

7- AND 8-MEMBERED OXASILACYCLOALKANES—I

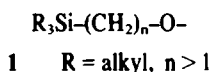
PREPARATION

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Abstract—Some new α -trimethylsiloxy- ω -methyl(ethoxy)silyl substituted alkanes of the formula $(\text{CH}_3)_3\text{SiO}(\text{CH}_2)_n\text{Si}(\text{CH}_3)_x(\text{OC}_2\text{H}_5)_{3-x}$ ($x = 0, 1, 2$; $n = 5, 6$) were synthesized. These compounds are stable and can undergo base catalysed decomposition producing 1-oxa-2-sila-2,2-disubstituted cycloalkanes of the formulae $(\text{C}_2\text{H}_5\text{O})_{2-x}(\text{CH}_3)_x\text{Si}(\text{CH}_2)_n\text{O}$ ($x = 0, 1, 2$; $n = 5, 6$).

It has been previously reported¹ that intramolecular coordination between oxygen and silicon in the ground state of the compounds **1** is enhanced by replacement of the alkyl group by

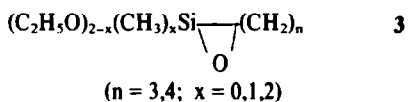
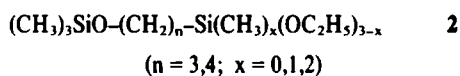


an electron attracting one, such as an ethoxy group, whereby the electron accepting ability of the silicon atom is increased.

The importance of such an interaction lies in the instability of such compounds which readily decompose producing cyclic products. For example, thermal decomposition of terminal alkoxysilyl substituted propoxysilanes²⁻⁴ as well as bis(trimethylsiloxy)methyl(hydroxypropyl)silane⁵ has led to the formation of cyclic products. This decomposition reaction was explained by the presence of weak coordination existing already between oxygen and silicon, this coordination might stabilize the transition state of the decomposition reaction which proceeds via nucleophilic attack at the silicon.⁶⁻⁸

Pola *et al.*¹ studied the intramolecular interaction of the compounds α -trimethylsiloxy- ω -methyl(ethoxy)silyl substituted alkanes **2**, in which they concluded that the formation of oxasilacycloalkanes **3** are increased as the number of ethoxy groups are increased and that six membered cycles are formed more easily than five membered ones.

In the present work we have prepared compounds of similar type to those discussed above but we increased the number of methylene groups intervening between silicon and oxygen with the aim of examining the tendency of the new compounds to undergo cyclization, in other words, whether higher membered cycles can be formed.



EXPERIMENTAL

All the temperature data in this work are uncorrected. All reactions of moisture sensitive compounds were carried out under an oxygen free-nitrogen atmosphere. The purity of the compounds prepared were checked by gas liquid chromatography. Some of the organosilane compounds as well as some of the starting materials were prepared in the laboratory according to the methods described in the literature.

1-Trimethylsiloxy-6-chlorohexane. One mole of hexamethylenchlorohydrin (136.5 g) was cooled and maintained at a temperature lower than 20° as one equivalent of hexamethyl-dimethylazane (81 g) was gradually added. A gentle reaction occurred during the addition and ammonia was evolved. The mixture was warmed slowly to boiling at 25 Torr and then distilled. The product was essentially pure 1-trimethylsiloxy-6-chlorohexane, b.p. 95°/10 Torr, the yield was quantitative. For elemental analysis see Table 1. An NMR analysis verified the correct structure.

1-Trimethylsiloxy-5-hexene. The method of preparation and the molar proportions of the materials used for the reaction were similar to those described above. The desired compound was obtained in quantitative yield, b.p. 154–56° and redistilled at 64–65°/16 Torr. An NMR analysis verified the correct structure.

Preparation of α -trimethylsiloxy- ω -methyl(ethoxy)silyl substituted pentanes and hexanes, general procedure. To a mixture of 0.1 mole of the desired 1-trimethylsiloxy alkene and 3 drops of freshly prepared chloroplatinic acid solution (0.01 molar solution in isopropanol), 0.1 mole of the required silylhydride was added over 0.5 h with stirring. After the addition was complete the reaction mixture was heated at 100–150°. The reaction temperature and the time allowed is dependent upon the compound used. The products of the reaction were obtained upon vacuum distillation at 3 Torr.

The compounds α -trimethylsiloxy- ω -methyl(ethoxy)silyl substituted pentanes and hexanes, their refractive indices, densities, yields, boiling points and elemental analysis are listed in Table 1. The NMR analyses of the compounds prepared verified the correct structures.

Preparation of 1-oxa-2-sila-2,2-disubstituted cycloheptanes and cyclooctanes, general procedure. A system consisting of a reaction flask and fractionating column prepared for vacuum distillation was set up. 0.01 or 0.02 mole of the required α -trimethylsiloxy- ω -methyl(ethoxy)silyl substituted alkanes together with 1% by weight of sodium ethoxide were introduced into the reaction flask. The reaction mixture was then heated until trimethylethoxysilane was observed to distill off. After this distillation is ceased, a viscous substance is formed which upon raising the reaction temperature and distillation under reduced pressure yields the desired product. The compound 2,2-dimethyl-2-silacycloheptane was distilled at atmospheric pressure. The compounds 1-oxa-2,2-disubstituted-2-silacycloheptanes and octanes, their physical constants and elemental analysis are listed in Table 2.

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Table 1. Yields, physical constants and element analysis of α -trimethylsiloxy- ω -methyl(ethoxy)silyl substituted alkanes and some intermediates

Compound	n_D^{25}	d_4^{25}	B.P.°C/ Torr	Yield %	M.P.	M.W.	Element%, Si	calc./found C	found H
$(CH_3)_3SiO(CH_2)_4Si(O_2C_2H_5)(CH_3)_2$	1.4141	0.8455	95-97/3	70	-	-	-	-	-
$(CH_3)_3SiO(CH_2)_5Si(O_2C_2H_5)(CH_3)_2$	1.4181	0.8551	100-104/3	42	$Si_2C_{12}H_{30}O_2$	262.6	21.40 20.29	54.90 55.02	11.52 11.19
$(CH_3)_3SiO(CH_2)_5Si(O_2C_2H_5)_2CH_3$	1.4185	0.8926	108-109/3	54	$Si_2C_{13}H_{32}O_3$	292.6	19.20 19.29	53.37 53.19	11.02 10.90
$(CH_3)_3SiO(CH_2)_5Si(O_2C_2H_5)_3$	1.4151	0.9065	127-128/3	87.4	$Si_2C_{14}H_{34}O_4$	322.59	17.42 17.96	52.12 51.89	10.62 10.45
$(CH_3)_3SiO(CH_2)_6Si(O_2C_2H_5)(CH_3)_2$	1.4232	0.8498	100/3	52	$Si_2C_{13}H_{32}O_2$	276.6	20.31 19.91	56.46 56.43	11.66 11.66
$(CH_3)_3SiO(CH_2)_6Si(O_2C_2H_5)_2CH_3$	1.4209	0.8929	121/3	53	$Si_2C_{14}H_{34}O_3$	306.6	18.23 18.54	54.84 54.50	11.18 10.98
$(CH_3)_3SiO(CH_2)_6Si(O_2C_2H_5)_3$	1.4179	0.9058	132-134/3	62.5	$Si_2C_{15}H_{36}O_4$	336.6	-	53.52 53.44	10.78 10.66
$(CH_3)_3SiO(CH_2)_5Cl$ ⁽⁹⁾	1.4268	0.9230	98/24	96	-	-	-	-	-
$(CH_3)_3SiO(CH_2)_6Cl$	1.4293	0.9223	104-105/23	quant.	$SiC_9H_{21}OCl$	208.65	13.45 13.67	51.77 51.70	10.14 10.00
$(CH_3)_3SiO(CH_2)_3CH=CH_2$ ⁽¹⁰⁾	1.4057	0.8062	144.5-45/760	83	-	-	-	-	-
$(CH_3)_3SiO(CH_2)_4CH=CH_2$	1.4115	0.8045	154-56/760	quant.	$SiC_9H_{20}O$	172.3	-	62.72 62.83	11.70 11.65

Table 2. Yields, physical constants and element analysis of 1-oxa-2-silacycloalkane compounds

Compound	n_D^{25}	d_4^{25}	B.p.°C/Torr	Yield %	M.P.	M.W.	Element%, Si	calc./found C	found H
$(CH_3)_2\overline{Si-(CH_2)_6-O}$	1.4451	0.8960	110-12/70	70	$SiC_8H_{18}O$	158.3	17.74 17.61	60.69 60.27	11.46 11.49
$CH_3(C_2H_5O)Si-(CH_2)_6-O$	1.4389	0.9342	109/35	62.5	$SiC_9H_{20}O_2$	188.3	14.91 14.78	57.40 57.88	10.70 10.67
$(C_2H_5O)_2\overline{Si-(CH_2)_6-O}$	1.4285	0.9698	120/35	74	$SiC_{10}H_{22}O_3$	218.3	12.86 12.97	55.00 54.89	10.15 10.14
$(CH_3)_2\overline{Si-(CH_2)_5-O}$	1.4291	0.8787	144-45/760	70	$SiC_7H_{16}O$	144.3	-	58.26 55.10	11.18 11.12
$CH_3(C_2H_5O)Si-(CH_2)_5-O$	1.4291	0.9392	96-98/35	85	$SiC_8H_{18}O_2$	174.3	16.11 15.69	55.12 55.10	10.41 10.34
$(C_2H_5O)_2\overline{Si-(CH_2)_5-O}$	1.4252	0.9784	112-14/35	67	$SiC_9H_{20}O_3$	204.3	13.75 13.74	52.90 52.90	9.87 9.91

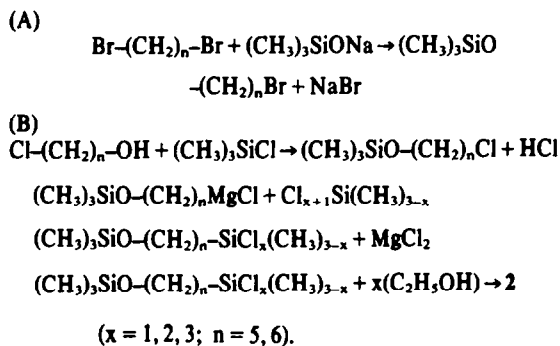
IR absorption measurements. The IR spectra of the compounds studied were recorded with a double-beam Zeiss, Model UR 20 spectrometer. The liquid phase spectra were recorded between KBr plates.

The spectra of α -trimethylsiloxy- ω -methyl(ethoxy)silyl substituted pentanes and hexanes show absorption maxima for Si-CH₃ arrangement at 840-875 cm⁻¹ due to Si-CH₃ rocking, 1255 cm⁻¹ due to Si-CH₃ bending, 2935.5 cm⁻¹ and 2980 cm⁻¹ due to C-H stretching and the band at 1392.5 cm⁻¹ due to C-CH₃ stretching vibrations. The presence of ethoxy groups in the compounds was confirmed by the absorption bands at 1167.5, 945-960 cm⁻¹ and the doublet at 1082-1107 cm⁻¹. A slight difference in the compounds having 5 methylene groups and those having 6 methylene groups is observed in the region 945-960 cm⁻¹ in which the signals of the former are of higher frequencies than the latter.

The spectra of the cyclic compounds $(C_2H_5O)_2\overline{Si-(CH_2)_n-O}$, $\overline{Si-(CH_2)_n-O}$ resemble to a large extent those of the linear compounds (structure 2, n = 5, 6). The compounds show an intensive absorption band ranging from 1005 to 1012 cm⁻¹ and broad weak bands in the region 519-530 cm⁻¹ which can be assigned to the vibration of the heterocycle.

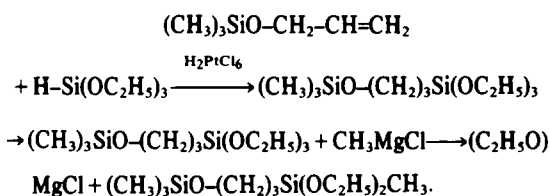
RESULTS AND DISCUSSION

Various ways for the preparation of the model compounds α -trimethylsiloxy- ω -methyl(ethoxy)silyl-substituted pentanes and hexanes were proposed. Among the methods which have been attempted are those presented in the following sequences of reactions:

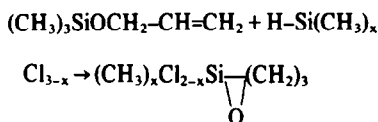


Dibromopentane as well as dibromohexane failed to react with sodium trimethylsilanolate (method A). In method B pentamethylene chlorohydrin and hexamethylene chlorohydrin react quantitatively with trimethylchlorosilane (or hexamethyldisilazane) with the formation of the desired product, but further reaction with magnesium failed to give the Grignard adduct, and hence no further reaction steps could be carried out. However, Pola¹ prepared similar compounds by using the last method but the yield was rather low.

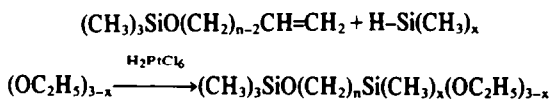
The formation of Si-C bonds by the addition of silylhydrides to carbon-carbon multiple bonds has been described by several authors.¹⁰⁻¹³ This addition was effected by using catalysts such as free radical sources, metals (Pt/C, Pt/C), metal salts such as potassium chloroplatinate and chloroplatinic acid. For example, addition of triethoxyhydroxilane to trimethylsiloxypropene takes place easily but substitution of the ethoxy group by a methyl one through a Grignard adduct takes place in low yield.¹



Kozlikov *et al.*¹⁰ tried to prepare similar chloro-substituted derivatives by the addition of chlorohydroxilane to trimethylsiloxy-2-propene but they failed and obtained, instead, a cyclic product:



In our work, we found that methyl(ethoxy)hydroxilanes instead of methyl(chloro)hydroxilanes should preferentially be used. The compounds under consideration here have been prepared by this way:

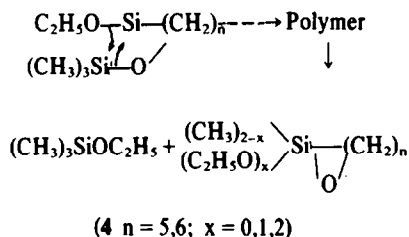


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This addition reaction, catalysed by chloroplatinic acid, is possible in the absence of a solvent. Stoichiometric amounts of the trimethylsiloxyalkene and of the silylhydride were used. A few drops of chloroplatinic acid (10^{-2} mole/l in isopropanol) solution were sufficient for the reaction to proceed. Higher concentration of the acid in the reaction mixture speeds the reaction but decreases the yield significantly. The reaction took place upon heating to the reflux temperature of the silylhydride used. The reaction period could be recognized by observing the increase in the reaction temperature up to a fixed degree. A polymeric substance remains after distillation of the desired compound. Its formation is attributed to the tendency of the reaction product to

polymerize in the presence of traces of acids (here chloroplatinic acid). The pure compounds are slightly stable at high temperature, e.g. trimethylsiloxy-triethoxysilyl substituted derivatives could be distilled under the atmospheric pressure.

Cyclization of α -trimethylsiloxy- α -methyl(ethoxy)silyl substituted alkanes. The product from the addition reaction described above could be converted into 1-oxa-2-sila-2,2-disubstituted cycloalkanes **4** under the influence of sodium ethoxide as catalyst:



The choice of the catalyst was determined by preliminary experiments made with *p*-toluenesulphonic acid, sodium hydroxide and sodium ethoxide. With *p*-toluenesulphonic acid, trimethylethoxysilane separated out but no cyclization occurred, a high boiling polymeric substance was formed which was partially distilled and shown to be a complex mixture as indicated by glc analysis. With sodium hydroxide, cyclization occurred but the yield was not satisfactory. With sodium ethoxide, better results were obtained and the cyclic compounds could be separated in fairly good yields.

The reaction proceeds smoothly on heating the compound under consideration with 1% (by weight) of sodium ethoxide. Trimethylethoxysilane is distilled off during the reaction process. The separation of a stoichiometric amount of the latter is an indication of the end of the reaction. The reaction does not lead directly to the formation of the cycles but, as has been observed, results in the formation of a polymeric viscous product. This polymer was then destroyed by high temperature heating whereby the cyclic compound was distilled off.

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