Anal. Calcd. for $(C_4H_8O_3Si)_x$: C, 36.3; H, 6.1; neut. equiv., 132. Found: C, 33.9; H, 6.2; neut. equiv., 130.

Stability of β-cyanoethyl(methyl)polysiloxane oil to silicon-carbon cleavage. Two grams (0.018 equivalent) of the β-cyanoethyl oil was refluxed with 50 ml. of 5% sodium hydroxide solution. Ammonia was evolved and the polymer had completely dissolved within 0.5 hr. After 24 hr. the solution was acidified with sulfuric acid (no odor of hydrogen cyanide), diluted to 200 ml., distilled, and the first 100-ml. portion of the distillate was titrated for propionic acid. Another 2-g. portion was refluxed for 24 hr. with 50 ml. of 5% sulfuric acid, diluted, distilled, and titrated. For comparison, 1-g. (0.018 mol.) samples of propionitrile were treated in the same manner.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Organosilicon Compounds. I. Synthesis of Some Long-Chain Tetraalkylsilanes[1]

HAROLD ROSENBERG, JAMES D. GROVES, AND CHRIST TAMBORSKI

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The preparation of several series of unsymmetrical tetraalkylsilanes and one series of mixed symmetrical tetraalkylsilanes by the reaction of the appropriate *n*-alkylchlorosilane with *n*-alkyllithium compounds is described. Certain of the physical properties of the products are presented and discussed. Many of the silanes synthesized exhibit extremely wide liquidus range and may be considered representative of a new class of thermally stable fluids.

A number of symmetrical tetraalkylsilanes of the type R_4Si[2–10] have been reported since Friedel and Crafts[11] first prepared tetraethylsilane in 1863. In connection with a program to develop high-temperature fluids, however, it was of interest to investigate the synthesis and properties of unsymmetrical and mixed symmetrical tetraalkylsilanes of the type $RSiR'_3$ and $R_2SiR'_2$ to determine the structural requirements for optimum liquidus range. Compounds representative of these two types have been previously prepared by the reactions of the Grignard reagents with alkylchlorosilanes,[12–15] by alkyllithium compounds with trialkylsilanes[16] and alkyllithium compounds with alkylalkoxysilanes.[17]

$$4-n\ \mathrm{RMgX} + \mathrm{R'}_n\mathrm{SiCl}_{4-n} \longrightarrow \mathrm{R}_n'\mathrm{SiR}\ 4-n + 4-n\ \mathrm{MgXCl}$$

$$\mathrm{RLi} + \mathrm{R'}_3\mathrm{SiH} \longrightarrow \mathrm{RSiR'}_3 + \mathrm{LiH}$$

$$4-n\ \mathrm{RLi} + \mathrm{R'}_n\mathrm{SiCl}_{4-n} \longrightarrow \mathrm{R'}_n\mathrm{SiR}_{4-n} + 4-n\ \mathrm{LiCl}$$

In an effort to extend the synthesis of both unsymmetrical ($RSiR'_3$) and mixed symmetrical ($R_2SiR'_2$) tetraalkylsilanes as classes, it was thought desirable to modify and combine the general methods of Bygden[12] and Gilman[16] in order to use the more reactive organolithium compounds (as compared to Grignard reagents) for obtaining increased yields with alkylchlorosilanes. Two series of long-chain tetraalkylsilanes of the type, $RSiR'_3$, and one series of the type, $R_2SiR'_2$, were thus prepared by the reaction of an appropriate *n*-alkylchlorosilane with various *n*-alkyllithium compounds.

$$n\text{-}\mathrm{C_{12}H_{25}SiCl_3} + 3\text{-}\mathrm{RLi} \longrightarrow n\text{-}\mathrm{C_{12}H_{25}SiR_3} + 3\mathrm{LiCl}$$

$$n\text{-}\mathrm{C_{18}H_{37}SiCl_3} + 3\text{-}\mathrm{RLi} \longrightarrow n\text{-}\mathrm{C_{18}H_{37}SiR_3} + 3\mathrm{LiCl}$$

$$(n\text{-}\mathrm{C_{12}H_{25}})_2\mathrm{SiCl_2} + 2\text{-}\mathrm{RLi} \longrightarrow (n\text{-}\mathrm{C_{12}H_{25}})_2\mathrm{SiR_2} + 2\mathrm{LiCl}$$

For the present study, *n*-dodecyl and *n*-octadecyl were chosen as typical examples of long-chain moieties while normal alkyl groups of from one to eighteen carbon atoms in length (with the exception of $n\text{-}C_{13}H_{27}$, $n\text{-}C_{15}H_{31}$, and $n\text{-}C_{17}H_{35}$) were selected for the other alkyl substituents.

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(1) Presented in part before the Division of Organic Chemistry at the 126th National Meeting, American Chemical Society, New York, N. Y., September 1954.

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Di(*n*-dodecyl)dimethyl- and di(*n*-dodecyl)diethylsilane were prepared by a reverse procedure to that utilized for the synthesis of the other di(*n*-dodecyl)dialkylsilanes. Thus, dimethyldichloro- and diethyldichlorosilanes were treated with *n*-dodecyllithium to give the corresponding tetraalkylsilanes in excellent yields. Although not a tetraalkylsilane, one aryl derivative, di(*n*-dodecyl)diphenylsilane, was similarly obtained from diphenyldichlorosilane and the alkyllithium.

When isopropyllithium was treated with *n*-dodecyltrichlorosilane under more vigorous conditions than those which were normally used for the preparation of the other tetraalkylsilanes, a mixture of products was obtained and the desired *n*-dodecyltri(isopropyl)silane could not be isolated.[18] Similarly, the reaction of cyclohexyllithium with *n*-dodecyltrichlorosilane failed to yield the expected cyclohexyl derivative.[19]

The yields, physical properties and analytical data for the two series of unsymmetrical tetraalkyl silanes are presented in Table I. The yields of 65–96% were somewhat lower than those obtained for the synthesis of symmetrical tetraalkylsilanes,[20] but were definitely superior to those obtained for unsymmetrical tetraalkylsilanes by the Grignard method.[12,13] In the case of the mixed symmetrical tetraalkylsilanes, the yields, as shown in Table II, ranged for 61–90% and were similarly superior to those obtained by other workers for related compounds of this type.[12,15,17]

EXPERIMENTAL

Materials. The *n*-alkyllithium compounds were prepared from Distillation Products, Inc. White Label *n*-alkyl bromides with the exception of those synthesized from 1-bromononane and 1-bromohendecane. The 1-bromononane was obtained in 59% yield by a Hundsdiecker reaction from capric acid while the 1-bromohendecane was prepared from *n*-undecanol and phosphorus tribromide in 61% yield.

n-Dodecyltrichlorosilane. The method used was a modification of that used by Whitmore.[13] To 79 g. (3.3 mol.) of magnesium turnings in 1250 ml. of anhydrous ethyl ether was added dropwise with stirring 777 g. (3.0 mol.) of *n*-bromododecane. The reaction was initiated by the addition of a small amount of previously prepared ethylmagnesium bromide. The mixture was stirred for an additional hour after all of the halide had been added. The yield of *n*-dodecylmagnesium bromide was 74.2% as determined by acid titration.

To a stirred solution of 382.5 g. (2.25 mol.) of redistilled silicon tetrachloride in 2 l. of anhydrous ethyl ether was added dropwise the Grignard reagent prepared above. The mixture was refluxed 12 hr. and the magnesium salts were filtered. After removal of the ether by distillation, additional salts were precipitated and filtered. The residue was fractionated *in vacuo* through a 24-in. column, packed with glass helices, to give 453 g. (66.5%) of *n*-dodecyltrichlorosilane, b.p. 82°/0.15 mm., $n_{\rm D}^{25}$ 1.4522. This compares with the 29% yield (no refractive index) obtained by Whitmore[13] for this compound.

n-Octadecyltrichlorosilane. This compound was prepared in 51% yield by the same method used for the synthesis of *n*-dodecyltrichlorosilane. The physical properties were found to be in agreement with those obtained for the compound prepared by other procedures.

Di(n-dodecyl)dichlorosilane. The dialkyldichlorosilane starting material was prepared by a procedure similar to that described for the preparation of disubstituted dihalosilanes.[21] To 182 g. (1.07 mol.) of silicon tetrachloride in 1200 ml. of anhydrous ethyl ether contained in a 5-l., 3 necked round bottomed flask fitted with a condenser, stirrer, and dropping funnel was added dropwise a 2200 ml. ethereal solution containing 2.85 moles of *n*-dodecylmagnesium bromide. The Grignard reagent was added with stirring over a period of 7 hr. and then gently refluxed overnight with continued stirring. The mixture was then filtered with suction and the salts were washed several times with anhydrous ethyl ether. The washings were added to the filtrate. After removal of the ether, the residue was fractionally distilled through a 12-in. column packed with glass helices. There was obtained 78.8 g. (16.8%) of the product, di(*n*-dodecyl) dichlorosilane, as a colorless liquid, b.p. 192° (0.23 mm.), $n_{\rm D}^{25}$ 1.4600. If after one half the Grignard reagent is added, 1 hr. is allowed to elapse before the remainder is added dropwise, the yield of product can be increased to 40–50%.

n-Dodecyltrialkyl (I) *and n-Octadecyltrialkylsilanes* (II). The method for the preparation of both series is illustrated by the synthesis of *n*-dodecyltri(*n*-propyl)silane. To a solution of 0.82 mol. of *n*-propyllithium (prepared by the same general method[22] used for the *n*-dodecyllithium previously described) in 550 ml. of anhydrous ether and maintained under a nitrogen atmosphere, 75.8 g. (0.25 mol.) of freshly distilled *n*-dodecyltrichlorosilane in 100 ml. of anhydrous ether was added dropwise with stirring. A constant reflux temperature of 34–35° was maintained throughout the addition which was complete in 90 min. The reaction mixture was refluxed for 24 hr. and the unreacted lithium filtered off. The filtrate was poured over 600 g. of cracked ice and the resulting solution was neutralized with 3*N* hydrochloric acid. The ether layer was phase separated, the water layer extracted three times with ethyl ether, and the combined ether layer and extracts were dried over anhydrous calcium sulfate. Following removal of the solvent by distillation, fractionation of the yellow liquid residue through a 30-cm. short-path Vigreux column gave 66.2 g. (81.1%) of *n*-dodecyltri(*n*-propyl)silane, b.p. 88° (0.09 mm.), $n_{\rm D}^{25}$ 1.4504, d_4^{25} 0.8069. See Table I for analysis.

Di(n-dodecyl)dialkylsilanes (III). The method for the preparation of this series is illustrated by the synthesis of di(*n*-dodecyl)di(*n*-hexyl)silane. To a solution of 0.7 mol. of *n*-hexyllithium (prepared by the general procedure of Gilman and co-workers,[22] and the yield determined by the double titration method[23]) in 200 ml. of anhydrous ethyl ether was added dropwise with stirring 78.0 gm. (0.18 mol.) of di(*n*-

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[18] Gilman and Clark, *J. Am. Chem. Soc.*, **69**, 1499 (1947), reported they were unable to prepare tetra(isopropyl)silane from silicon tetrachloride and isopropyllithium.

[19] This result was not entirely unexpected since Nebergall and Johnson [W. H. Nebergall and O. H. Johnson, *J. Am. Chem. Soc.*, **71**, 4022 (1949)] were unable to replace the chlorine in tricyclohexylsilane with methyl and ethyl groups. This failure was apparently due to steric effects arising from the crowding of three cyclohexyl groups around the silicon atom. In the case of germanium, unlike silicon, alkyltricyclohexylgermanes may be prepared [O. H. Johnson and W. H. Nebergall, *J. Am. Chem. Soc.*, **71**, 1721 (1949)], presumably because of the increased size of the germanium atom.

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TABLE I

UNSYMMETRICAL TETRAALKYLSILANES, RSiR′$_3$

								Analyses[a]							
								MR$_D$		Carbon, %		Hydrogen, %		Silicon, %	
R	R′	Formula	Yield, %	B.P.	Mm.	n_D^{25}	d_4^{25}	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
n-$C_{12}H_{25}$	CH_3	$C_{15}H_{34}Si$	75	69	0.19	1.4350	0.7782	81.32	81.32	74.29	74.35	14.13	13.87	11.58	11.31
n-$C_{12}H_{25}$	C_2H_5	$C_{18}H_{40}Si$	96	95	0.20	1.4495	0.8038	95.26	95.06	75.96	76.07	14.17	13.98	9.87	9.59
n-$C_{12}H_{25}$	n-C_3H_7	$C_{21}H_{46}Si$	81	88	0.09	1.4504	0.8069	109.2	108.8	77.21	77.06	14.19	13.90	8.60	8.49
n-$C_{12}H_{25}$	n-C_4H_9	$C_{24}H_{52}Si$	79	98	0.05	1.4530	0.8095	123.1	123.1	78.17	79.09	13.22	13.73	7.62	7.30
n-$C_{12}H_{25}$	n-C_5H_{11}	$C_{27}H_{58}Si$	91	152	0.05	1.4548	0.8144	137.1	136.8	78.93	79.03	14.23	13.97	6.84	7.23
n-$C_{12}H_{25}$	n-C_6H_{13}	$C_{30}H_{64}Si$	87	165	0.07	1.4565	0.8170	151.0	150.8	79.56	79.82	14.24	13.95	6.20	6.38
n-$C_{12}H_{25}$	n-C_7H_{15}	$C_{33}H_{70}Si$	92	212	0.10	1.4584	0.8187	165.0	165.1	80.07	80.15	14.26	14.35	5.67	5.94
n-$C_{12}H_{25}$	n-C_8H_{17}	$C_{36}H_{76}Si$	95	221	0.15	1.4595	0.8224	178.9	178.7	80.50	80.60	14.26	14.30	5.23	5.22
n-$C_{12}H_{25}$	n-C_9H_{19}	$C_{39}H_{82}Si$	77	235	0.10	1.4600	0.8245	192.9	192.4	80.88	81.59	14.27	14.41	4.85	4.29
n-$C_{12}H_{25}$	n-$C_{10}H_{21}$	$C_{42}H_{88}Si$	95	240	0.03	1.4613	0.8255	206.8	206.6	81.20	81.37	14.28	14.53	4.52	4.81
n-$C_{12}H_{25}$	n-$C_{11}H_{23}$	$C_{45}H_{94}Si$	65	268	0.06	1.4619	0.8268	220.8	220.5	81.48	82.31	14.28	14.00	4.23	3.84
n-$C_{12}H_{25}$	n-$C_{12}H_{25}$	$C_{48}H_{100}Si$	90	280	0.13	1.4630	0.8276	234.7	234.4	81.73	81.83	14.30	14.31	3.98	4.21
n-$C_{12}H_{25}$	n-$C_{14}H_{29}$	$C_{54}H_{112}Si$	75	305	0.15	1.4638	0.8294	262.6	262.6	82.14	82.24	14.30	14.41	3.56	3.73
n-$C_{18}H_{37}$	n-C_6H_{13}	$C_{36}H_{76}Si$	79	209	0.04	1.4599	0.8263	178.9	178.0	80.50	80.71	14.26	14.20	5.23	5.22
n-$C_{18}H_{37}$	n-C_8H_{17}	$C_{42}H_{88}Si$	87	250	0.10	1.4618	0.8284	206.8	206.0	81.20	81.47	14.28	14.24	4.52	4.94
n-$C_{18}H_{37}$	n-$C_{10}H_{21}$	$C_{48}H_{100}Si$	93	283	0.10	1.4632	0.8294	234.7	234.3	81.73	81.65	14.30	14.45	3.98	4.12
n-$C_{18}H_{37}$	n-$C_{12}H_{25}$	$C_{54}H_{112}Si$	85	296	0.05	1.4640	0.8304	262.6	262.4	82.14	82.25	14.30	14.32	3.56	3.60
n-$C_{18}H_{37}$	n-$C_{14}H_{29}$	$C_{60}H_{124}Si$	81	323	0.10	1.4648	0.8321	290.5	290.1	82.48	82.50	14.31	14.26	3.22	3.18

[a] Analyses by Schwarzkopf Microanalytical Laboratories, Woodside, N. J.

TABLE II

DI(n-DODECYL)DIALKYLSILANES, (n-$C_{12}H_{25}$)$_2$SiR$_2$

							Analyses[a]							
							MR$_D$		Carbon, %		Hydrogen, %		Silicon, %	
R	Empirical Formula	Yield, %	B.P.	Mm.	n_D^{25}	d_4^{25}	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3	$C_{26}H_{56}Si$	88.5	177	0.12	1.4507	0.8064	132.4	132.4	78.69	78.75	14.27	14.12	7.08	7.19
C_2H_5	$C_{28}H_{60}Si$	83.0	197	0.17	1.4563	0.8159	141.7	141.6	79.15	79.22	14.24	14.09	6.61	6.80
n-C_3H_7	$C_{30}H_{64}Si$	88.2	208	0.50	1.4572	0.8181	151.0	150.8	79.55	79.52	14.24	14.00	6.20	6.00
n-C_4H_9	$C_{32}H_{68}Si$	81.5	185	0.05	1.4579	0.8192	160.3	160.2	79.91	80.19	14.26	13.96	5.84	5.63
n-C_5H_{11}	$C_{34}H_{72}Si$	75.0	202	0.08	1.4585	0.8204	169.6	169.4	80.22	80.29	14.26	13.95	5.52	5.56
n-C_6H_{13}	$C_{36}H_{76}Si$	61.0	209	0.04	1.4594	0.8212	178.9	178.9	80.50	80.61	14.26	14.00	5.23	5.39
n-C_7H_{15}	$C_{38}H_{80}Si$	82.8	228	0.15	1.4599	0.8211	188.2	188.2	80.76	80.74	14.27	14.11	4.97	5.18
n-C_8H_{17}	$C_{40}H_{84}Si$	73.0	256	0.12	1.4605	0.8261	197.5	197.3	80.99	14.27	14.27	14.17	4.74	4.74
u-C_9H_{19}	$C_{42}H_{88}Si$	77.3	263	0.06	1.4609	0.8250	206.8	206.6	81.20	81.27	14.28	14.34	4.52	4.76
n-$C_{10}H_{21}$	$C_{44}H_{92}Si$	75.5	259	0.25	1.4615	0.8259	216.1	215.9	81.39	81.44	14.28	14.15	4.33	4.71
n-$C_{12}H_{23}$	$C_{46}H_{96}Si$	80.0	260	0.04	1.4619	0.8266	225.4	225.2	81.57	81.72	14.29	14.26	4.15	4.24
n-$C_{12}H_{25}$	$C_{48}H_{100}Si$	79.8	280	0.13	1.4622	0.8276	234.7	234.4	81.73	81.83	14.29	14.31	3.98	4.21
n-$C_{14}H_{29}$	$C_{52}H_{108}Si$	79.0	290	0.05	1.4635	0.8309	253.3	252.6	82.01	81.95	14.30	14.12	3.69	4.27
n-$C_{18}H_{37}$	$C_{60}H_{124}Si$	86.5	355	0.10	1.4648	0.8337	290.5	290.1	82.52	82.48	14.30	14.12	3.20	3.87

[a] Analyses by Schwarzkopf Microanalytical Laboratories, Woodside, N. J.

dodecyl)dichlorosilane in 100 ml. of anhydrous ethyl ether over a period of 2 hr. After the addition was completed the mixture was stirred for an additional hour and then refluxed overnight (*ca.* 20 hr.). The excess lithium particles were filtered off with suction and the filtrate was poured slowly over ice to decompose the excess alkyllithium. The solution was then neutralized with 3*N* hydrochloric acid and the ether layer phase separated. The water layer was extracted three times with 100 ml. of ethyl ether and the extracts, together with the ether layer, were dried over anhydrous calcium sulfate. After removal of the ether by distillation, fractionation of the liquid residue through a 30-cm. short-path Vigreux column gave 59.1 gm. (61.0%) of the product, b.p. 209° (0.04 mm.), n_D^{25} 1.4594, d_4^{25} 0.8212. See Table II for analysis.

Di(n-dodecyl)diphenylsilane. This aralkyl derivative, as well as the corresponding dimethyl and diethyl derivatives, was prepared by the reverse reaction of that used for the preparation of the di(*n*-dodecyl)dialkylsilanes. Thus, 127.0 g. (0.5 mol.) of diphenyldichlorosilane was added dropwise to an ether solution of 1.4 mol. of *n*-dodecyllithium (prepared by the same procedure used for the *n*-hexyllithium described above) over a period of 4 hr. The mixture was stirred for an additional hour and the unreacted lithium metal and salts were removed by suction filtration. The filtrate was treated in the same manner as described in the preparation of the di(*n*-dodecyl)di(*n*-hexyl)silane. The product was obtained, upon fractional distillation through a glass helices-packed column, as a colorless liquid, weighing 17.4 g. (79.1%), b.p. 216° (0.05 mm.), n_D^{25} 1.5053, d_4^{25} 0.9023.

Anal. Calcd. for $C_{36}H_{60}Si$: Si, 5.39; MR_D, 171.45. Found, Si, 5.68; MR_D, 171.30.

Acknowledgment. The authors gratefully acknowledge the technical assistance of Dr. Marvin Rausch in this investigation.

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER]

Organosilicon Compounds. II. 1,1-Disubstituted Silacyclohexanes

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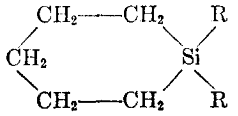
1,1-Disubstituted-silacyclohexanes were prepared by the reaction of 1,1-dichlorosilacyclohexane with an alkyl- or aryllithium compound. Attempts to effect cyclization of 1,5-dilithiopentane and a dialkyl(or diaryl)dichlorosilane were unsuccessful. Certain physical properties of the 1,1-dialkylsilacyclohexanes are presented.

In the first paper of this series,[1] the preparation and properties of two classes of long-chain tetraalkylsilanes were reported as part of a program on thermally stable fluids in which various properties of different types of organosilanes were correlated with molecular structure. The present paper describes the synthesis and properties of a series of cyclic organosilicon compounds, the 1,1-disubstituted-silacyclohexanes. In this class of compounds, represented by I, silicon is contained in a six-membered ring in which two alkyl or aryl groups are attached to the heterocyclic atom.



I

A review of previous attempts to prepare cyclic organosilicon compounds is contained in a paper by West.[2] The first 1,1-disubstituted-silacyclohexane to be prepared was reported by Bygden[3] more than forty years ago. He synthesized 1,1-dimethylsilacyclohexane by reacting methylmagnesium bromide with 1,1-dichlorosilacyclohexane, which was prepared from the Grignard reagent of 1,5-dibromopentane and silicon tetrachloride.

$$BrMg(CH_2)_5MgBr + SiCl_4 \longrightarrow (CH_2)_5SiCl_2 + 2MgBrCl$$

$$(CH_2)_5SiCl_2 + 2CH_3MgBr \longrightarrow (CH_2)_5Si(CH_3)_2 + 2MgBrCl$$

This compound was also prepared by West[2] in somewhat greater yield (72%) by the reaction of 1-chloro-1-methylsilacyclohexane with the Grignard reagent obtained from methyl iodide. The only other compound of this type described in the literature is the diethyl derivative of I, 1,1-diethylsilacyclohexane.[4] This was apparently prepared through a Wurtz type reaction in which a mixture of 1,5-dibromopentane and diethyldichlorosilane was treated with sodium metal. However, no details of the synthetic procedure used, yield

$$Br(CH_2)_5Br + (C_2H_5)_2SiCl_2 + 2Na \longrightarrow (CH_2)_5Si(C_2H_5)_2 + 2NaCl$$

obtained, or physical properties of the product were reported.

Bygden[3] also attempted the preparation of the diethyl derivative by the reaction of the Grignard reagent of 1,5-dibromopentane and diethyldichlorosilane but failed to obtain a pure product.

In the present work, a series of alkyl derivatives of I was prepared in good yield by the reaction of 1,1-dichlorosilacyclohexane with an alkyllithium in a 1 to 2 molar ratio:

$$(CH_2)_5Si(Cl)_2 + 2RLi \longrightarrow I + 2LiCl$$

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[1] H. Rosenberg, J. D. Groves, and C. Tamborski, *J. Org. Chem.*, **25**, 243 (1960).

[2] R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

[3] A. Bygden, *Ber.*, **48**, 1236 (1915).

[4] G. Gruttner and M. Wiernik, *ibid.*, **48**, 1474 (1915).