this work is being undertaken. Results of the biological tests will be reported by Dr. Otho E. Easterday of the Brookhaven National Laboratory.

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Phenyl and *p*-Trimethylsilylphenyl Compounds of Silicon, Germanium, and Tin

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We wish to report several new compounds of silicon, germanium, and tin, containing phenyl and *p*-trimethylsilylphenyl substituents (Table I) which have been synthesized by treatment of an appropriate chlorine compound with *p*-trimethylsilylphenyllithium.

$$2p\text{-}(CH_3)_3SiC_6H_4Li + (C_6H_5)_2SiCl_2 \longrightarrow [p\text{-}(CH_3)_3SiC_6H_4]_2Si(C_6H_5)_2 + 2LiCl$$

TABLE I

Compounds Prepared from *p*-Trimethylsilylphenyllithium

Reagent	Moles of RLi / Moles of the chlorine compound	Reaction Time, Hr.	Product	M.P., °C.	Yield, %	Formula	Analyses: Element	Analyses: Calcd.	Analyses: Found
$(C_6H_5)_3SiCl$	1.2	8[a]	Triphenyl(*p*-trimethylsilylphenyl)silane	163–165[b]	83	$C_{27}H_{28}Si_2$	Si	13.8	13.5, 13.8
$(C_6H_5)_2SiCl_2$	2.3	1[a]	Diphenylbis(*p*-trimethylsilylphenyl)silane[c]	163.5–165[b]	86	$C_{30}H_{36}Si_3$	Si	17.5	17.4, 17.3
$SiCl_4$	6.3	12[d]	Tetrakis(*p*-trimethylsilylphenyl)silane	355–357[e]	77	$C_{36}H_{52}Si_5$	Si	22.4	22.3, 22.2
$GeCl_4$	5.3	12[f]	Tetrakis(*p*-trimethylsilylphenyl)germane	351–354[g]	49	$C_{36}H_{52}GeSi_4$	Si	16.8	17.1, 17.2
$SnCl_4$	4.5	12[a]	Tetrakis(*p*-trimethylsilylphenyl)tin	343–345[h]	58	$C_{36}H_{52}Si_4Sn$	Si Sn	15.7 16.6	15.5, 15.6 16.6, 16.0

[a] Reaction carried out at 0 to 25°. [b] Recrystallized from absolute ethanol. A mixed melting point between these compounds was depressed.[c] A mixture of the *o*-, *p*- and *m*-isomers has been reported previously by H. A. Clark, U. S. Patent **2,507,515** [*Chem. Abstr.*, **45**, 2197 (1951)]; Brit. Patent **669,179** [*Chem. Abstr.*, **46**, 8894 (1952)].[d] Reaction carried out at reflux temperature. [e] Recrystallized from absolute ethanol–chloroform (2:1) and from absolute ethanol–methyl ethyl ketone (2:1). [f] The ether was distilled off and replaced by toluene at reflux temperature. [g] The crude product was freed from a less soluble impurity by extraction with a minimum volume of cold benzene, and then was recrystallized from benzene–absolute ethanol. [h] Recrystallized from absolute ethanol–benzene (1:1) and from petroleum ether (b.p. 100–120°).

The last three compounds (Table I), which differ only in the central atom, have nearly the same melting points. When these compounds are admixed in pairs the melting points are not depressed below those of the lower melting components. Presumably they constitute an isomorphic series. Similarly it has been reported[1] that mixtures of tetraphenylsilane and tetraphenylgermane show no depression in melting point, although mixtures of tetraphenylgermane and tetraphenyltin do show a slight depression.

EXPERIMENTAL[2]

Diphenylbis(p-trimethylsilylphenyl)silane. *p*-Trimethylsilylphenyllithium[3] was prepared by adding 22.9 g. (0.1 mole) of trimethyl(*p*-bromophenyl)silane[4] in 100 ml. of ether to 1.8 g. (0.26 g.-atom) of lithium in 140 ml. of ether during 90 min. under spontaneous reflux. The yield was 80%, determined by titration of the total base formed on hydrolysis. The excess lithium was removed by filtration. A solution of 8.85 g. (0.035 mole) of diphenyldichlorosilane in 100 ml. of ether was added during 30 min. at 0 to 5°. The mixture was allowed to warm to room temperature during 30 min., by which time Color Test I[5] was negative. After hydrolyzing the reaction mixture with cold dilute sulfuric acid, the ether layer was separated, dried over sodium sulfate, and distilled, leaving a residue, which after crystallization from absolute ethanol melted at 160–163.5° and weighed 14.4 g. (86%). A second recrystallization gave 13.5 g. (80%) of crystals, m.p. 162.5–164.5°. The analytical sample melted at 163.5–165°.

Anal. Calcd. for $C_{30}H_{36}Si_3$: Si, 17.5. Found: Si, 17.4, 17.3.

Elementary analyses. It has been observed in this laboratory that silicon analyses performed by the sulfuric acid digestion procedure[6] give erratically low results with com-

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(1) H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.* 1480 (1935). It might be mentioned in this connection that Dr. T. C. Wu in this laboratory has observed that a mixture of all of the tetraphenyl derivatives of carbon, silicon, germanium, tin, and lead melted at 218–220°.

(2) Melting points are uncorrected. All operations involving organolithium compounds were carried out under an atmosphere of dry, oxygen-free nitrogen, in sodium-dried ethyl ether.

(3) Adapted from procedures kindly supplied by Dr. Horace W. Melvin of this laboratory.

(4) C. A. Burkhard, *J. Am. Chem. Soc.*, **68**, 2103 (1946); H. Gilman, H. W. Melvin, and J. J. Goodman, *J. Am. Chem. Soc.*, **76**, 3219 (1954).

(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(6) H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

pounds containing trimethylsilyl groups. This difficulty was not encountered with tetrakis(*p*-trimethylsilylphenyl)tin which was readily soluble in concentrated sulfuric acid. Nitric acid was added in small portions until oxidation was complete. Tin was determined by difference after volatilization from silica with ammonium iodide.[7]

The remaining four compounds, Table I, were analyzed by fusion with sodium peroxide in a Parr bomb.[8] The germanium in the Ge-Si compound volatilized as germanium tetrachloride incidental to the work-up of the fusion mixture.

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[7] E. R. Caley and M. G. Burford, *Ind. Eng. Chem., Anal. Ed.*, **8**, 114 (1936).

[8] F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *J. Am. Chem. Soc.*, **68**, 475 (1946).

Carbonation of Lithium Derivatives of Certain Quinolines and Isoquinolines

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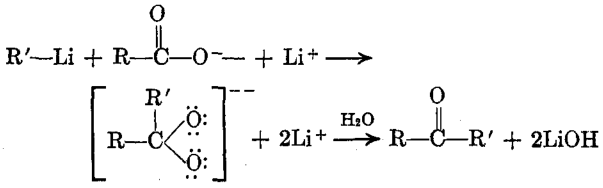
In a recent splendid investigation, Normant[1] found that excellent yields of the Grignard reagents could be obtained with alkyl and aryl chlorides by employing tetrahydrofuran as the solvent. This solvent has been used in this laboratory to include the preparation of phenyllithium from chloro- and fluoro benzene[2] with lithium wire, and 2-quinolyllithium from 2-bromoquinoline by menas of a halogen-metal interconversion reaction with *n*-butyllithium at −60°.

On carbonating 2-quinolyllithium, which was prepared in tetrahydrofuran, by pouring jet-wise onto a slurry of dry ice–tetrahydrofuran, the 2-quinolinecarboxylic acid was obtained in a yield of 50%. The same intermediate, however, when made in diethyl ether and carbonated by employing a dry ice–ether slurry, yielded 2,2′-diquinolyl ketone in 34% yield and a trace of acid. When this intermediate in diethyl ether was carbonated at −100°, both acid and ketone were obtained.

Ketone formation on carbonation of organolithium derivatives has been noted earlier.[3] This reaction has been shown to involve the initial formation of the carboxylic salt which is again attacked by the organolithium reagent.[4] The intermediate was found to be the dilithio ketal which resisted further substitution or loss of lithium oxide (I).[4]



$$R'\text{—}Li + R\text{—}\overset{O}{\overset{\|}{C}}\text{—}O^- + Li^+ \longrightarrow \left[R\text{—}\overset{R'}{\overset{|}{C}}\begin{matrix}\ddot{O}\!:\\ \ddot{O}\!:\end{matrix}\right]^{--} + 2Li^+ \xrightarrow{H_2O} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}R' + 2LiOH$$

I

Since the stability of the ketal was shown to be enhanced by the presence of electron-attracting groups,[5] the electrostatic effect of the nitrogen atom can be considered to have been involved in the stabilization of the quinolyl ketal. Further evidence in support of this hypothesis was the isolation of only the acids on carbonation of 3-quinolyl- and 4-isoquinolyllithium under the same conditions.

The greater basicity and solvating effect of tetrahydrofuran may have been responsible for reducing the effective formation of the intermediate ketal, thereby favoring the production of the acids in preference to the ketones.

2-Quinolyl- and 1-isoquinolyllithium have been prepared for the first time. The general procedure used was a low temperature halogen-metal interconversion reaction with *n*-butyllithium. Each of these organolithium compounds was characterized by a reaction with benzophenone to give the corresponding tertiary alcohols. 3-Quinolyllithium was reported earlier,[6] and 2-quinolylmagnesium bromide has been prepared with difficulty and in low yield.[7]

EXPERIMENTAL[8]

2-Quinolyllithium and α,α-diphenyl-2-quinolinemethanol. To a rapidly stirred solution of 0.025 mole of *n*-butyllithium in 50 ml. of anhydrous ether which was cooled by means of a dry ice–acetone bath to −50°, there was introduced very quickly 5.2 g. (0.025 mole) of 2-bromoquinoline. The color of the reaction mixture became yellow and, finally, dark red. Color Test II[9] was negative, but Color Test I[10] was positive within 15 min.

To the 2-quinolyllithium which was maintained at −50°, there was added 4.5 g. (0.025 mole) of benzophenone in 100 ml. of anhydrous ether. After 70 ml. of this solution had been added, Color Test I[10] was negative. The reaction mixture was dark brown in color and contained a yellow precipitate. After hydrolysis with saturated ammonium chloride solution, a solid which was insoluble in both the ether and water layer was separated by filtration. The yield of this crude product was 5.45 g. or 70% (m.p. 189–191°). The melting point of the purified compound which was crystallized from an ethanol-benzene solvent pair was 193.5–195.0°.

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[1] Normant, *Compt. rend.*, **239**, 1510 (1954).

[2] Oita, Doctoral Dissertation, Iowa State College, Ames, Iowa, March, 1955.

[3] Gilman and Van Ess, *J. Am. Chem. Soc.*, **55**, 1258 (1933).

[4] Bluhm, Donn, and Zook, *J. Am. Chem. Soc.*, **77**, 4406 (1955).

[5] Tegner, *Acta. Chem. Scand.*, **6**, 782 (1952).

[6] Gilman and Spatz, *J. Am. Chem. Soc.*, **63**, 1553 (1941).

[7] Wibaut and Herringa, *Rec. trav. chim.*, **74**, 1003 (1955).

[8] All melting points are uncorrected.

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

[10] Gilman and Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).