487; M_D calcd. 70.3; found, 70.1.

Anal. Calcd. for $C_{13}H_{22}OSi$: Si, 12.6. Found: Si, 12.4.

Trimethyl-1-naphthylsilane.—Trimethylchlorosilane was treated with 1-naphthyllithium by the same procedure to give trimethyl-1-naphthylsilane in 70% yield. 1-Bromonaphthalene is a persistent impurity in this compound and careful fractionation is required to remove it; b. p. 99° at 0.2 mm., n^{20}_{D} 1.5810, d^{20}_{4} 0.9870; M_D calcd. 67.4; found 67.6.

Anal. Calcd. for $C_{13}H_{16}Si$: Si, 14.0. Found: Si, 13.8.

Trimethyl-9-fluorenylsilane.—To 17 g. (0.11 mole) of fluorene in 70 ml. of ether was added 48 ml. of an ether solution of 0.12 mole of *n*-butyllithium. After the spontaneous reflux and gas evolution had subsided, the mixture was refluxed for sixteen hours. To this solution of 9-fluorenyllithium was added dropwise 13 g. (0.12 mole) of trimethylchlorosilane in 50 ml. of ether. After the addition was complete, the mixture was refluxed for two hours, then hydrolyzed, and the ether distilled. The residue, after crystallization from dilute ethanol, weighed 12.8 g., corresponding to a yield of 49%, and melted at 97.5–99.5°.

Anal. Calcd. for $C_{16}H_{18}Si$: Si, 11.7. Found: Si, 11.4.

Triphenyl-2-thienylsilane.—The procedure described above for the preparation of trimethyl-9-fluorenylsilane was used to prepare triphenyl-2-thienylsilane in 63% yield from thiophene, *n*-butyllithium and triphenylchlorosilane; m. p. 196–198° with softening at 195°.

Anal. Calcd. for $C_{22}H_{18}Si$: Si, 8.19. Found: Si, 8.19.

Diphenyl-*p*-tolylsilanol.—A solution of 24.8 g. (0.099 mole) of diphenyldichlorosilane in 50 ml. of ether was cooled to −20°. To this was added dropwise with vigorous stirring 0.099 mole of *p*-tolyllithium (122 ml. of 0.82 *M* solution in ether) while keeping the temperature between −15 and −20°. At the end of the addition the mixture was stirred at room temperature for thirty minutes, then hydrolyzed and the ether distilled. The residue was crystallized from petroleum ether (b. p. 90–120°) to give 22 g. (77%) of diphenyl-*p*-tolylsilanol, m. p. 87–88°.

Anal. Calcd. for $C_{19}H_{18}OSi$: Zerewitinoff H, 1.00. Found: Zerewitinoff H, 1.01.

Cleavage and Attempted Cleavage of Silanols and Silanes.—The procedure for the cleavage of triphenylsilanol by *n*-butyllithium will be described in detail. All other cleavages and attempted cleavages of silanols or silanes, except those for which individual procedures are described below, were carried out under the same conditions, and the results are to be found in the Tables. In the case of triphenylsilanol alone the silanol formed as a result of the cleavage was isolated and identified. In other cases only the acid fraction was examined. All reaction products except those hitherto unreported in the literature were identified by mixed melting point determinations with authentic specimens.

Active hydrogen was determined by the Zerewitinoff method, using methyllithium rather than methylmagnesium iodide as the source of methane. The methyllithium was prepared in the usual manner from methyl iodide and lithium in di-*n*-butyl ether. The silanol to be analyzed was dissolved in dry xylene, since this was found to be a better solvent for aryl silanols than is di-*n*-butyl ether. Methyllithium has the advantage over methylmagnesium iodide that the lithium salts of the silanols are soluble in xylene while the magnesium salts form a thick, gelatinous precipitate which tends to prevent adequate mixing of the solutions and to entrap the methane evolved.

A solution of 0.12 mole of *n*-butyllithium in ether was added slowly with vigorous agitation to an ethereal solution of 11 g. (0.04 mole) of triphenylsilanol in an atmosphere of dry nitrogen. During the addition of the first 0.04 mole of *n*-butyllithium spontaneous reflux occurred, and the lithium salt of triphenylsilanol separated as a white precipitate. The suspension was heated to reflux for twenty-four hours, at the end of which time the precipitate had redissolved to give a pale yellow solution. This was poured jetwise on crushed Dry Ice; the carbonated mix-

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[5] For similar cleavage reactions see Whitmore and co-workers, THIS JOURNAL, 68, 1083 (1946); 69, 1551 (1947); 70, 2869 (1948).

[6] R cannot be hydrogen. For the reaction of R_3SiH compounds with *n*-butyllithium, see Gilman and Massie, *ibid.*, 68, 1128 (1946); Meals, *ibid.*, 68, 1880 (1946).

[7] Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925).

ture was acidified with dilute hydrochloric acid, and the ether layer was separated. Extraction of this ether solution with aqueous sodium carbonate, followed by acidification of the extract, gave 4.2 g. of acid melting at 116–117°. Recrystallization from hot water gave 3.2 g. (76%) of pure benzoic acid.

The ether solution of the non-acid portion of the reaction product was washed thoroughly with dilute hydrochloric acid and with water in order to remove all traces of nonvolatile acids and bases which catalyze the condensation of silanols to disiloxanes. After drying the solution over sodium sulfate and removing the ether, the residue was distilled under reduced pressure to give 8.8 g. (86%) of diphenyl-*n*-butylsilanol; b. p. 165–166° at 0.3 mm., n^{20}_{D} 1.5178, d^{20}_{4} 0.9700; M_D calcd. 79.2; found, 79.9.

Anal. Calcd. for $C_{16}H_{20}OSi$: Si, 10.9; Zerewitinoff H, 1.00. Found: Si, 10.6; Zerewitinoff H, 0.96.

Diphenyl-*p*-tolylsilanol and *n*-Butyllithium.—To 5.00 g. (0.0173 mole) of diphenyl-*p*-tolylsilanol in 50 ml. of ether was added 0.043 mole of *n*-butyllithium (75 ml. of 0.64 *M* solution in ether). This mixture was refluxed for twenty-four hours, then carbonated, acidified and extracted with sodium carbonate as described in the general procedure for cleavages. The sodium carbonate extract was placed in a separatory funnel, covered with an equal volume of ether, and acidified with dilute hydrochloric acid. The ether solution of organic acids was separated; the aqueous layer was washed with ether and the ether solution and washings were combined. The ether was evaporated without drying and the wet residue was dissolved in 30 ml. of 10% sodium hydroxide solution. To this was added 1 g. of potassium permanganate and the solution was refluxed six hours. It was then acidified with hydrochloric acid to precipitate the organic acids and reduce the manganese dioxide. The acids were taken up in ether; the ether solution was dried and evaporated. The residue of mixed benzoic and terephthalic acids was separated by extraction in a Soxhlet apparatus with chloroform, according to the method of Gilman and Kirby.[8] The yield of benzoic acid was 0.13 g. (6%), and of terephthalic acid, 0.54 g. (18%).

Triphenyl-2-thienylsilane and *n*-Butyllithium.—To a warm 1:1 ether–benzene mixture was added 2 g. (0.0058 mole) of triphenyl-2-thienylsilane and a solution of 0.0116 mole of *n*-butyllithium in 80 ml. of ether. After refluxing for three hours the mixture was carbonated, acidified and extracted with alkali in the usual way. There was obtained, after crystallization from dilute alcohol, 1.5 g. (45%) of triphenyl-2-thienyl-5-carboxysilane[9] melting at 188–190° with some preliminary softening.

Anal. Calcd. for $C_{23}H_{18}O_2SSi$: Si, 7.25, neut. equiv., 386. Found: Si, 7.29; neut. equiv., 383.

Triethyl-*p*-anisylsilane and *n*-Butyllithium.—To 8 g. (0.036 mole) of triethyl-*p*-anisylsilane in 40 ml. of ether was added 70 ml. of ether containing 0.032 mole of *n*-butyllithium. After being refluxed for sixteen hours the mixture was carbonated, acidified and extracted with aqueous alkali. On acidification of the alkaline extract 4.5 g. (47%) of a carboxy-4-methoxyphenylsilane was obtained. Purification was effected by redissolving the solid in aqueous sodium carbonate, extracting with ether and reprecipitating with hydrochloric acid. The material thus obtained melted at 52–56° with some preliminary softening. Calcd.: neut. equiv., 266. Found: neut. equiv., 264.

To 2 g. (0.0075 mole) of this acid in 80 ml. of glacial acetic acid was added 1.6 g. (0.01 mole) of bromine along with 0.25 g. of iodine. The solution was stirred at room temperature for twenty-two hours and then poured into water. Upon standing, crystals separated which were filtered off and washed with a concentrated sodium bisulfite solution. Crystallization from hot water gave 1 g. (58%) of 2-methoxy-5-bromobenzoic acid (mixed m. p.). Thus, metalation of triethyl-*p*-anisylsilane occurs *ortho* to the ether linkage, which is the conventional position.[10]

Trimethyl-9-fluorenylsilane and *n*-Butyllithium.—Three grams (0.0126 mole) of trimethyl-9-fluorenylsilane was refluxed four and one-half hours with 0.014 mole of *n*-butyllithium in ether. The mixture was carbonated and worked up in the usual way to give 1.3 g. (37%) of fluorene-9-carboxylic acid (mixed m. p.). In a second run the trimethyl-9-fluorenylsilane was refluxed with the *n*-butyllithium solution for sixteen hours before carbonation and an 82% yield of fluorene-9-carboxylic acid was obtained.

In another trial the trimethyl-9-fluorenylsilane was refluxed with the *n*-butyllithium solution for twenty hours and the mixture was then hydrolyzed immediately without carbonating. There was recovered unchanged 89% of pure trimethyl-9-fluorenylsilane. This indicates that the cleavage observed above is not caused by the *n*-butyllithium, but rather by the instability of the resultant β-oxygenated silane.

Hexaphenyldisiloxane and *n*-Butyllithium.—Ten grams (0.02 mole) of hexaphenyldisiloxane was refluxed forty-eight hours with 0.02 mole of *n*-butyllithium, then carbonated and worked up in the usual way. The yield of pure benzoic acid was 1.6 g. (66%). On concentration of the ether solution containing the alkali insoluble reaction products, 0.5 g. (5%) of hexaphenyldisiloxane precipitated. Complete removal of the ether left an oil which, when taken up in methanol, deposited 2.4 g. (50%) of triphenyl-*n*-butylsilane.

Summary

1. *n*-Butyllithium has been shown to cleave triarylsilanols which are not sterically hindered to give diaryl-*n*-butylsilanols and aryllithiums.

2. Hexaphenyldisiloxane is cleaved by *n*-butyllithium to give triphenyl-*n*-butylsilane and phenyllithium.

3. The tetraaryl- and mixed arylalkylsilanes examined in this study are not cleaved by *n*-butyllithium. However, those aromatic silanes which contain activating groups may be metalated in the aromatic nucleus.

4. It has been established that metalation of triethyl-*p*-anisylsilane takes place ortho to the methoxy group.

5. When trimethyl-9-fluorenylsilane is treated with *n*-butyllithium and carbonated, cleavage of the carboxy-alkyl group from silicon has been found to occur.

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[8] Gilman and Kirby, THIS JOURNAL, **54**, 351 (1932).

[9] The structure of this acid was not proved, but in view of the usual metalation of 2-substituted thiophenes in the 5-position the assumed structure is probably reliable. See Gilman and Breuer, *ibid.*, **56**, 1123 (1934); Benkeser and Currie, *ibid.*, **70**, 1780 (1948); Gilman and Shirley, *ibid.*, **71**, 1870 (1949).

[10] For orientation studies in metalation reactions see Gilman and co-authors, *ibid.*, **56**, 1123, 1412 (1934); **61**, 109 (1939); **62**, 987 (1940); Morton, Little and Strong, *ibid.*, **65**, 1339 (1943).