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# SILICON HETEROCYCLIC COMPOUNDS

# II*. THE SYNTHESIS OF MEDIUM SIZED SILACYCLOALKANES BY A MODIFIED CLEMMENSEN REDUCTION OF SILAACYLOINS

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## Summary

The compounds 1,1-dimethyl-1-silacyclooctane, 1,1-dimethyl-1-silacyclononane, 1,1-dimethyl-1-silacyclodecane and 1,1-dimethyl-1-silacycloundecane were prepared by a modified Clemmensen reduction of the corresponding silacycloacyloins.

## Introduction

Since only a small amount of 1,1-dimethyl-1-silacyclooctane and no 1,1-dimethyl-1-silacyclononane could be prepared by hydrosilation ring closure of 8-dimethylsilyl-1-octene [1], other methods of medium-ring product formation were investigated.

The preparation of various medium size silicon heterocyclic compounds has been rather extensively studied. Benkeser [2] and Weber [3] independently prepared seven-, eight-, and nine-membered silacycloalkanones by a modified acyloin condensation or a modified Dieckmann reaction of the corresponding silyl diesters. Later, Mazerolles and co-workers [4,5] reported the preparation of eleven-, twelve-, thirteen-, and fourteen-membered silacycloalkanones. However, little or no work has been concerned with the preparation of eight-, nine-, ten-, and eleven-membered silacycloalkanes.

## Result and discussion

Searching for an improved method to prepare silyl diesters a modified Reformatsky reaction of ethylbromoacetate with dimethyldichlorosilane in zinc dust was attempted. This was unsuccessful, which is in agreement with Fessenden's report [6].

It is well known that the ester group inhibits formation of the Grignard reagents of haloesters. However, Meyers and co-workers [7] have developed a

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* For part I see ref. 1.

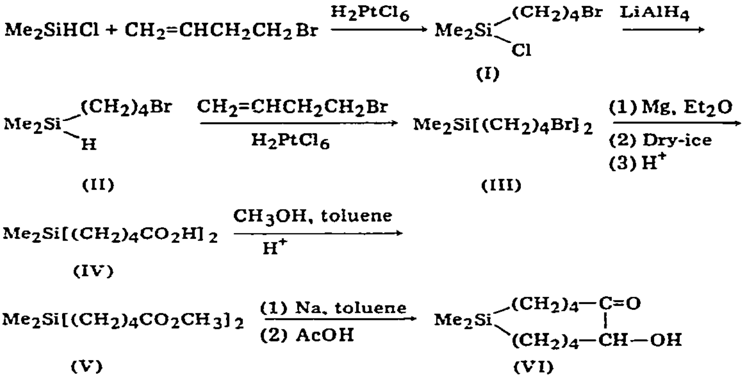
carboxyl protecting group, oxazolinyl, which is stable to Grignard reagent formation. Employing this idea, many attempts were made to prepare silyl diesters but all failed because of the formation of an *N*-silyl quarternary salt.

## Preparation of silacycloacyloins

Since no general method could be developed, several routes were used to obtain the diesters needed for the eight-, nine-, ten-, and eleven-membered silacycloacyloins.

Entry into the eleven-membered system was accomplished as shown in Scheme 1. This approach is similar to the one used by Mazerolles [4,8]. The diacid (IV) was not isolated, but was converted directly into its diester (V) by treatment with absolute methanol under acidic conditions. An acyloin ring closure of (V) then afforded 1,1-dimethyl-7-hydroxysila-6-cycloundecanone (VI) [4] in an over-all 8.8% yield.

SCHEME 1

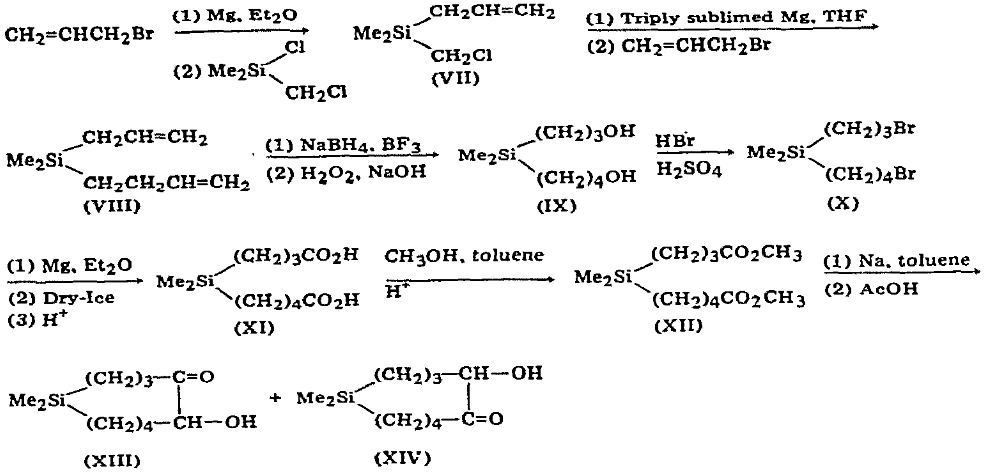


A synthetic route for preparing the ten-membered system, in 4.8% overall yield is shown in Scheme 2. Hydroboration of compound (VIII) [10] followed by oxidation with hydrogen peroxide in base gave the diol (IX) [3], which was not isolated but was converted directly into its dibromide (X) by treatment with 48% hydrobromic acid and concentrated sulfuric acid. The conversion of dibromide (X) into the desired silacycloacyloin isomers, 1,1-dimethyl-5-hydroxysila-6-cyclodecanone (XIII) and 1,1-dimethyl-6-hydroxysila-5-cyclodecanone (XIV) followed the route shown.

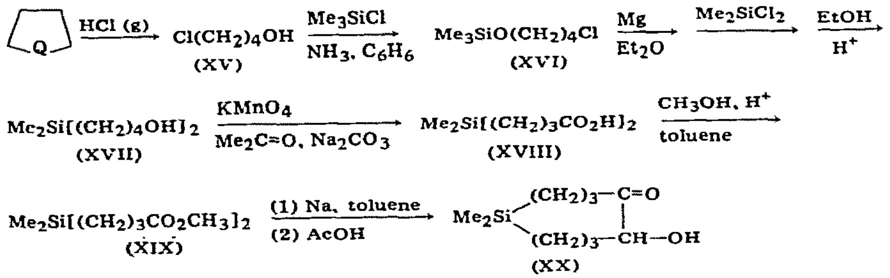
A modification of Benkeser's method [2] was used for synthesizing the nine-membered system, and is shown in Scheme 3. The diacid (XVIII) was obtained by permanganate oxidation of (XVII), and again without isolation, was converted directly into its diester (XIX) [2] by treatment with absolute methanol under acidic conditions. The acyloin ring closure of (XIX) gave 1,1-dimethyl-6-hydroxysila-5-cyclononanone (XX) [2] in an overall 1.6% yield.

A modification of Weber's method [3] was used for synthesizing the eight-membered system, as shown in Scheme 4. The diol (IX), obtained previously (Scheme 2) was converted into the desired silacycloacyloin isomers, 1,1-dimethyl-4-hydroxysila-5-cyclooctanone (XXIII) and 1,1-dimethyl-5-hydroxysila-4-cyclooctanone (XXIV), in 11.8% overall yield (from converted 3-bromo-1-propene).

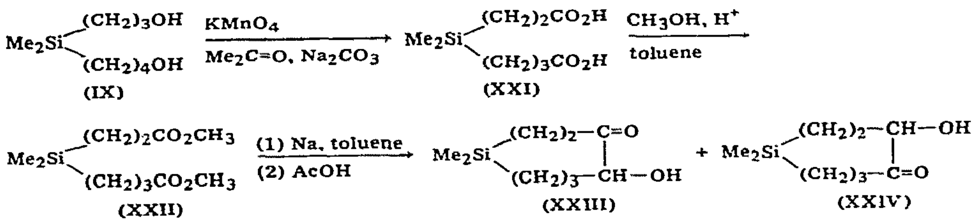
SCHEME 2



SCHEME 3



SCHEME 4

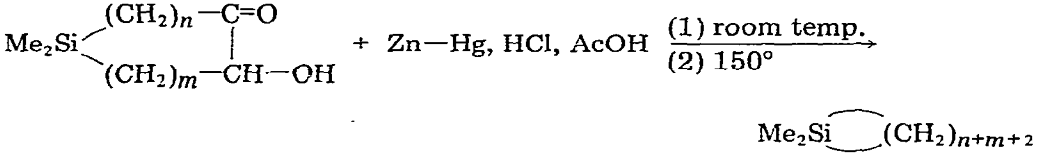


## Preparation of silacycloalkanes

Cope and co-workers [12] had reported that when sebacoin was reduced to cyclodecanone with zinc dust, glacial acetic acid, and concentrated hydrochloric acid, a considerable amount of cyclodecane was formed when the reaction temperature was over 80°. Allinger and Cram [13] have prepared *p,p'*-tetramethylene-1,5-dicyclohexylpentane by first refluxing 2-hydroxy-3-keto-*p,p'*-pentamethylene-1,4-dicyclohexylbutane with amalgamated zinc, concentrated hydrochloric acid, and acetic acid and followed by hydrogenation in the presence of platinum oxide catalyst. Based on the consumption of hydrogen, the acyloin was probably first reduced to the olefin at the reflux temperature of the reaction. Additionally, it is known that the carbonyl group of ketones or aldehydes can be reduced to the methylene group by Clemmensen reduction [14] using zinc amalgam and concentrated hydrochloric acid.

Considering the above findings, the conversion of silacycloacyloins to silacycloalkanes using a mixture of amalgamated zinc, concentrated hydrochloric acid and acetic acid was performed in two stages. Initially, the reaction was kept at room temperature for 48 h with the addition of 7 ml portions of concentrated hydrochloric acid at 12 h intervals. The purpose of this was to reduce the silacycloacyloin to silacycloalkanone and prevent the formation of olefin. After this, the reaction was kept at 150° for an additional 48 h to reduce the silacycloalkanone to silacycloalkane. The completion of the reaction could be easily determined by the disappearance of amalgamated zinc.

Under the conditions described above, 1,1-dimethyl-1-silacycloundecane (XXV), 1,1-dimethyl-1-silacyclodecane (XXVI), 1,1-dimethyl-1-silacyclononane (XXVII) and 1,1-dimethyl-1-silacyclooctane (XXVIII) were prepared.



(XXV) 61.5%, $n,m = 4$

(XXVI) 71.7% $\left\{ \begin{array}{l} n = 3, m = 4 \\ n = 4, m = 3 \end{array} \right.$

(XXVII) 66.0%, $n,m = 3$

(XXVIII) 74.5% $\left\{ \begin{array}{l} n = 2, m = 3 \\ n = 3, m = 2 \end{array} \right.$

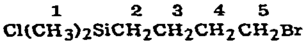
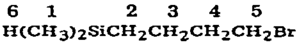
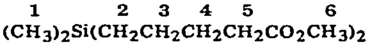
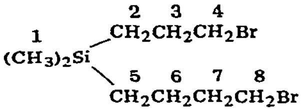
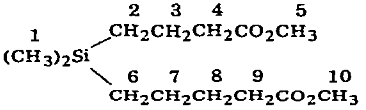
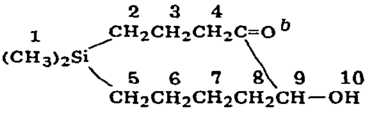
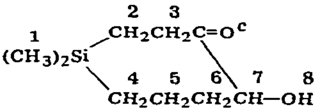
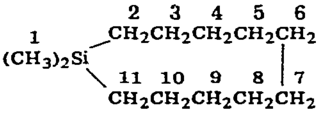
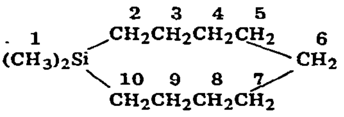
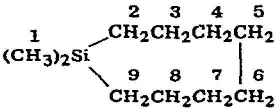
The two isomers, (XIII) and (XIV), were not separated since the Clemmensen reduction of these two isomers would give the same product (XXVI). Also, the two isomers, (XXIII) and (XXIV), were not separated for the same reason.

## Experimental

All boiling points reported here are uncorrected. All reaction products were identified by their NMR and IR spectra. The NMR spectra and the physical properties, including elemental analyses, of the new compounds are listed in Tables 1 and 2, respectively. The IR spectra were determined with a Perkin—Elmer Grating 457 Spectrophotomer. The NMR spectra were obtained with a Varian A-60 NMR Spectrometer. All elemental analyses are performed by M-H-W Laboratories, Garden City, Michigan.

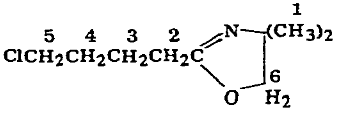
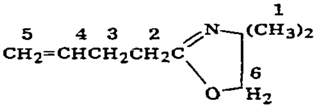
TABLE 1

NMR SPECTRA OF NEW COMPOUNDS[a]

| Compound | τ value |
|---|---|
|  $\overset{1}{\mathrm{Cl(CH_3)_2Si}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\overset{5}{\mathrm{CH_2Br}}$ (I) | 9.60 (s, $H^1$), 8.98-9.37 (m, $H^2$), 7.86-8.73 (m, $H^{3,4}$), 6.61 (t, J 6.5 Hz, $H^5$) |
|  $\overset{6}{\mathrm{H}}\overset{1}{\mathrm{(CH_3)_2Si}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\overset{5}{\mathrm{CH_2Br}}$ (II) | 9.97 (d, J 4 Hz, $H^1$), 9.18-9.60 (m, $H^2$), 7.85-8.78 (m, $H^{3,4}$), 6.65 (t, J 6.5 Hz, $H^5$), 6.07 (h, J 3.5 Hz, $H^6$) |
|  $\overset{1}{\mathrm{(CH_3)_2Si}}(\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\overset{5}{\mathrm{CH_2}}\overset{6}{\mathrm{CO_2CH_3}})_2$ (V) | 10.00 (s, $H^1$), 9.22-9.62 (m, $H^2$), 8.03-8.90 (m, $H^{3,4}$), 7.70 (t, J 6.5 Hz, $H^5$), 6.33 (s, $H^6$) |
|  (X) | 10.00 (s, $H^1$), 9.20-9.71 (complex, $H^{2,5}$), 7.87-8.87 (complex, $H^{3,6,7}$), 6.70 (t, J 7 Hz, $H^4$), 6.68 (t, J 7 Hz, $H^8$) |
|  (XII) | 10.02 (s, $H^1$), 9.25-9.67 (m, $H^{2,6}$), 8.08-8.97 (complex, $H^{3,7,8}$), 7.73 (t, J 6 Hz, $H^{4,9}$), 6.45 (s, $H^{5,10}$) |
|  (XIII) and (XIV) | 9.96-10.03 (m, $H^1$), 9.15-9.65 (complex, $H^{2,5}$), 7.33-8.83 (complex, $H^{3,4,6,7,8}$), 6.30 (broad singlet, $H^{10}$), 5.55-5.82 (complex, $H^9$) |
|  (XXIII) and (XXIV) | 9.95-10.05 (m, $H^1$), 9.00-9.55 (m, $H^{2,4}$), 7.10-8.35 (complex, $H^{3,5,6}$), 6.20 (broad singlet, $H^8$), 5.50-5.84 (complex, $H^7$) |
|  (XXV) | 10.05 (s, $H^1$), 9.19-9.60 (m, $H^{2,11}$), 8.60 (broad peak, $H^{3,4,5,6,7,8,9,10}$) |
|  (XXVI) | 10.06 (s, $H^1$), 9.32 (t, J 6 Hz, $H^{2,10}$), 8.53 (broad peak, $H^{3,4,5,6,7,8,9}$) |
|  (XXVII) | 9.96 (s, $H^1$), 9.12-9.46 (envelope, $H^{2,9}$), 8.50 (broad peak, $H^{3,4,5,6,7,8}$) |

(continued)

TABLE 1 (continued)

| Compound | $\tau$ value |
|---|---|
| <br>(XXIX) | 8.83 (s, $H^1$), 8.12-8.60 (m, $H^{3,4}$), 7.93 (t, $J$ 6 Hz, $H^2$), 6.65 (t, $J$ 6 Hz, $H^5$), 6.37 (s, $H^6$) |
| <br>(XXX) | 8.83 (s, $H^1$), 7.55-7.78 (complex, $H^{2,3}$), 6.18 (s, $H^6$), 4.78-5.20 (m, $H^5$), 3.80-4.48 (m, $H^4$) |

[a] Unless otherwise stated, these spectra were determined either with neat samples or in carbon tetrachloride with tetramethylsilane as internal standard. [b] The mixture of (XIII) and (XIV) were determined in deuteriochloroform solution. [c] The mixture of (XXIII) and (XXIV) were determined in deuteriochloroform solution.

The sources of the reagents were as follows: dimethylchlorosilane, dimethyldichlorosilane, chloromethyldimethylchlorosilane, and 4-bromo-1-butene, PCR Incorporated; 2-amino-2-methyl-1-propanol, Eastman Chemical Company; n-butyllithium, Lithium Corporation of America.

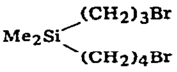
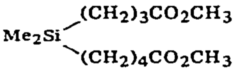
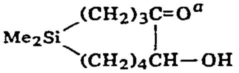
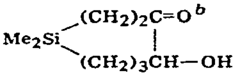
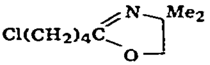
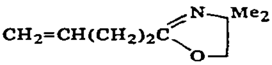
*Dimethylchloro(4-bromobutyl)silane (I).* To a 300 ml three-necked flask equipped with a pressure-equalizing dropping funnel, a magnetic stirrer, and a condenser with a calcium chloride drying tube, 100 ml of cyclohexane and a few drops of chloroplatinic acid (0.2 *M* in isopropyl alcohol) were added. An equimolar mixture of 20 g (0.15 mole) of 4-bromo-1-butene and 13.8 g (0.15 mole) of dimethylchlorosilane was added dropwise with stirring. After the addition, the reaction mixture was refluxed for 50 h. After the solvent had been distilled off, vacuum distillation of the residue afforded 20.73 g (61%) of product: b.p. 64—65° (2.5 mm); $n_D^{24}$ 1.4713; $\nu$(Si—$CH_3$) 1250 $cm^{-1}$ (in NaCl).

*Dimethyl(4-bromobutyl)silane (II).* In a 300 ml three-necked flask fitted with a pressure-equalizing dropping funnel, a magnetic stirrer and a condenser with a calcium chloride drying tube, 125 ml of ether and 1.15 g (0.03 mole) of lithium aluminum hydride were placed. To this flask 20.16 g (0.088 mole) of compound (I) was added dropwise with stirring. After the addition, the mixture was refluxed for 24 h, cooled, and poured into 200 ml of cold water. Dilute hydrochloric acid was added with stirring until the ether and aqueous layers were clearly separated. The aqueous layer was separated and extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and the ether was removed by aspirator. The residue was distilled under reduced pressure to give 14.0 g (81.5%) of product: b.p. 70—71° (18 mm); $n_D^{26}$ 1.4582; $\nu$(Si—H) 2120 and $\nu$(Si—$CH_3$) 1250 $cm^{-1}$ (in NaCl).

*Dimethylbis(4-bromobutyl)silane (III).* The apparatus and procedure were identical to that described for the preparation of (I) except 14.0 g (0.072 mole) of compound (II) and 9.68 g (0.072 mole) of 4-bromo-1-butene were used. Distillation of the residue under reduced pressure gave 17.5 g (73.5%) of product, b.p. 110—112° (0.05 mm), $n_D^{26}$ 1.4926 (lit. [8] b.p. 119° (0.4 mm), $n_D^{20}$ 1.4966).

TABLE 2

PHYSICAL PROPERTIES OF NEW COMPOUNDS

| Compound | | B.p. (°C/mm) | $n_D$ (°C) | Analysis, found (calcd.) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| $ClMe_2Si(CH_2)_4Br$ | (I) | 64-65 (2.5) | 1.4713 (24 | 31.55<br>(31.38) | 6.19<br>(6.14) | |
| $HMe_2Si(CH_2)_4Br$ | (II) | 70-71 (18) | 1.4582 (26) | 36.92<br>(36.92) | 8.00<br>(7.75) | |
| $Me_2Si[(CH_2)_4Br]_2$ | (V) | 105-106 (0.1) | 1.4460 (24) | 58.29<br>(58.29) | 9.93<br>(9.78) | |
|  $Me_2Si(CH_2)_3Br(CH_2)_4Br$ | (X) | 87-89 (0.05) | 1.4841 (27) | 34.46<br>(34.19) | 6.54<br>(6.38) | |
|  $Me_2Si(CH_2)_3CO_2CH_3(CH_2)_4CO_2CH_3$ | (XII) | 103-105 (0.2) | 1.4400 (32.4) | 56.78<br>(56.89) | 9.60<br>(9.55) | |
|  [a] | (XIII)<br>and<br>(XIV) | 84-88 (0.2) | 1.4804 (29) | 61.40<br>(61.63) | 10.40<br>(10.34) | |
|  [b] | (XXIII)<br>and<br>(XXIV) | 69-71 (0.45) | 1.4788 (33) | 57.88<br>(58.01) | 9.66<br>(9.74) | |
|  | (XXV) | 134 (23.5) | 1.4740 (27) | 72.60<br>(72.64) | 12.87<br>(13.21) | |
|  | (XXVI) | 122 (32) | 1.4682 (31) | 71.76<br>(71.65) | 13.09<br>(13.12) | |
|  | (XXVII) | 83 (17.5) | 1.4635 (22.3) | 70.35<br>(70.50) | 12.96<br>(13.02) | |
|  | (XXIX) | 77 (0.4) | | 56.78<br>(56.99) | 8.57<br>(8.50) | 7.49<br>(7.39) |
|  | (XXX) | 46-47 (3.7) | 1.4422 (20) | 70.74<br>(70.55) | 10.06<br>(9.87) | 9.29<br>(9.56) |

[a] The mixture of (XIII) and (XIV). [b] The mixture of (XXIII) and (XXIV).

*Dimethylbis(4-carbomethoxybutyl)silane (V).* A 300 ml three-necked flask equipped with a pressure-equalizing dropping funnel, a condenser with a calcium chloride drying tube, and a magnetic stirrer was flamed out under nitrogen. In the flask was placed 100 ml of ether and 4.69 g (0.19 g-atom) of magnesium turnings. To this was added 15.94 g (0.048 mole) of compound (III) dropwise with stirring. When formation of the Grignard reagent was complete, an excess of crushed Dry-ice was added in portions. The reaction mixture was then hydrolyzed by adding dilute hydrochloric acid until the layers were clearly separated. The aqueous layer was separated and extracted with ether. The combined ether solutions were extracted with 20% sodium hydroxide until the extract was basic. The basic solution was then acidified with 20% sulfuric acid and extracted with ether. After drying and removal of the ether, the crude diacid (IV) was then refluxed overnight in 100 ml of toluene with 100 ml of absolute methanol containing 0.5 ml of concentrated sulfuric acid. The volume was then reduced to one-third by distillation. The reaction mixture was then cooled, and extracted with ether. After drying and removal of the ether, the residue was distilled under reduced pressure to give 7.21 g [51.5% based on converted dibromide (III) of product: b.p. 105—106° (0.1 mm); $n_D^{24}$ 1.4460; $\nu$(C=O) 1740 and $\nu$(Si—$CH_3$) $cm^{-1}$ (in NaCl).

*Dimethylallyl(3-butenyl)silane (VIII).* A 500 ml three-necked flask was fitted with a condenser with a calcium chloride drying tube, a pressure-equalizing dropping funnel, a magnetic stirrer, and an inlet for nitrogen. To this flask 120 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride), 12.15 g (0.5 g-atom) of triply sublimed magnesium turnings, and several drops of methyl iodide were added. After the reaction was initiated, 63.4 g (0.427 mole) of dimethylallylchloromethylsilane (VII), prepared according to the method of Connolly [9], in 50 ml of dried tetrahydrofuran was added dropwise with stirring and refluxing under a nitrogen atmosphere. When one half of the solution had been added, the reaction mixture was diluted with 80 ml of dried tetrahydrofuran. After the addition was completed, the reaction mixture was stirred and refluxed overnight. It was then cooled, and poured through an L-shaped tube loosely plugged with glass wool into a pressure-equalizing funnel which was attached to an apparatus identical to that described above. In this flask 120 ml of dried tetrahydrofuran and 51.7 g (0.472 mole) of 3-bromo-1-propene were introduced. The Grignard reagent was added dropwise with stirring and refluxing. After the addition was completed, the reaction mixture was stirred and refluxed for 12 h. Following hydrolysis, drying, and removal of the ether, the residue was distilled under reduced pressure affording 47.5 g (72%) of product, b.p. 67—68° (30 mm), $n_D^{28}$ 1.4390 (lit. [10] b.p. 71—72° (40 mm), $n_D^{20}$ 1.4336).

*Dimethyl(3-hydroxypropyl) (4-hydroxybutyl)silane (IX).* This was prepared by the hydroboration with $NaBH_4$—$BF_3$ and then oxidation with $H_2O_2$ in NaOH of 15.8 g (0.1 mole) of compound (VIII). The residue was distilled under reduced pressure giving a 10 ml forerun of the mono-adduct, dimethyl-(3-butenyl) (3-hydroxypropyl)silane boiling at 75—76° (0.13 mm). The product itself was not isolated but was used in the next reaction.

*Dimethyl(3-bromopropyl) (4-bromobutyl)silane (X).* This was prepared by following the general method described by Kamm and Marvel [15]. To the above crude diol (IX) residue 42.9 g of hydrobromic acid (48%) and 8.01 ml of concentrated sulfuric acid were added. The mixture was refluxed for 6 h, then poured into 200 ml of cold water, and extracted with ether. The aqueous portion was saturated with ammonium sulfate, and again extracted with ether. The combined ether extracts were washed with saturated ammonium sulfate, and dried over anhydrous magnesium sulfate. After removal of ether, the residue was distilled under reduced pressure affording 12.4 g (39.2% based on converted diene (VIII)) of product: b.p. 87—89° (0.05 mm); $n_D^{27}$ 1.4841; $\nu$(Si—$CH_3$) 1255 $cm^{-1}$ (in NaCl).

*Dimethyl(3-carbomethoxypropyl) (4-carbomethoxybutyl)silane (XII).* The apparatus and procedure were the same as that described in the preparation of compound (V) except 13.71 g (0.043 mole) of compound (X) and 4.69 g (0.19 g-atom) of magnesium turnings were used. After the removal of ether, the residue was distilled under reduced pressure giving 5.02 g (42.2% based on converted dibromide (X) of product: b.p. 103—105° (0.2 mm); $n_D^{32}$ 1.4400; $\nu$(C=O) 1740 $cm^{-1}$ (in NaCl).

*Dimethylbis (3-carboxypropyl)silane (XVIII).* To the crude diol (XVII), made by Benkesers' method [2] from 14.5 g (0.08 mole) of trimethyl(4-chlorobutoxy)silane (XVI) was added 8 g (0.05 mole) of potassium permanganate, 0.05 g of sodium carbonate, and 125 ml of acetone. The reaction mixture was refluxed for 28 h, and then poured into 200 ml of cold water. Traces of permanganate were destroyed by adding sodium sulfite. Acetone removal was followed by ether extraction, leading to the recovery of a small amount of starting diol. The basic solution was then acidified with 20% sulfuric acid solution, and its ethereal extracts were dried over anhydrous magnesium sulfate. After the solvent was removed by aspirator, the crude diacid product (XVIII) was used in the next reaction without further purification.

*Dimethylbis(3-carbomethyoxypropyl)silane (XIX).* The above crude diacid (XVIII) was esterified by refluxing it with absolute methanol, toluene and a few drops of concentrated sulfuric acid to produce the product, b.p. 98—104° (0.23 mm), $n_D^{21.7}$ 1.4442 (lit. [2] b.p. 106—120° (0.5 mm), $n^{29.7}$ 1.4436). The yield was 2.13 g [20.5% based on 14.5 g of (XVI) converted to product].

*Dimethyl(2-carbomethoxyethyl) (3-carbomethyoxypropyl)silane (XXII).* This product was prepared from 15.2 g (0.098 mole) of dimethylallyl(3-butenyl)-silane (VIII). This compound (VIII) was first hydroborated using sodium borohydride—boron trifluoride and then oxidized with hydrogen peroxide in sodium hydroxide to the diol (IX), which was not isolated but converted directly to diacid (XXI) by the same procedure used to prepare compound (XVIII). Using the same esterification procedure previously described the crude diacid was converted into 9.36 g [38.6% based on 15.2 g of converted diene (VIII)] of diester, b.p. 94—97° (0.35 mm), $n_D^{30.8}$ 1.4402 (lit. [3] b.p. 105° (0.2 mm)).

*General procedure for acyloin ring closure.* A 300 ml three-necked flask was equipped with a condenser with a calcium chloride drying tube, a pressure-equalizing dropping funnel, a magnetic stirrer, and a nitrogen inlet. The system was heated and purged with dry nitrogen. There was then added 60 ml of toluene (purified by refluxing with sodium overnight and then distilled into the reaction vessel). The solvent was brought to reflux under nitrogen (some vapor was allowed to escape to remove residual moisture) and 1.6 g (0.07 g-atom) of sodium (cut into small pieces) was added to the flask. The molten sodium was dispersed by high-speed stirring while at reflux. To the solution was added 4.48 g (0.015 mole) of compound (V) in 15 ml of toluene over a 2 h period with stirring and refluxing. Stirring and refluxing were continued for 10 h longer. The reaction mixture was cooled in an icebath and hydrolyzed by adding 20 ml of a 1/1 acetic acid—toluene mixture with continued cooling and stirring, followed by 50 ml of water. The toluene layer was separated, and the aqueous layer was extracted with toluene. After drying and the removal of toluene by distillation, the residue was distilled under reduced pressure to give 1.3 g (38.2%) of product, b.p. 95—96° (0.1 mm), $n_D^{24}$ 1.4883 (lit. [4] b.p. 121° (1.2 mm),

$n_D^{40}$ 1.4871). Other products by this method are: (XIII) and (XIV) (yield 1.29 g, 48.9%), (XX) [2] (Yield 0.73 g, 44.5%) and (XXIII) and (XXIV) (yield 1.56 g, 51.7%).

*Reduction of silaacyloins to the silacycloalkanes.* The following procedure for the preparation of 1,1-dimethylsilacyclooctane (XXVIII) is typical. The other silacycloalkanes were prepared in a similar manner and are listed in Table 2. Amalgamated zinc was prepared in a 250 ml round bottomed flask with 16 g of zinc dust and 0.67 g of mercuric chloride in 40 ml of water. After addition of 0.3 ml of concentrated hydrochloric acid, the mixture was swirled for five minutes. The liquid was decanted, and 1.17 g (6.27 mmole) of a mixture of (XXIII) and (XXIV) was introduced along with 15 ml each of concentrated hydrochloric acid and acetic acid. A condenser was then connected to this flask. The mixture was stirred at room temperature for 48 h with the addition of 4 ml portions of concentrated hydrochloric acid at 12 h intervals. The reaction mixture was then stirred at 150° for another 48 h. After cooling, the contents were poured into 100 ml of water, and extracted with ether. The ether extracts were washed with saturated sodium carbonate until the evolution of carbon dioxide ceased, and then dried over anhydrous magnesium sulfate. After the removal of solvent by aspirator, the NMR spectrum of the colorless liquid residue indicated that it was about 90% pure. Distillation gave 0.73 g (74.5%) of product: b.p. 101.6 (53 mm); $n_D^{31.5}$ 1.4580; $\nu$(Si—$CH_3$) 1250 $cm^{-1}$ (in NaCl) (lit. [1] b.p. 78° (20 mm), $n_D^{28}$ 1.4605).

*2-(4-Chlorobutyl)-4,4-dimethyl-2-oxazoline (XXIX).* A modification of Meyers' method [17] was used. In a 1-l, three-necked flask equipped with a pressure-equalizing dropping funnel, a magnetic stirrer, and a dry nitrogen inlet were placed 15 g (0.13 mole) of 2,4,4-trimethyl-2-oxazoline [18] dissolved in 150 ml of dry tetrahydrofuran, and cooled to —78° under a nitrogen atmosphere. To this magnetically stirred solution was added 65 ml of n-butyllithium (80% in hexane). There was an immediate precipitate of yellow anion. 1-Bromo-3-chloropropane (20.5 g, 0.13 mole) obtained from the treatment of trimethylene chlorohydrin with phosphorus tribromide was added in a dropwise manner over half an hour period. After the addition, the mixture was allowed to slowly warm to room temperature during which time the yellow precipitate disappeared. The mixture was poured into 500 ml of ether and the ether solution was washed with cold water. The ether solution was extracted with cold 3 *N* hydrochloric acid and then the acid solution was immediately neutralized with cold 40% sodium hydroxide solution and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate. The dried ether solution was evaporated and distilled under reduced pressure to yield 1.65 g (6.7%) of product; b.p. 77° (0.4 mm); $\nu$C=N) 1670 $cm^{-1}$ (in $CCl_4$).

During the above distillation, a white precipitate formed, which was probably the *N*-quarternary salt [19] resulting from the displacement of the halogen by nitrogen. This precipitate was soluble in water and the aqueous solution gave a positive test when mixed with silver nitrate. The bromo-analog gave the same result even without heating.

*2-(3-butenyl)-4,4-dimethyl-2-oxazoline (XXX).* The apparatus and procedure were the same as that described above except 13 g (0.1 mole) of 2,4,4-trimethyl-2-oxazoline, 13.8 g (0.1 mole) of 3-bromo-propene, and 50 ml of n-butyl lithium (80% in hexane) were used. The residue was distilled under reduced pressure and gave 12 g (69.6%) of product: b.p. 46—47° (3.7 mm); $n_D^{20}$ 1.4422; $\nu$(C=C) 3080, 1640 and $\nu$(C=N) 1670 $cm^{-1}$ (in NaCl).

*Attempted preparation of dimethylbis [4-(4,4-dimethyl-2-oxazolinyl)butyl]-silane.* The Grignard reagent of compound (XXIX) was added to dimethyldichlorosilane in tetrahydrofuran. The color of the reaction mixture changed from green to red, and then to brown. The reaction was stopped at this point. None of the expected product could be isolated.

*Attempted hydrosilation of 2-(3-butenyl)-4,4-dimethyl-2-oxazoline (XXX) with dimethylchlorosilane.* The general method of hydrosilation in cyclohexane with a catalytic amount of chloroplatinic acid was followed. When compound (XXX) was added to dimethylchlorosilane a white precipitate was formed immediately. The white precipitate when dissolved in water, gave a positive test when mixed with silver nitrate.

*Attempted hydrosilation of 2-(3-butenyl)-4,4-dimethyl-2-oxazoline (XXX) with dimethylsilane.* Dimethylsilane generated by treating dimethylchlorosilane with lithium aluminum hydride was passed through a mixture containing compound (XXX), hexane, and a few drops of chloroplatinic acid. After refluxing for 48 h, no reaction had taken place.

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