Silicon Heterocyclic Compounds. I. Synthesis of the 3-Sila-1-heterocyclohexanes[1]

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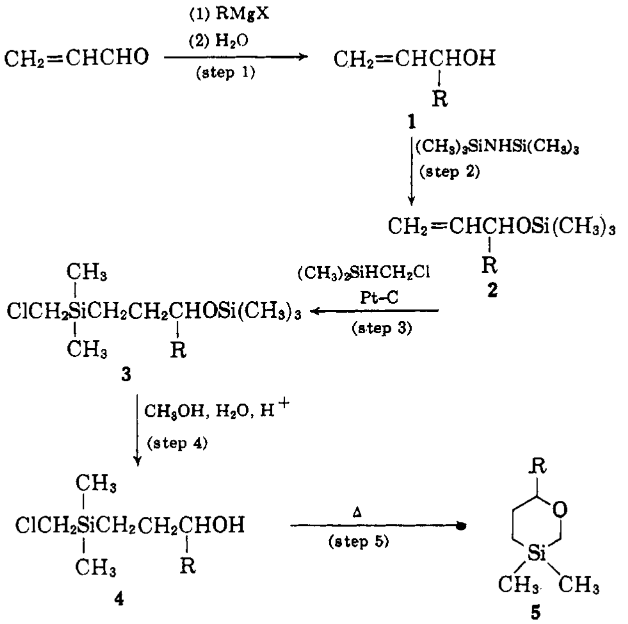
A series of 1-sila-3-heterocyclohexanes of the general formula $(CH_3)_2\overline{SiCH_2CH_2CH(R)ZCH_2}$ where R is H and Z is O (**5**), $SiCl_2$ (**7**), S (**8**), and n-$C_4H_9N \cdot HBr$ (**9**) have been synthesized. The 6-alkyl derivatives (R = CH_3, C_2H_5, and C_3H_7) were prepared in the case where Z = O. Compound **5** (R = H) was prepared by the following sequence, starting with allyl alcohol (**1**). Reaction of **1** and $[(CH_3)_3Si]_2NH$ gave $CH_2{=}CHCH(R)OSi(CH_3)_3$ (**2**). Condensation of **2** with $(CH_3)_2SiH(CH_2Cl)$ using platinum on carbon as catalyst gave $ClCH_2Si(CH_3)_2CH_2CH_2CH(R)OSi(CH_3)_3$ (**3**). Cleavage of **3** to $ClCH_2Si(CH_3)_2CH_2CH_2CH(R)OH$ (**4**) was carried out by refluxing with acid and methanol. Atmospheric distillation of **4** yielded **5**. In the cases of R = CH_3, C_2H_5, and C_3H_7, the starting alcohol, $CH_2{=}CHCH(R)OH$ (**1**), was prepared from acrolein and the corresponding Grignard reagent. The other members of the series were prepared from $XCH_2Si(CH_3)_2CH_2CH_2CH_2X$ (**6**). Reaction of **4** with $SOCl_2$ gave **6a**, X = Cl, and cleavage of **5** with hydrobromic and sulfuric acids gave **6b**, X = Br. Treatment of the di-Grignard reagent of **6a** with $SiCl_4$ gave **7**. Reaction of **6b** with Na_2S gave **8** and with n-butylamine gave **9**.

There has been an expanding interest in silicon heterocyclic chemistry. In general, the reports have concerned themselves with the syntheses and properties of the silacyclohexanes and related silacycloalkanes.[2] Silaheterocycles which contain another heteroatom in the ring are well known.[3] With the exception of systems such as phenoxsilins,[4] these dihetero ring systems generally are of the type which contain the silicon adjacent to the other heteroatom.[5] As a consequence, these silaheterocyclic compounds exhibit a chemistry similar to that of their open-chain analogs. Simple heterocyclic systems in which a silicon atom and another heteroatom are separated by at least one methylene group have not been reported.[6] Extrapolating from the chemistry of carbon-functional organosilicon compounds,[7] one would expect that this type of heterocyclic compound would exhibit interesting chemical properties.

This report is concerned with the synthesis of a series of 1-sila-3-heterocyclohexanes. Subsequent reports will deal with the preparation of the corresponding silaheterocycloheptanes, the limitations of the synthetic method, as well as the chemistry, spectra, and physical properties of these new heterocyclic compounds.

The synthetic route used for the preparation of 3,3-dimethyl-3-sila-1-oxacyclohexane (**5**, R = H) and the 6-alkyl silaoxacyclohexanes (**5**) is shown in Chart I.

CHART I



The synthesis of the parent member of this series, 3,3-dimethyl-3-sila-1-oxacyclohexane (**5**, R = H), was carried out with isolation and characterization of each intermediate. In the preparations of the 6-alkyl derivatives (**5**, R = CH_3, C_2H_5, C_3H_7), only the ring-closed products were characterized.

In the synthesis of **5**, R = H, the starting material was allyl alcohol. Because a silicon hydride reacts with an alcohol in the presence of a catalyst,[8] it was necessary to protect the hydroxyl group prior to step 3. The trimethylsiloxyl group was chosen as blocking group on the basis of its ease of formation by treatment of the alcohol with hexamethyldisilazane,[9] its ease of removal,[10] and its inertness to a silicon hydride in the presence of platinum on carbon.[11] In the reaction with allyl alcohol, the hexamethyldisilazane was freshly prepared from trimethylchlorosilane and ammonia in petroleum ether (b.p. 30-60°).[12] After filtration of the ammonium chloride, this solution was used directly. For the other alcohols (**1**), freshly distilled hexamethyl-

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(1) This work was supported by a grant (GP-315) from the National Science Foundation.

(2) (a) R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954); (b) **76**, 6015 (1954); (c) R. A. Benkeser and E. W. Bennett, *ibid.*, **80**, 5414 (1958); (d) G. D. Oshesky and F. F. Bentley, *ibid.*, **79**, 2047 (1957).

(3) (a) J. W. Curry, *ibid.*, **78**, 1686 (1956); (b) L. H. Sommer and O. F. Bennett, *ibid.*, **79**, 1009 (1957); (c) R. W. West, *ibid.*, **77**, 2339 (1955); (d) L. H. Sommer and G. A. Baum, *ibid.*, **76**, 5002 (1954); (e) W. H. Knoth and R. V. Lindsey, *J. Org. Chem.*, **23**, 1392 (1958); (f) W. H. Knoth and R. V. Lindsey, *J. Am. Chem. Soc.*, **80**, 4106 (1958); (g) K. A. Andrianov and S. E. Yakushkina, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1396 (1962); *Chem. Abstr.*, **58**, 2466 (1963); (h) G. Fritz and G. Teichmann, *Ber.*, **95**, 2361 (1962); (i) N. S. Nametkin and A. V. Topchiev, *Issled. v Obl. Kremniiorgan. Soedin. Sinez i Fiz.-Khim. Svoistva Akad. Nauk SSSR Inst. Neftekhim. Sinteza Sb. Statei*, 190 (1962); *Chem. Abstr.*, **58**, 6852 (1963); (j) K. A. Andrianov, V. I. Pakhomov, and N. E. Lapteva, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 2039 (1962); *Chem. Abstr.*, **58**, 9112 (1963); (k) N. Wieber and N. Schmidt, *Ber.*, **96**, 1019 (1963); (l) H. Niederpruem and W. Simmler, *ibid.*, **96**, 965 (1963).

(4) D. Wittenberg, H. A. McNinch, and H. Gilman, *J. Am. Chem. Soc.*, **80**, 5418 (1958).

(5) Ref. 3e and f.

(6) The syntheses of disilacycloalkanes have been reported; see ref. 3e, h, i, and l.

(7) (a) C. Eaborn, "Organosilicon Compounds," Academic Press, Inc., New York, N. Y., 1960, Chapter 14; (b) P. D. George, M. Prober, and J. R. Elliott, *Chem. Rev.*, **56**, 1065 (1956).

(8) Ref. 7a, p. 200 and 294, and the references therein.

(9) R. J. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961).

(10) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **19**, 441 (1954).

(11) Unpublished research, R. J. Fessenden.

(12) R. C. Osthoff and S. W. Kantor, *Inorg. Syn.*, **5**, 55 (1957).

disilazane was used. Hexamethyldisiloxane, the hydrolysis product of the disilazane,[13] was a contaminant in the lower boiling alkoxenylsilanes (**2**), but did not interfere with the condensation (step 3).

Step 3, the condensation of (chloromethyl)dimethylsilane with silyl-blocked alkenyl alcohols (**3**),[14] proceeded with substantial evolution of heat. With the lower boiling reactants and, in particular, with allyloxytrimethylsilane, the reaction proceeded with almost explosive violence. The procedure outlined in the Experimental has been used with safety in runs varying from 0.1 to 6.0 moles. In some runs, the catalyst failed, due to the presence of free alcohol in **2**, allowing a buildup of reactants, but addition of a new portion of catalyst (caution) resulted in continuation of the reaction.

The removal of the siloxyl-blocking group from **3** (step 4) was carried out in high yields (79–81%) by the "transesterification" reaction characteristic of alkoxy silanes.[15] A large excess of aqueous methanol with a trace of acid was used. The resulting methoxytrimethylsilane and hexamethyldisiloxane, as well as the excess methanol and water, were removed by distillation prior to water work-up and fractional distillation. The combination of steps 3 and 4, with filtration to remove the Pt–C prior to distillation, resulted in overall yields of 63 to 74%.

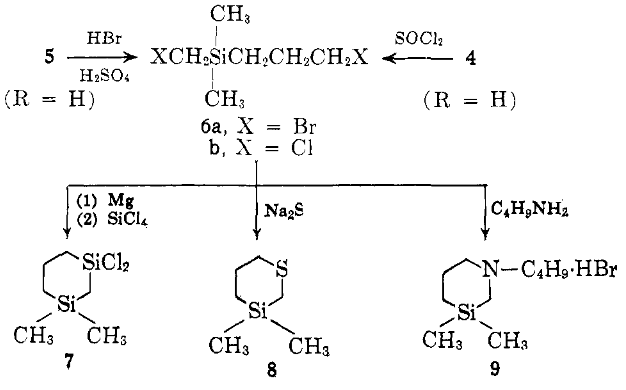
Substantial difficulty was encountered in obtaining an analytical sample of **4** (R = H) because of the tendency of this compound to undergo ring closure to **5**. The desired sample was obtained only after repeated vacuum distillation.

The ring **5** (R = H) was obtained in 54 to 58% yields by slow atmospheric distillation of **4**. The distillate was collected in a flask containing solid sodium carbonate to minimize the contact time of **5** with hydrogen chloride. With the 6-alkyl compounds, higher yields of the cyclic product were obtained: R = CH_3, 73%; R = C_2H_5, 81%; R = C_3H_7, 68%.

The syntheses of other 1-sila-3-heterocyclohexanes by extension of the synthetic scheme are summarized in Chart II. The preparation of the 6-alkyl derivatives of these rings was not attempted.

The key intermediate for the synthesis of 1,1-dichloro-3,3-dimethyl-1,3-disilacyclohexane (**7**), 3,3-dimethyl-3-sila-1-thiacyclohexane (**8**), and 3,3-dimethyl-3-sila-1-butyl-1-azacyclohexane hydrobromide (**9**) was the dihalogen compound, **6a** or **6b**. Compound **6a**, α-bromopropyl(bromomethyl)dimethylsilane, was obtained from **5**, R = H, in 73 to 83% yields using 48% hydrobromic acid and concentrated sulfuric acid. The procedure employed was developed for the conversion of tetrahydropyran to 1,5-dibromopentane[16] (80–82% yield). This reaction is indicative that **5** should show a chemistry similar to that of tetrahydropyran.

CHART II



Compound **6b** was obtained in yields of 63 to 80% by treatment of **4**, R = H, with thionyl chloride, followed by distillation of the crude reaction mixture at atmospheric pressure. The classical procedures[17] gave substantially lower yields (32–40%).

A Grignard ring-closure reaction was used to obtain compound **7**. The di-Grignard reagent of **6a** was prepared in the usual manner,[18] and the ring closure was carried out using inverse addition. The work-up procedure described in the Experimental is a modification of that employed by West for the synthesis of 1,1-dichlorosilacyclohexane (51% yield).[19] Compound **7** was obtained from this reaction in 42 to 50% yields.

The silathiacyclohexane **8** was prepared in 69% yield from **6a** and in 47% yield from **6b**. The procedure used was that of Tarbell,[20] which was developed for the synthesis of tetramethylene sulfide (64% yield).

The reaction of **6a** with *n*-butylamine, spontaneous and exothermic, gave the ring **9** in 51% yield. No attempt has yet been made to prepare other 1-alkyl derivatives of **9**. All attempts to synthesize the parent 3-sila-1-azacyclohexane have met with failure.

Experimental[21]

Silaoxacyclohexanes. (Chloromethyl)dimethylsilane.—To 37.9 g. (1.0 mole) of lithium aluminum hydride in 1 l. of anhydrous ether was added dropwise with cooling, over a period of 1 hr., 429 g. (3.0 moles) of (chloromethyl)dimethylchlorosilane (b.p. 115–117°). After the addition had been completed, the reaction mixture was heated at reflux for 1 hr., then cooled and filtered, using suction and Filter-Cel, to remove the insoluble inorganic salts. The clear filtrate was returned to the reaction flask and water was added (vigorous reaction). After the reaction had subsided, the resulting white salts were decomposed using dilute hydrochloric acid, and finally the reaction mixture was made neutral using sodium bicarbonate solution. The ethereal layer was separated, the aqueous layer was extracted with two 200-ml. portions of ether. The ethereal extracts were combined and dried with magnesium sulfate. Distillation

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(13) R. O. Sauer and R. H. Hasek, *J. Am. Chem. Soc.*, **68**, 241 (1946).

(14) That the direction of addition of the silicon hydride to the double bond is as indicated is shown by the stability of the resulting alcohol to refluxing acid. If the addition had occurred in the reverse direction, the product of step 5 would have been a β-hydroxyalkyl silane [*i.e.*, Cl—$CH_2Si(CH_3)_2CH(CH_3)CH_2OH$] which would be expected to be acid unstable [F. C. Whitmore, L. H. Sommer, J. R. Gold, and R. E. Van Strein, *ibid.*, **69**, 1551 (1947)]. Further evidence for the structure assignment is found in the n.m.r. spectrum of **4**, R = H, which shows an ill-defined pentuplet at δ 1.65 (—CH_2—$\mathit{CH_2}$—CH_2—) and a triplet at 0.20 (Si-$\mathit{CH_2}$—CH_2—). The areas under these two peaks were in the ratio of 2:2, in agreement with structure **4**.

(15) Ref. 10.

(16) D. W. Andrus, *Org. Syn.*, **23**, 67 (1943).

(17) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, p. 269, and the references cited therein.

(18) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice Hall, Englewood Cliffs, N. J., 1962, p. 449.

(19) Ref. 2a.

(20) D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, **63**, 2939 (1941).

(21) All boiling points are uncorrected. Distillations, unless otherwise noted, were made at atmospheric pressure using a 3-ft. modified Podbielniak column (*cf.* ref. 18, p. 237). The infrared spectra were recorded using a Beckman IR-4 spectrophotometer. The n.m.r. data were obtained using a Varian A-60 instrument, carbon tetrachloride solution with TMS as internal reference. The carbon, hydrogen, chlorine, and nitrogen analyses were performed by the Berkeley Microanalytical Laboratory. Silicon analyses were performed in this laboratory.

yielded 223 g. (69%) of (chloromethyl)dimethylsilane, b.p. 80–82°, n^{25}D 1.4182; lit.[22] b.p. 81°, n^{25}D 1.4165. The yields varied from 60 to 73%.

Allyloxytrimethylsilane.—Ammonia gas was passed through a solution of 364 g. (8.4 moles) of trimethylchlorosilane dissolved in 2.4 l. of petroleum ether (b.p. 30–60°) until the reaction vessel became cool to the hand. The addition of the ammonia required approximately 5 hr. The mixture was then filtered to remove the ammonium chloride, and the filter cake was washed thoroughly with petroleum ether to remove any hexamethyldisilazane. To the filtrate, containing crude hexamethyldisilazane and petroleum ether, was added 370 g. (6.4 moles) of allyl alcohol. The mixture was heated at reflux for 24 hr. and then distilled without further work-up to yield 568 g. of allyloxytrimethylsilane, b.p. 100°, n^{24}D 1.3950; lit.[23] b.p. 100°, n^{30}D 1.3905. The yields varied from 61 to 86%. Gas phase chromatography of the alloxytrimethylsilane indicated that it contained approximately 3% hexamethyldisiloxane (b.p. 100°). No attempt was made to further purify the alloxytrimethylsilane.

γ-(Trimethylsiloxy)propyl(chloromethyl)dimethylsilane.—To a 1-l. flask containing 0.1 g. of Pt–C (5%) was added 50 g. of a mixture of 202.3 g. (1.89 moles) of (chloromethyl)dimethylsilane and 245.3 g. (1.89 moles) of allyloxytrimethylsilane. The mixture was heated to about 80°, at which point a very vigorous reaction ensued (caution). After the reaction had subsided, the remaining mixture of reactants was added dropwise while the temperature of the reaction mixture was maintained at greater than 120°. In some runs, the addition of another 0.1 g. of Pt–C (caution) was required to maintain the temperature of the reaction. The addition of the reactants required about 1 hr. After the addition had been completed, the mixture was heated at reflux for 1.5 hr. During the reflux period, the reflux temperature rose from 130° to about 175°. The mixture was then cooled, filtered, and distilled. There was obtained 366 g. (81%) of γ-(trimethylsiloxy)propyl(chloromethyl)dimethylsilane, b.p. 222–225°, n^{25}D 1.4386.

Anal. Calcd. for $C_9H_{23}ClOSi_2$: C, 45.28; H, 9.64; Cl, 14.88. Found: C, 45.51; H, 9.66; Cl, 14.86.

Yields varied from 74 to 84%. The infrared spectrum showed the characteristic absorption bands at 8.0 (Si–CH$_3$) and 9.1 μ (Si–O–C).

γ-Hydroxypropyl(chloromethyl)dimethylsilane.—A mixture of 307 g. (1.29 moles) of γ-(trimethylsiloxy)propyl(chloromethyl)-dimethylsilane, 400 ml. of methanol, 80 ml. of water, and 4 ml. of 6 *N* sulfuric acid was heated at reflux for 15 min. The mixture then was distilled without further work-up, and material boiling up to 70° was discarded. The residue was diluted with 500 ml. of water and extracted with ether. Fractional distillation of the ethereal extracts resulted in 172 g. (81%) of γ-hydroxypropyl-(chloromethyl)dimethylsilane, b.p. 125° (30 mm.), n^{22}D 1.4662. The yields varied from 78 to 81%.

Gas phase chromatography indicated that the hydroxy compound was contaminated with a lower boiling material, shown later to be 3,3-dimethyl-3-sila-1-oxacyclohexane (**5**). An analytical sample was finally obtained after repeated distillation with b.p. 80° (3.0 mm.).

Anal. Calcd. for $C_6H_{15}ClOSi$: C, 43.24; H, 9.00; Cl, 21.40; Si, 16.8. Found: C, 43.12; H, 8.96; Cl, 21.52; Si, 16.7.

The infrared spectrum of the hydroxy compound was in agreement with the assigned structure, showing the expected bands at 3.0 (OH) and 8.0 μ (SiCH$_3$).

In other runs, the aqueous methanol and sulfuric acid were added directly to the crude γ-(trimethylsiloxy)propyl(chloromethyl)dimethylsilane reaction flask, the mixture was heated at reflux for 15 min., filtered to remove the Pt–C, and then distilled. The over-all yields based on allyloxytrimethylsilane and (chloromethyl)dimethylsilane ranged from 63 to 77%.

3,3-Dimethyl-3-sila-1-oxacyclohexane.—In a 1-l. round-bottomed flask was placed 500 g. (3.0 moles) of γ-hydroxypropyl-(chloromethyl)dimethylsilane, and the material was distilled at atmospheric pressure while the distillate was collected on solid sodium carbonate. The distillation was carried out over a period of 12 hr. The boiling point of the distillate was maintained between 120 and 135°. There remained after the distillation 165 g. of residue which was not characterized, but which was used for the preparation of compound **6b**. The distillate was washed with three 100-ml. portions of saturated sodium carbonate solution, dried with anhydrous sodium carbonate, then fractionally distilled to yield 215 g. (54%) of 3,3-dimethyl-3-sila-1-oxacyclohexane, b.p. 135–138°, n^{22}D 1.4444. The yields using this procedure varied from 46 to 57%.

Anal. Calcd. for $C_6H_{14}OSi$: C, 55.38; H, 10.77; Si, 21.54. Found: C, 55.65; H, 10.70; Si, 21.50.

6-Alkyl Silaoxacyclohexanes.—The following procedure was used to prepare the 6-alkyl 3,3-dimethyl-3-sila-1-oxacyclohexanes. In all cases, only the final silaoxacyclohexane was completely characterized.

Preparation of Alcohols.—To the alkyl Grignard reagent was added acrolein, and the reaction mixture was worked up in the standard fashion. Runs were carried out on a 4.0-mole basis. The yields and physical constants of the crude alcohols were 3-hydroxy-1-butene, 58%, b.p. 96–97°, lit.[24] b.p. 96–97°; 3-hydroxy-1-pentene, 43%, b.p. 112–114°, n^{25}D 1.4242, lit.[25] b.p. 114–114.5°; 3-hydroxy-1-hexene, 46%, b.p. 70–75° (150 mm.), n^{21}D 1.4295, lit.[26] b.p. 79–82° (100 mm.).

Preparation of Silyl-Blocked Alcohols.—Purified hexamethyldisilazane (b.p. 124–126°) was heated to reflux in a 1-l. round-bottomed flask, and the alcohol was added in small portions through the condenser. The addition for a 2.0-mole run required about 1 hr. After the mixture was heated at reflux for an additional 15 to 24 hr., the reaction mixture was distilled. The yields and physical constants of the crude siloxy derivatives were 3-trimethylsiloxy-1-butene, 91%, b.p. 107°, n^{27}D 1.3934; 3-trimethylsiloxy-1-pentene, 91%, b.p. 130°, n^{24}D 1.4047; 3-trimethylsiloxy-1-hexene, 63%, b.p. 151°, n^{24}D 1.4101.

Condensation with (Chloromethyl)dimethylsilane.—A mixture of the silyl-blocked alcohol and the (chloromethyl)dimethylsilane (0.5 to 1.0-mole runs) was made, and the procedure described for the preparation of γ-(trimethylsiloxy)propyl(chloromethyl)dimethylsilane was followed. After the reflux period, the reaction mixture was filtered, then an equal volume of aqueous methanol (15% water by volume) with a trace of hydrochloric acid was added. The mixture was heated at reflux for 0.5 hr., distilled at atmospheric pressure until distillation became difficult, then distilled at reduced pressure. The yields and physical constants of the crude hydroxy compounds were γ-hydroxybutyl(chloromethyl)dimethylsilane, 86%, b.p. 87° (2.8 mm.), n^{25}D 1.4618; γ-hydroxypentyl(chloromethyl)dimethylsilane, 82%, b.p. 92° (2.7 mm.), $n^{25.5}$D 1.4620; γ-hydroxyhexyl(chloromethyl)-dimethylsilane, 71%, b.p. 109–110°, n^{25}D 1.4620.

Ring Closure.—The ring-closure reactions of the γ-hydroxyalkyl (chloromethyl)silanes were carried out using the procedure as described for 3,3-dimethyl-3-sila-1-oxacyclohexane. The yields and physical properties are summarized in Table I.

TABLE I

YIELDS AND PHYSICAL PROPERTIES OF THE 6-ALKYL 3,3-DIMETHYL-3-SILA-1-OXACYCLOHEXANES

Compound	Yield, %	B.p., °C.	n^{25}D
6-Methyl-[a]	73	147–148	1.4394
6-Ethyl-[b]	81	163–169	1.4418
6-Propyl-[c]	68	190–191	1.4440

[a] *Anal.* Calcd. for $C_7H_{16}OSi$: C, 58.32; H, 11.10; Si, 19.50. Found: C, 58.12; H, 11.04; Si, 19.24. [b] *Anal.* Calcd. for $C_8H_{18}OSi$: C, 60.75; H, 11.38; Si, 17.76. Found: C, 60.73; H, 11.49; Si, 17.64. [c] *Anal.* Calcd. for $C_9H_{20}SiO$: C, 62.79; H, 11.63; Si, 16.29. Found: C, 62.89; H, 11.43; Si, 16.13.

Other Silaheterocyclohexanes. γ-Bromopropyl(bromomethyl)dimethylsilane.—A mixture of 32.5 g. (0.25 mole) of 3,3-dimethyl-3-sila-1-oxacyclohexane, 74 g. of concentrated sulfuric acid, and 253 g. of 48% hydrobromic acid was heated under reflux for 3 hr. and then cooled to room temperature. The reaction mixture was diluted with 100 ml. of water, and the organic material was extracted with 100 ml. of ether. The ethereal material was washed with two 50-ml. portions of saturated sodium bicarbonate solution and dried with magnesium sulfate. Fractional distillation yielded 52.7 g. (78%) of γ-bromopropyl-(bromomethyl)dimethylsilane, b.p. 103° (8.5 mm.), n^{24}D 1.5066.

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[22] (a) L. H. Sommer, W. P. Burie, and D. R. Wegenberg, *J. Am. Chem. Soc.*, **81**, 251 (1959); (b) R. Merker and M. J. Scott, *ibid.*, **81**, 975 (1959).

[23] E. Masuhara, K. Kojima, and N. Tarumi, *Skika Zairo Kenkyu-jo Hokoku*, **2**, 18 (1954); *Chem. Abstr.*, **52**, 1671 (1958).

[24] S. A. Morell and A. H. Auernheimer, *J. Am. Chem. Soc.*, **66**, 795 (1944).

[25] K. Rosenmund and H. Bach, *Ber.*, **94**, 2394 (1961).

[26] H. Normant, *Compt. rend.*, **240**, 314 (1955); *Chem. Abstr.*, **50**, 229 (1950).

Anal. Calcd. for $C_6H_{14}Br_2Si$: C, 26.28; H, 5.11; Br, 58.39. Found: C, 26.31; H, 5.31; Br, 58.28.

γ-Chloropropyl(chloromethyl)dimethylsilane. A.—To 29.7 g. (0.25 mole) of thionyl chloride was added in small portions (caution) 41.7 g. (0.25 mole) of γ-hydroxypropyl(chloromethyl)-silane. After the evolution of gases had subsided, the mixture was heated at reflux for 1 hr. and distilled without further work-up to yield 28.9 g. (63%) of the dichloro derivative, b.p. 212°, $n^{23}D$ 1.4656. Yields using this procedure varied from 63 to 80%. Reactions using pyridine as solvent gave yields ranging from 32 to 40%.

Anal. Calcd. for $C_6H_{14}ClSi$: C, 38.92; H, 7.56; Cl, 38.37. Found: C, 38.90; H, 7.54; Cl, 38.18.

B.—A mixture of 81.3 g. (0.685 mole) of thionyl chloride and 114 g. of the residue from the preparation of 3,3-dimethyl-3-sila-1-oxacyclohexane yielded, after a 3-hr. reflux and distillation, 100.8 g. of the dichloro derivative.

1,1-Dichloro-3,3-dimethyl-1,3-disilacyclohexane.—Using the general procedure as outlined by Cason and Rapoport,[18] the di-Grignard reagent of γ-bromopropyl(bromomethyl)dimethylsilane (54.2 g., 0.19 mole) was prepared using 9.2 g. (0.38 g.-atom) of magnesium turnings and 200 ml. of ether. The Grignard reagent was then transferred to a dropping funnel and added dropwise to a solution of 32.4 g. (0.19 mole) of silicon tetrachloride in 500 ml. of ether. The mixture was heated under reflux for 19 hr., then filtered with suction using Filter-Cel. The filtrate was distilled to yield 25.4 g. (62%) of the disilacyclohexane, b.p. 97° (20 mm.), $n^{23}D$ 1.4798. An analytical sample was obtained using a gas phase preparative column.

Anal. Calcd. for $C_6H_{14}Cl_2Si_2$: C, 33.80; H, 6.57. Found: C, 34.04; H, 6.55.

3,3-Dimethyl-3-sila-1-thiacyclohexane.—A mixture of 29.7 g. (0.104 mole) of γ-bromopropyl(bromomethyl)dimethylsilane, 26.2 g. (0.109 mole) of sodium sulfide, 50 ml. of water, and 200 ml. of ethanol was heated under reflux for 16 hr. The reaction mixture then was distilled to dryness. The first 75 ml. of the distillate, b.p. 79–81°, was diluted with water, and the oil which separated was extracted with 50 ml. of petroleum ether (b.p. 30–60°). A saturated solution of mercuric chloride was added to the remainder of the distillate until solid material ceased to form (*ca.* 1 l. was required). The solid mercuric salt was collected, washed with ethanol and water, then steam distilled. About 500 ml. of distillate was collected. The organic material was extracted from the distillate with petroleum ether (b.p. 30–60°). Combination of the extracts followed by drying over magnesium sulfate and distillation yielded 10.9 g. (69%) of the silathiacyclohexane, b.p. 181°, $n^{26}D$ 1.4978.

Anal. Calcd. for $C_6H_{14}SSi$: C, 49.31; H, 9.59; S, 21.91; Si, 19.17. Found: C, 49.53; H, 9.65; S, 21.62; Si, 19.19.

In a run using the same conditions except that γ-chloropropyl-(chloromethyl)dimethylsilane was used in place of the dibromo derivative, there was obtained a 47% yield of the silathiacyclohexane.

3,3-Dimethyl-3-sila-1-butyl-1-azacyclohexane Hydrobromide.—To 30.0 g. (0.11 mole) of γ-bromopropyl(bromomethyl)dimethylsilane was added 16.1 g. (0.22 mole) of *n*-butylamine. A spontaneous exothermic reaction occurred almost immediately, the temperature rising to 170°. After the reaction had subsided, the mixture was heated to 260°. Upon cooling, the mixture solidified. The solid was dissolved in boiling water, clarified with activated carbon, and crystallized, yielding 15.1 g. (52%) of the crude product. Recrystallization from ethanol (95%) gave an analytical sample, m.p. 210–211°.

Anal. Calcd. for $C_{10}H_{24}BrNSi$: C, 45.11; H, 9.02; N, 5.26; Si, 10.54. Found: C, 45.37; H, 8.88; N, 5.11; Si, 10.61.

Some Reactions of Carbomethoxymercuric Salts

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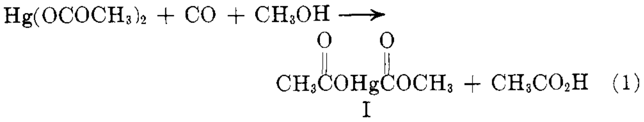
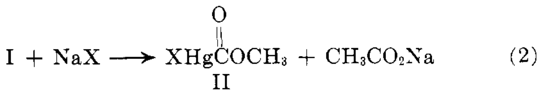
Carbomethoxymercuric acetate (I) yielded benzyl acetate and methyl benzyl ether when treated with excess benzyl bromide. Carbomethoxymercuric bromide (II, X = Br), mercurous bromide, and mercuric bromide were also isolated. On reaction with benzyl bromide, carbomethoxymercuric bromide yielded methyl benzyl ether, carbon monoxide, and mercuric bromide. Photochemical decomposition of carbomethoxymercuric iodide (II, X = I) in benzene solution afforded methyl benzoate and a compound tentatively identified as toluene. Reaction of a methanolic solution of I with ethylene yielded β-methoxyethylmercuric acetate.

A methanolic solution of mercuric acetate will react readily with carbon monoxide to form carbomethoxymercuric acetate (I) (eq. 1). Furthermore, the acetate group of I may be easily replaced by halide (eq. 2) to form compounds of structure II[2] (X = Cl, Br, or I). Although the structures for these compounds caused some controversy in the early literature,[2-5] a recent investigation by Halpern and Kettle[6] has proven structures I and II to be correct.



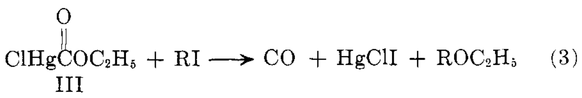
$$Hg(OCOCH_3)_2 + CO + CH_3OH \longrightarrow \underset{\text{I}}{CH_3\overset{O}{\overset{\|}{C}}OHg\overset{O}{\overset{\|}{C}}OCH_3} + CH_3CO_2H \quad (1)$$



$$\text{I} + NaX \longrightarrow \underset{\text{II}}{XHg\overset{O}{\overset{\|}{C}}OCH_3} + CH_3CO_2Na \quad (2)$$

Since the chemistry of this class of organomercury compounds appears to have been little studied, the reactions of I and II (X = Br) with benzyl bromide, the photochemical decomposition of II (X = I), and the reaction of I with ethylene were investigated. The results of these studies are herein reported.

Reaction with Benzyl Bromide.—In 1920, Manchot reported the reactions of methyl iodide with carbomethoxymercuric acetate (I) and *n*-propyl iodide with carbethoxymercuric chloride (III), although the structures he proposed for I and III were incorrect.[4] The former reaction was reported to yield carbon monoxide, mercuric iodide, and mercuric acetate, whereas carbon monoxide and mercury halides were isolated from the latter. Equation 3 was suggested to account for the latter reaction, although the ethyl ether apparently was not isolated.



$$\underset{\text{III}}{ClHg\overset{O}{\overset{\|}{C}}OC_2H_5} + RI \longrightarrow CO + HgClI + ROC_2H_5 \quad (3)$$

Since Manchot identified no organic compounds from his reactions, the reaction of compound I with an ex-

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(1) Northern Regional Research Laboratory, Peoria, Ill.

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(3) W. Schoeller, *ibid.*, **53**, 2144 (1920).

(4) W. Manchot, *ibid.*, **53**, 984 (1920).

(5) W. Manchot, *ibid.*, **54**, 571 (1921).

(6) J. Halpern and S. F. A. Kettle, *Chem. Ind.* (London), 668 (1961).