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Synthesis of siloxanes

XX *. Stereochemical investigations of substitution reactions at cyclotrisiloxanes with new types of model compounds **

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Abstract

Functional cyclotrisiloxanes [(RMeSiO)(R'$_2$SiO)(ClMeSiO)] (R = OSiMe$_3$, OSi (OSiMe$_3$)$_3$; R' = OSiMe$_3$) and [(PhMeSiO)$_2$-(XMeSiO)] (X = H, Cl), each as a mixture of two configurational isomers, have been prepared and shown to be useful as model compounds for studying the stereochemical course of substitution reactions at siloxane silicon atoms by ^{29}Si or ^{1}H NMR spectroscopy. As an example, the acetolysis of the chlorocyclotrisiloxanes was studied and found to proceed with retention of configuration.

1. Introduction

Recently, we described the preparation of 2-substituted 2,4,6-trimethyl-4,6-bis(trimethylsiloxy)cyclotrisiloxanes (Fig. 1; R = OSiMe$_3$; X = Cl, Br, OAc, OMe, H) which were made for an investigation of the stereochemistry of nucleophilic substitution reactions at silicon atoms in cyclosiloxanes [2,3]. The signals of the ^{1}H and ^{29}Si NMR spectra of these compounds were assigned to the three possible configurational isomers and the proportions of the isomers in the obtained mixtures were determined. From the intensities and the chemical shifts of the signals from the isomers in the starting material and in the product mixtures, the relative rate constants of the isomers and the stereochemistry of the reactions could be evaluated. In some reactions, this type of model compound did not allow conclusions to be reached about the stereochemical outcome owing to the superimposition of isomer signals in the NMR spectra, and so we were interested in reducing the number of configurational isomers to two. Two different routes were used for this purpose.

2. Experimental

2.1. Solvents and reagents

All reagents and solvents were dried by standard methods prior to use. Trimethylsilanol [4], 3,3-dihydroxy-1,1,1,5,5,5-hexamethyltrisiloxane (**1**) [5], 3-hydroxy-3-trimethylsiloxy-1,1,1,5,5,5-hexamethyltrisiloxane (**2**) [6], 1,1,3,3-tetrachloro-1,3-dimethylsiloxane (**3**) [7], and *meso*-1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane (**4**) [8], were prepared by published methods.

2.2. Spectra

The NMR spectra were recorded on a Bruker WP 80 SY (^{1}H) or a Bruker MSL 300 (^{29}Si) NMR spectrometer operating in the FT mode at 80.13 and 59.63 MHz, respectively, with Me$_4$Si as internal standard.

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** Dedicated to my old friend Professor M.G. Voronkov in recognition of his very important contributions to organosilicon chemistry.

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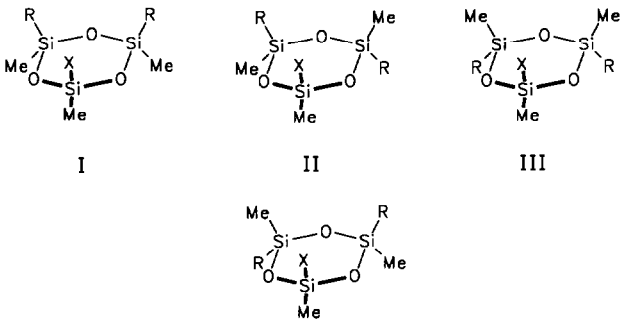


I II III

Fig. 1. Cyclotrisiloxanes forming three configurational isomers I–III.

The chemical shifts are reported in ppm with positive shifts downfield from Me_4Si.

2.3. Preparations

2.3.1. 1,1,3-Trichloro-1,3,5,5,5-pentamethyltrisiloxane (5)

A solution of trimethylsilanol (18.0 g, 0.2 mol) in diethyl ether (150 ml) was added to a stirred mixture of **3** (62.4 g, 0.2 mol) and pyridine (15.8 g, 0.2 mol) in diethyl ether (600 ml). After 30 min further stirring, the pyridine hydrochloride was filtered off, the solvent evaporated from the filtrate, and the residue fractionated under vacuum.

Yield 16.7 g, 28%. B.p. 96–98°C/5.3 kPa. d_4^{20} 1.072, n_D^{20} 1.4015. Hydrolysable Cl found: 36.05. $C_5H_{15}Cl_3O_2Si_3$ calc.: 35.80%. ^{29}Si NMR ($CDCl_3$): δ −42.91 (MeSiCl), −17.43 ($MeSiCl_2$), 14.12 (Me_3Si).

2.3.2. 1,1,3-Trichloro-1,3,7,7,7-pentamethyl-5,5-bis(trimethylsiloxy)tetrasiloxane (6)

This was prepared by the same procedure but starting from **2** (62.4 g, 0.2 mol) instead of trimethylsilanol.

Yield 72.7 g, 70%. B.p. 102–103°C/0.08 kPa. d_4^{20} 1.037, n_D^{20} 1.4019. Hydrolysable Cl found: 20.33. $C_{11}H_{33}Cl_3O_5Si_6$ calc.: 20.50%. ^{29}Si NMR ($CDCl_3$): δ −107.01 (SiO_4), −43.50 (MeSiCl), −17.19 ($MeSiCl_2$), 10.31 (Me_3Si).

2.3.3. 2-Chloro-2,4-dimethyl-4,6,6-tris(trimethylsiloxy)cyclotrisiloxane (7)

Solutions of **1** (24.0 g, 0.1 mol) and **5** (29.8 g, 0.1 mol) each in diethyl ether (100 ml) were added dropwise and simultaneously to a stirred solution of pyridine (15.8 g, 0.2 mol) in diethyl ether (600 ml). After overnight standing, the pyridine hydrochloride was filtered off, the solvent evaporated from the filtrate, and the residue fractionated under vacuum.

Yield 13.5 g, 29%. B.p. 77–78°C/0.05 kPa. d_4^{20} 1.008, n_D^{20} 1.4009. Hydrolysable Cl found: 7.60. $C_{11}H_{33}ClO_6Si_6$ calc.: 7.64%. Isomer proportions: 44.5% (**IV**); 55.5% (**V**). ^{1}H NMR ($CDCl_3$): δ 0.50 (s, 3H, MeSiCl, **IV**), 0.52 (s, 3H, MeSiCl, **V**). ^{29}Si NMR ($CDCl_3$): δ −101.61 (SiO_4, **V**); −101.43 (SiO_4, **IV**); −56.74 ($MeSiO_3$, **IV**); −55.75 ($MeSiO_3$, **V**); −31.61 (MeSiCl, **IV**); −31.38 (MeSiCl, **V**); 10.57 ($Me_3SiOSiMeO_2$, **V**); 10.73 ($Me_3SiOSiMeO_2$, **IV**); 11.11 and 11.73 ($Me_3SiOSiOSiMe_3$, **IV**); 11.47 and 11.50 ($Me_3SiOSiOSiMe_3$, **V**).

2.3.4. 2-Chloro-2,4-dimethyl-4-tris(trimethylsiloxy)silyl-6,6-bis(trimethylsiloxy)cyclotrisiloxane (8)

This was prepared by the same procedure but from **6** (52.0 g, 0.1 mol) instead of **5**.

Yield 17.2 g, 25%. B.p. 124–126°C/0.06 kPa. d_4^{20} 0.992, n_D^{20} 1.4020. Hydrolysable Cl found: 5.16. $C_{17}H_{51}ClO_9Si_9$ calc.: 5.18%. Isomer proportions: 38% (**IV**), 62% (**V**). ^{1}H NMR ($CDCl_3$): δ 0.48 (s, 3H, MeSiCl, **IV**), 0.50 (s, 3H, MeSiCl, **V**). ^{29}Si NMR ($CDCl_3$): δ −108.32 (SiO_4 exocyclic, **IV**), −108.23 (SiO_4 exocyclic, **V**), −101.61 (SiO_4 endocyclic, **V**), −101.33 (SiO_4 endocyclic, **IV**), −57.92 ($MeSiO_3$, **IV**), −57.32 ($MeSiO_3$, **V**), −31.50 (MeSiCl, **IV**), −31.18 (MeSiCl, **V**), 9.60 ($(Me_3SiO)_3Si$, **V**), 9.54 ($(Me_3SiO)_3Si$, **IV**), 11.07 and 11.91 ($Me_3SiOSiOSiMe_3$, **IV**), 11.36 and 11.66 ($Me_3SiOSiOSiMe_3$, **V**).

2.3.5. 2-Hydrido-2,4,6-trimethyl-4,6-diphenylcyclotrisiloxane (9)

This was prepared by the same procedure but from **4** (29.0 g, 0.1 mol) and methyldichlorosilane (11.5 g, 0.1 mol) instead of **1** and **5**.

Yield 9.3 g, 28%. B.p. 122–123°C/0.05 kPa. d_4^{20} 1.067, n_D^{20} 1.5108. Isomer proportions: 58.5% (**I**), 41.5% (**III**). ^{29}Si NMR ($CDCl_3$): δ −22.27 (MeSiH, **I**), −22.13 (MeSiH, **III**), −20.74 (MeSiPh, **I**), −20.59 (MeSiPh, **III**).

2.3.6. 2-Chloro-2,4,6-trimethyl-4,6-diphenylcyclotrisiloxane (10)

Over a period of 15 min, a saturated solution of chlorine (0.08 mol) in carbon tetrachloride was added dropwise to a stirred mixture of **9** (16.6 g, 0.05 mol), pyridine (4.0 g, 0.05 mol) and a small amount of ionol in carbon tetrachloride (100 ml). Then the mixture was stirred for a further 30 min, the pyridine hydrochloride filtered off, the solvent evaporated from the filtrate, and the residue distilled under vacuum.

Yield 13.6 g, 74%. B.p. 130–132°C/0.05 kPa. d_4^{20} 1.099, n_D^{20} 1.5087. Hydrolysable Cl found: 9.71. $C_{15}H_{19}ClO_3Si_3$ calc.: 9.69%. Isomer proportions: 40% (**I**), 60% (**III**). ^{1}H NMR ($CDCl_3$): δ 0.54 (s, 6H, MeSiPh, **I**), 0.56 (s, 3H, MeSiCl, **III**), 0.58 (s, 6H, MeSiPh, **III**), 0.66 (s, 3H, MeSiCl, **I**). ^{29}Si NMR ($CDCl_3$): δ −30.92

(MeSiCl, **I**), −30.46 (MeSiCl, **III**), −18.97 (MeSiPh, **I**), −18.91 (MeSiPh, **III**).

The procedure as described for the preparation of **9**, but using methyltrichlorosilane (15.0 g, 0.1 mol) instead of methyldichlorosilane, afforded a mixture of **10** (33%) and 1,1,7,7-tetrachloro-1,3,5,7-tetramethyl-3,5-diphenyltetrasiloxane (**11**) (7%) which could not be separated by distillation. The yields were calculated from the ^{29}Si NMR spectrum.

^{29}Si NMR ($CDCl_3$): δ −29.24 (MeSiPh), −19.58 ($MeSiCl_2$).

2.3.7. Kinetic investigations

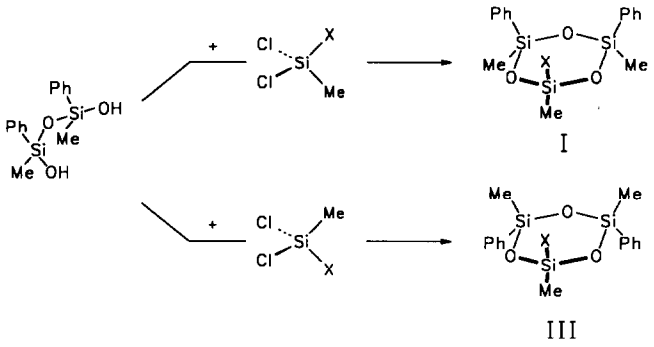
The acetolyses were monitored by ^{29}Si NMR spectroscopy. Acetic acid (0.24 g, 4 mmol), acetic anhydride (0.4 ml), Me_4Si (0.1 ml) and $CDCl_3$ (1.2 ml) were mixed in an NMR tube and the reactions were started by adding the chlorocyclotrisiloxane (1.4 mmol). Spectra were recorded over periods of between 15 min and 72 h. The relative rate constants of the isomers were determined by the competition method.

3. Results and discussion

The first method of reducing the number of isomers in the products involved changing the substitution pattern of the model compounds in such a way that the cyclotrisiloxanes could only occur in two configurational isomers (Fig. 2). Compound 2-chloro-2,4,4,6-tetramethyl-6-trimethylsiloxycyclotrisiloxane (**12**) (Fig. 2) would have been closest in structure to the model compounds used in our previous work (Fig. 1, R = $OSiMe_3$), but the need to use the very unstable dimethylsilanediol in the final synthetic step would have caused difficulties. Thus, we decided to use the readily available and stable trisiloxanediol, **1**, as an alternative cyclization component while not changing the general structure of the cyclotrisiloxane, and this yielded **7** and **8** (Fig. 2).

IV V

Fig. 2. Cyclotrisiloxanes forming two configurational isomers **IV** and **V**. **7**: R = $OSiMe_3$, R′ = $OSiMe_3$; **8**: R = $OSi(OSiMe_3)_3$, R′ = $OSiMe_3$; **12**: R = $OSiMe_3$, R′ = Me.



I III

Fig. 3. Route to cyclotrisiloxanes forming two configurational isomers **I** and **III** starting from the *meso*-dimethyldiphenyldisiloxanediol. **9**: X = H; **10** X = Cl.

In an alternative approach, we tried to use a starting compound for the ring closure step having a stereochemically fixed structure. Thus, when we introduced phenyl groups to provide steric hindrance (Fig. 3), we were able to prepare cyclotrisiloxanes from the pure *meso* diastereomer of the disiloxanediol. In this way, only two out of three possible configurational isomers could be formed (Fig. 1). As the cyclization step with methyltrichlorosilane also afforded a considerable amount of acyclic tetrasiloxane, which proved difficult to separate from the cyclotrisiloxane, a route involving the preparation of hydridocyclotrisiloxane and its subsequent chlorination was used to prepare **10**.

For both types of model compounds, the ^{29}Si and ^{1}H NMR spectra showed that the proportions of the

TABLE 1. Acetolysis of chlorocyclotrisiloxanes: relative rate constants for the configurational isomers, stereoprecision, and ^{29}Si NMR signals used in monitoring the reactions

Cyclotrisiloxane	Relative rate constants	Stereoprecision [a] (stereochemistry)	^{29}Si NMR			
			Si–Cl		Si–OAc	
			IV	**V**	**IV**	**V**
7	1:4.3 [b]	93% (RET)	−31.61	−31.38	−49.53	−48.83
8	1:5.1 [b]	96% (RET)	−31.50	−31.18	−49.11	−48.46
			I	**III**	**I**	**III**
10	1:8.2 [c]	92% (RET)	−30.92	−30.46	−49.51	−47.96

[a] As a percentage of the predominant stereochemistry. [b] **IV**:**V** (Fig. 2). [c] **I**:**III** (Fig. 3).

configurational isomers in the mixtures obtained differed considerably from the statistical 1:1 ratio. Taking into account the differences in the degrees of steric hindrance associated with the relative positions of the bulky substituents in the planar cyclotrisiloxane molecules, the NMR signals were assigned to the *trans* and *cis* isomers. In addition, our own and other previous studies on the NMR assignment of configurationally isomeric cyclosiloxanes, assisted us in our analysis, particularly in the case of the isomeric products from the acetolysis reactions [9,10].

When using the competition method, we observed that the product signals in the ^{29}Si NMR spectra appeared in the same sequence as the signals from the starting material disappeared. Thus, for all three chlorocyclotrisiloxanes we showed that the acetolysis proceeds with retention of configuration (see Table 1). The isomer with the sterically hindering substituents *trans* to the leaving group always showed the highest reactivity. Thus, the retention stereochemistry is supported, since the attack of the nucleophile from the side of the leaving group should be less hindered in these isomers.

The retention stereochemistry for leaving chloride ions from cyclotrisiloxanes contrasts sharply with the generally observed inversion of configuration in nucleophilic displacement reactions of chlorosubstituted acyclic silanes and silacyclohexanes [11]. This strong tendency towards retention stereochemistry resembles that found for silacyclo-pentanes and -butanes, but cannot be attributed, as it was for the latter species, to a small endocyclic bond angle at the silicon reaction centre (90–96°) because in cyclotrisiloxanes, there are O–Si–O bond angles of 105–108° [12–14].

We suggest that ring strain relief *via* an axial-equatorial arrangement of the siloxane cycle in the trigonal-bipyramidal intermediate of the nucleophilic substitution reaction accounts for the strong preference of the retention pathway. Recent X-ray diffraction studies of anionic pentacoordinated silicates with five- and six-membered oxygen-containing rings serving as models for S_N2 transition states have revealed a trigonal-bipyramidal structure with the rings located in axial-equatorial sites [15,16]. Those reports also illustrate the importance of stereochemical control in nucleophilic displacement reactions at silicon brought about by variations in ring constraints.

Work is underway to isolate a single configurational isomer of a functional phenyl-substituted cyclotrisiloxane in order to confirm our NMR assignment system by an X-ray structural study.

References

1 K. Käppler, A. Porzel, U. Scheim and K. Rühlmann, *J. Organomet. Chem., 402* (1991) 155.
2 U. Scheim, K. Rühlmann, H. Grosse-Ruyken and A. Porzel, *J. Organomet. Chem., 314* (1986) 39.
3 R. Gewald, K. Rühlmann, U. Scheim and A. Porzel, *J. Organomet. Chem., 377* (1989) 9.
4 L. Birkofer, A. Ritter and H. Dickopp, *Chem. Ber., 96* (1963) 1473.
5 K. A. Andrianov and V. V. Severny, *Zh. Obshch. Khim., 32* (1962) 1633.
6 U. Scheim, H. Grosse-Ruyken, K. Rühlmann and A. Porzel, *J. Organomet. Chem., 312* (1986) 27.
7 N. N. Sokolov and K. A. Andrianov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1957) 806.
8 J. Hickton, A. Holt, J. Homer and A. W. Jarvie, *J. Chem. Soc. C*, (1966) 149.
9 H. Jancke, *Dissertation*, Berlin, 1969.
10 E. Pelletier and J. F. Harrod, *Organometallics, 3* (1984) 1070.
11 R. Corriu, C. Guerin and J. Moreau, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, New York, 1989, Part I, p. 305.
12 N. G. Bokii, G. N. Zakharova and Yu. T. Struchkov, *Zh. Strukt. Khim., 13* (1972) 291.
13 R. P. Hernandez, *Acta Crystallogr., Sect. A, 34* (1978) 5406.
14 N. Oberhammer, W. Zeil and G. Fogarasi, *J. Mol. Struct., 18* (1973) 309.
15 R. O. Day, C. Sreelatha, J. A. Deiters, S. E. Johnson, J. A. Holmes, L. Howe and R. R. Holmes, *Organometallics, 10* (1991) 1758.
16 K. C. K. Swamy, C. Sreelatha, R. O. Day, J. A. Holmes and R. R. Holmes, *Inorg. Chem., 30* (1991) 3126.