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Alkoxysilanes. VII. The Preparation of Alkylalkoxysiloxanes

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Trimethylsiloxytri-*t*-butoxysilane (I), bis(trimethylsiloxy)di-*t*-butoxysilane (II), and bis(trimethylsiloxy)bis-(tri-*t*-butoxysiloxy)silane (III) were prepared by the reaction of trimethylchlorosilane with tri-*t*-butoxysilanol, di-*t*-butoxysilanediol, and bis(tri-*t*-butoxysiloxy)silanediol respectively. Bis(tri-*t*-butoxysiloxy)dimethylsilane (IV) was also obtained by the reaction of dimethyldichlorosilane with tri-*t*-butoxysilanol. The reaction of dimethyldichlorosilane with di-*t*-butoxysilanediol or bis(tri-*t*-butoxysiloxy)silanediol gave tetramethyltetra-*t*-butoxy (V) or tetramethyltetra(tri-*t*-butoxysiloxy)cyclooctasiloxane (VI). These compounds were identified by means of elemental analysis, molecular-weight determination, and a study of the IR and NMR spectra.

Alkylalkoxysiloxanes have been obtained by the hydrolysis of alkylalkoxychlorosilanes and alkylalkoxysilanes,[1,2] but the preparation of the alkylalkoxysiloxanes[3] by the reaction of alkoxysilanols with alkylchlorosilanes has not been described. In this paper, we wish to report an investigation of the preparation of alkylalkoxysiloxanes bearing methyl and *t*-butoxy groups as organic radicals.

Since we had already prepared several alkoxysilanols, tri-*t*-butoxysilanol,[4] di-*t*-butoxysilanediol,[5] and bis-(tri-*t*-butoxysiloxy)silanediol, we expected that the reaction of these silanols with alkylchlorosilanes would lead to the formation of mixed siloxanes. Furthermore, polyalkylalkoxysiloxanes may be obtained by the reactions of the silanediols with dichlorosilanes. It was found that the following reactions, (A) and (B), easily afforded the products (I), (II), (III), and (IV):

$$Me_3SiCl + (RO)_{4-n}Si(OH)_n + nC_5H_5N \rightarrow (RO)_{4-n}Si(OSiMe_3)_n + nC_5H_5NHCl \quad (A)$$

where R=Bu^t and n=1: (I), n=2: (II)
R=(Bu^{t}O)$_3$Si and n=2: (III)

$$Me_2SiCl_2 + 2(RO)_3SiOH + 2C_5H_5N \rightarrow [(RO)_3SiO]_2SiMe_2 + 2C_5H_5NHCl \quad (B)$$

where R=Bu^t (IV)

These products could be distilled as a colorless viscous liquid (IV) which solidified as soon as distilled. As Table 1 shows, the results of the elemental analysis and molecular-weight determination agreed with the calculated values for the compounds. The IR spectra of these comopunds are essentially identical and show absorption peaks at 1388 and 1360 (branching of the alkyl group), 1240 and 1255 (Si–Me$_3$, methyl group), 1052 (Si–O–Si), 841 (Si–Me$_3$), and 799 (Si–Me$_2$)cm^{-1}.[6] The NMR spectra of the compound (I) also show the proton signals at 8.73 (Bu^t) and 9.90 (Me) τ. The formation of these compounds indicates that the hydroxy groups in the silanols are easily replaced by the trimethylsiloxy group, although they are sterically hindered. It is generally known that it is difficult to replace the X group in the alkoxysilanes $(RO)_{4-n}SiX_n$

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Table 1. Alkylalkoxysiloxanes

Reactants (g) A	B		Products	Yield (%)	Bp °C/mmHg	n_D^{20}	Mol wt Found (Calcd)	Found Anal % (Calcd) Si
14.1	34.2	10.2	(I)	57	102/16[a]	1.3974	336 (337)	15.89 (16.69)
5.1	4.8	3.3	(II)	21	110—111/23[a]	1.3946	364 (353)	22.33 (23.89)
3.2	8.8	2.4	(III)	20	167—169/1	1.4141	600 (687)	16.23 (16.35)
8.9	36.3	10.9	(IV)	28	150—153/1 38.5—40 (Mp)	—	535 (585)	14.44 (14.40)

A: Chlorosilane, B: Silanol, a) Fractionally distilled

Table 2. Cyclic Alkylalkoxysiloxanes

Reactants (g) A	B		Products	Yield (%)	Mp °C	Mol wt Found (Calcd)	Found Anal % (Calcd) C	H	Si
21.0	34.0	25.4	(V)	66	109—110[a]	527 (529)	45.31 (45.51)	9.56 (9.15)	21.31 (21.24)
1.5	6.6	1.8	(VI)	35	132—133[b]	1294 (1290)	47.71 (48.41)	8.82 (9.32)	17.62 (17.42)

A: Dichlorosilane, B: Silanediol, a) Recrystallized from *n*-hexane, b) Recrystallized from ethanol

(n=halogen, amino group; R=t-alkyl group; n=1 or 2) by a bulky alkoxy group.[7-9] In the present case, however, the replacement is very easy. This difference seems to result from the difference in the bond length between the Si–O–C and Si–O–Si bonds.

Since it was found that the reaction of (A) and (B) easily afforded the alkylalkoxysiloxanes, we can expect that the reaction of dialkyldichlorosilanes with silanediols will produce polyalkylalkoxysiloxanes. With this view, the following reaction was carried out:

$$Me_2SiCl_2 + (RO)_2Si(OH)_2 + 2C_5H_5N \rightarrow \text{cyclic tetrasiloxane (OR, Me)} + 2C_5H_5NHCl \quad (C)$$

where R=Bu^t: (V), R=(Bu^{t}O)$_3$Si: (VI)

The products obtained (V and VI) could be distilled or recrystallized. As is shown in Table 2, (V) solidified as soon as distilled (mp 109—110°C); (VI) could not be distilled because of the decomposition (240°C/1mmHg), but it was recrystallized from ethanol (mp 132—133°C). These products were soluble in common organic solvents. The analytical data and the results of the molecular-weight determination agreed with the calculated values for the cyclooctasiloxanes shown by Equation (C).

The formation of these compounds was also confirmed by the spectroscopic data; the IR spectra of these compounds show the absorption peaks at 1388 and 1360 (Bu^t), 1252 and 1240 (Si–Me), 1060 (Si–O–Si), and 799 (Si–Me$_2$) cm^{-1}. The NMR spectra of (V) show proton signals at 8.72 (Bu^t) and 9.87 (Me) τ. In this reaction, the formation of the cyclic alkylalkoxysiloxanes may be ascribed to the steric effect of the t-butoxy and tri-t-butoxy-siloxy groups.

Experimental

All the experiments were carried out under a dry atmosphere. The melting and boiling points are uncorrected.

Materials. Commercially-available trimethylchlorosilane and dimethyldichlorosilane were redistilled before use.[10] The aldoxysilanols used were prepared by a method already described.[4,5]

Preparation of Alkylaldoxysiloxanes. To a solution of silanol or silanediol and pyridine in toluene, dimethyldichlorosilane in the same solvent was added, drop by drop, about 0°C. After the mixture had been refluxed for 2 hr, pyridine hydrochloride was filtered off; then the solvent was removed, and the residue was recrystallized or distilled *in vacuo*, giving crystals or a liquid.

Instruments. The molecular weight was determined by the cryoscopic method in benzene. The IR spectra were measured in a liquid film or KBr disk by means of a Hitachi EPI-S2 spectrometer. The NMR spectra were measured with a Varian A-60 spectrometer in a carbon tetrachloride solution, with tetramethylsilane as the internal standard.

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