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Synthesis of siloxanes

XXII *. Synthesis and crystal structure of 2-t-butoxy-2,4,6-trimethyl-4,6-diphenyl-(2α,4α,6α)-cyclotrisiloxane

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Abstract

The structure of 2-t-butoxy-2,4,6-trimethyl-4,6-diphenyl-(2α,4α,6α)-cyclotrisiloxane has been determined by an X-ray crystallographic study. The structure revealed confirms the validity of the basis of our ^{29}Si and ^{1}H NMR assignments previously made to configurational isomers of several model compounds, which are suitable for studying the stereochemistry of substitutions at silicon atoms in siloxanes

1. Introduction

We recently reported the preparation of several substituted cyclotrisiloxanes (*e.g.* Fig. 1; R = $OSiMe_3$, Ph; X = Cl, Br, OAc, OMe, H) that were made in order to enable investigation of the stereochemistry of nucleophilic substitution reactions at silicon atoms in cyclosiloxanes by NMR spectroscopy [2–4]. Showing a strong tendency to react with retention of configuration, these cyclotrisiloxanes showed stereochemical behaviour different from that of the optically active acyclic and cyclic six-membered ring silanes [5].

The assignments of the configurational isomers were previously made on the basis of NMR data. For further studies and more detailed discussion of the stereochemistry, we thought it appropriate to establish a stereochemical assignment by crystallography. This has now provided a firm basis for the stereochemical assignment of cyclotrisiloxane isomers.

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* For Part XXI, see ref. 1.

2. Experimental details

2.1. Materials

All substances and solvents were dried by standard methods prior to use. 1,3-Dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane (*meso* : *rac* = 1 : 1), **1** [6], *meso*-1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane, **2** [6], 2-hydrido-2,4,6-trimethyl-4,6-diphenylcyclotrisiloxane, **3** [2], 2-chloro-2,4,6-trimethyl-4,6-diphenylcyclotrisiloxane, **4** (isomeric ratio: 40% **a**, 60% **c**) [2] and t-butoxydichloromethylsilane, **5** [7], were prepared as described previously.

2.2. 2-t-Butoxy-2,4,6-trimethyl-4,6-diphenylcyclotrisiloxane, 6a–6c

Separate solutions of **1** (29.0 g, 0.1 mol) and **5** (18.7 g, 0.1 mol), each dissolved 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). The mixture was left overnight and the pyridine hydrochloride then filtered off, the solvent evaporated from the filtrate, and the residue fractionated under vacuum. Yield (13.7 g, 34%), b.p. 141–

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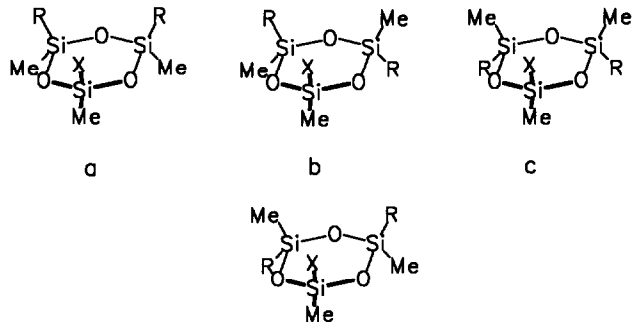


a b c

Fig. 1. Structure of the three configurational isomers **a**–**c** of cyclotrisiloxanes. **3**: R=Ph, X=H; **4**: R=Ph, X=Cl; **6**: R=Ph, X=O^{t}Bu.

143°C/0.02 kPa, d_4^{20} 1.028, n_D^{20} 1.4979. Isomer proportions: 23.0% (**a**), 51.0% (**b**), 26.0% (**c**).

^{1}H NMR ($CDCl_3$): δ 0.10 (s, 3H, MeSiO^{t}Bu, **a**), 0.17 (s, 3H, MeSiO^{t}Bu, **b**), 0.26 (s, 3H, MeSiO^{t}Bu, **c**), 0.36 (s, 3H, MeSiPh, **a**), 0.42 (s, 3H, MeSiPh, **b**), 0.45 (s, 3H, MeSiPh, **b** and s, 3H, MeSiPh, **c**), 1.10 (s, 9H, SiO^{t}Bu, **c**), 1.25 (s, 9H, SiO^{t}Bu, **b**), 1.38 (s, 9H, SiO^{t}Bu, **a**). ^{29}Si NMR ($CDCl_3$): δ −55.21 (SiO^{t}Bu, **b**), −55.13 (SiO^{t}Bu, **c**), −54.85 (SiO^{t}Bu, **a**), −21.43 to −21.27 (SiPh, **a**–**c**).

2.3. 2-t-Butoxy-2,4,6-trimethyl-4,6-diphenyl-(2α,4β,6β)-cyclotrisiloxane, 6c

A solution of t-butanol (3.7 g, 0.05 mol) in diethyl ether (50 ml) was added to a stirred mixture of **4** (18.3 g, 0.05 mol) and pyridine (15.8 g, 0.2 mol) in diethyl ether (150 ml). After 30 min further stirring, the pyridine hydrochloride was filtered off, the solvent evaporated from the filtrate, and the residue fractionated under vacuum. The isomeric mixture of 94% **c** and 6% **a** obtained crystallized after standing overnight at −20°C (m.p. 26–29°C, yield: 81%). Recrystallization from methanol at −20°C afforded the pure isomer **c**.

Yield (12.5 g, 62%), b.p. 141–143°C/0.02 kPa, m.p. 33°C (Found: C, 56.7; H, 6.7. $C_{19}H_{28}O_4Si_3$ calc.: C, 56.4; H, 6.9%). ^{1}H NMR ($CDCl_3$): δ 0.26 (s, 3H, MeSiO^{t}Bu), 0.45 (s, 3H, MeSiPh), 1.10 (s, 9H, SiO^{t}Bu).

2.4. 2-t-Butoxy-2,4,6-trimethyl-4,6-diphenyl-(2α,4α,6α)-cyclotrisiloxane, 6a

Attempts to obtain a single crystal suitable for X-ray structural analysis were carried out in methanol at −20°C and were successful only when the isomeric mixture containing 94% **c** and 6% **a** was used. Surprisingly, the selected crystal studied was found by X-ray crystallographic analysis to be isomer **a**.

M.p. 59°C. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 3H, MeSiO^{t}Bu), 0.36 (s, 3H, MeSiPh), 1.38 (s, 9H, SiO^{t}Bu).

2.5. Spectra

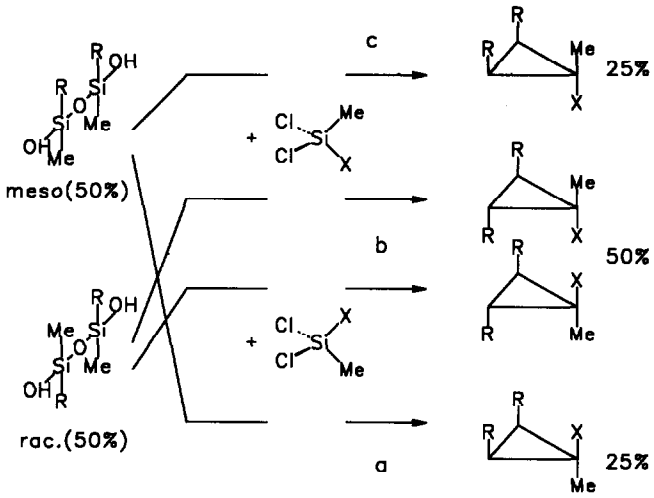
The NMR spectra were recorded on a Bruker WP 80 SY (^{1}H) or a Bruker MSL 300 (^{29}Si) NMR spectrometer operating in the FT mode at 80.13 and 59.63 MHz, respectively, with Me_4Si as internal standard. The chemical shifts are reported in ppm with positive shifts downfield from Me_4Si.

2.6. X-Ray data collection and reduction

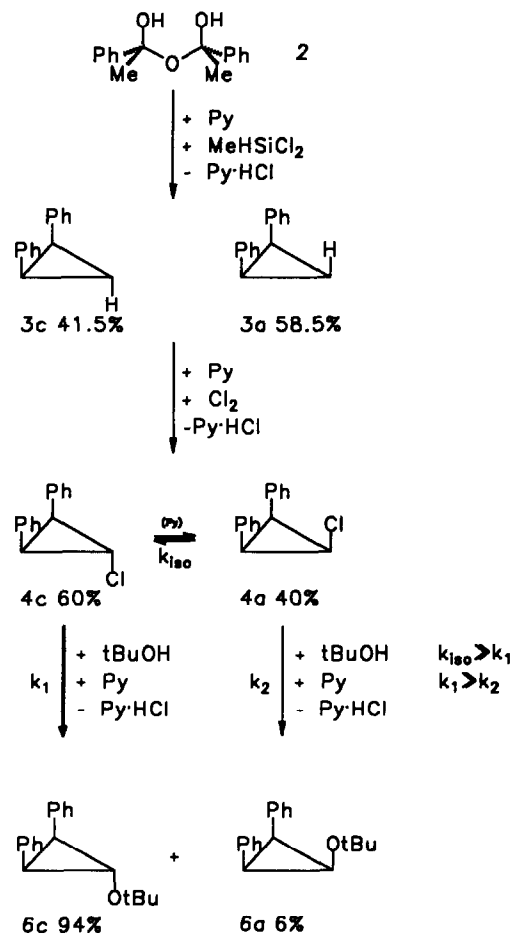
A colorless crystal of dimensions 0.52 × 0.34 × 0.20 mm^3 was used for data collection on a STOE STADI IV automated four-circle diffractometer, using graphite monochromated Mo-Kα radiation (λ = 71.069 pm). Crystal data: $C_{19}H_{28}O_4Si_3$, M = 404.7, monoclinic, space group $P2_1/n$, a = 1072.0(8), b = 893.9(5), c = 2385.8(20) pm, β = 98.80(6)°, V = 2259.10^6 pm^3, Z = 4, D_c = 1.190 g cm^{-3}, μ(Mo-Kα) 1.88 cm^{-1}. A total of 6697 reflections in the range 2θ = 55° were collected at a temperature of 210K by a 2θ–ω scan, and the structure was solved by the direct method followed by the successive Fourier method carried out with the programs SHELXS-76 [11] and SHELXS-86 [12]. After the block diagonal least square refinement for non-hydrogen atoms with anisotropic temperature factors, the positions of the hydrogen atoms were calculated geometrically and verified from the difference Fourier map, and then included in the refinement with isotropic temperature factors. The final R factor was 0.048 (R_w = 0.039) for 3663 reflections with $I > 2\sigma(I)$. Tables of hydrogen atom coordinates and thermal parameters and lists of observed and calculated structure factors are available from the authors.

3. Results and discussion

We first prepared the 2-t-butoxy-2,4,6-trimethyl-4,6-diphenylcyclotrisiloxane as a mixture of three configurational isomers by ring closure of 1,3-dihydroxy-1,3-dimethyl-1,3-diphenyldisiloxane (*meso*:*rac* = 1:1) with t-butoxydichloromethylsilane (Scheme 1). In accordance with our previous NMR assignment studies on similar compounds, we observed that the proportions of the configurational isomers deviated from the statistical 1:2:1 ratio. Thus, by considering the different amounts of steric hindrance associated with the relative positions of the bulky phenyl and t-butoxy substituents in the planar cyclotrisiloxane molecule, two of the NMR signals were assigned to isomers **a** and **c**. The signal with double intensity was then readily assigned to isomer **b**, which exists in two enantiomers. Other recent studies on the NMR assignment of configurationally isomeric cyclotrisiloxanes served to confirm our findings [8–10]. In order to confirm the NMR assignment system on which our stereochemical investigations of substitution reactions at functional cyclotrisiloxane have so far been based, we set out to prepare and isolate a single configurational isomer suitable for X-ray crystallographic study.



Scheme 1. Formation of configurational isomers in the synthesis of cyclotrisiloxanes [(RMeSiO)2(XMeSiO)], with statistical isomeric distribution.



Scheme 2. Route to 2-t-butoxy-2,4,6-trimethyl-4,6-diphenyl-(2α,4β, 6β)-cyclotrisiloxane.

TABLE 1. Atomic coordinates for non-hydrogen atoms in compound **6a**

Atom	x	y	z	U_{eq} / U_{iso}
Si(1)	0.16089(7)	0.3797(1)	0.14993(3)	0.0392(2)
Si(2)	0.25675(8)	0.4927(1)	0.04549(3)	0.0443(3)
Si(3)	0.42481(7)	0.4941(1)	0.15764(3)	0.0432(3)
O(1)	0.1530(2)	0.4272(2)	0.08321(7)	0.457(6)
O(2)	0.3874(2)	0.5191(2)	0.08911(7)	0.0490(7)
O(3)	0.3062(2)	0.4079(2)	0.17931(7)	0.0431(6)
O(4)	0.1198(2)	0.2080(2)	0.15636(7)	0.0445(7)
C(1)	0.0567(3)	0.4947(4)	0.1859(2)	0.055(1)
C(2)	0.1490(3)	0.0716(3)	0.1282(1)	0.045(1)
C(3)	0.1201(4)	−0.0542(4)	0.1667(2)	0.058(1)
C(4)	0.0647(5)	0.0645(5)	0.0713(2)	0.069(2)
C(5)	0.2871(4)	0.0680(4)	0.1212(2)	0.064(1)
C(6)	0.1961(5)	0.6689(5)	0.0127(2)	0.071(2)
C(7)	0.2878(3)	0.3544(3)	−0.0082(1)	0.047(1)
C(8)	0.1967(4)	0.3187(5)	−0.0542(2)	0.074(2)
C(9)	0.2209(6)	0.2151(6)	−0.0944(2)	0.103(2)
C(10)	0.3351(6)	0.1458(6)	−0.0892(2)	0.115(3)
C(11)	0.4261(5)	0.1781(5)	−0.0450(2)	0.096(2)
C(12)	0.4020(4)	0.2822(4)	−0.0052(2)	0.071(2)
C(13)	0.4494(5)	0.6763(4)	0.1933(2)	0.062(1)
C(14)	0.5636(3)	0.3694(4)	0.1713(1)	0.045(1)
C(15)	0.6580(3)	0.3719(4)	0.1374(1)	0.062(1)
C(16)	0.7606(3)	0.2764(5)	0.1476(2)	0.079(2)
C(17)	0.7714(3)	0.1777(5)	0.1913(2)	0.077(2)
C(18)	0.6804(4)	0.1731(5)	0.2264(2)	0.077(2)
C(19)	0.5775(3)	0.2678(4)	0.2157(1)	0.063(1)

In our previous investigations we had found that the use of pure *meso*-disiloxanediol as starting material in the ring closure step led to the formation of only two out of the three possible configurational isomers (Scheme 2). With the number of isomers reduced to two, the substitution of the chlorocyclotrisiloxane by reaction with t-butanol afforded an isomeric mixture that was highly enriched in isomer **c** (Scheme 2). This considerable change of the isomeric ratio can be attributed to a highly stereoselective retention stereochemistry in the substitution of chloro by alkoxy substituents in cyclotrisiloxanes in association with an equilibrium between the chloro-substituted isomers **a** and **c** in the presence of pyridine, with the alkoxycyclotrisiloxanes configurationally stable under the reaction conditions [3]. In the case of bulky nucleophiles such as t-butanol the rate of isomerization (k_{iso}) of the starting material markedly exceeds the rates of the substitutions (k_1, k_2) (Scheme 2). In addition, for steric reasons isomer **4c** reacts much faster than **4a** with the nucleophile that attacks from the side of the leaving group [3]. From the isomeric mixture obtained (**6a** : **6c** = 6 : 94) **6c** (m.p. 33°C) was isolated by recrystallisation from methanol.

Surprisingly, it was not recrystallization of the pure isomer **6c**, but that of the isomeric mixture (**a** : **c** = 6 : 94) that yielded colorless crystals suitable for structure

TABLE 2. Bond lengths (Å) for compound **6a**

Si(1)–O(1)	1.637(2)	C(2)–C(4)	1.513(5)
Si(1)–O(3)	1.627(2)	C(2)–C(5)	1.515(5)
Si(1)–O(4)	1.610(2)	C(7)–C(8)	1.391(5)
Si(1)–C(1)	1.826(4)	C(7)–C(12)	1.377(5)
Si(2)–O(1)	1.641(2)	C(8)–C(9)	1.386(7)
Si(2)–O(2)	1.629(2)	C(9)–C(10)	1.360(9)
Si(2)–C(6)	1.834(5)	C(10)–C(11)	1.354(8)
Si(2)–C(7)	1.846(3)	C(11)–C(12)	1.382(6)
Si(3)–O(2)	1.638(2)	C(14)–C(15)	1.389(4)
Si(3)–O(3)	1.637(2)	C(14)–C(19)	1.385(5)
Si(3)–C(13)	1.838(4)	C(15)–C(16)	1.385(6)
Si(3)–C(14)	1.848(3)	C(16)–C(17)	1.357(6)
O(4)–C(2)	1.449(4)	C(17)–C(18)	1.381(6)
C(2)–C(3)	1.515(5)	C(18)–C(19)	1.383(6)

determination, and these proved to be crystals of **6a**. These crystals belong to the monoclinic space group $P2_1/n$ and the unit cell contains four molecules. Final atomic coordinates, bond lengths and angles are given in Tables 1–3. Figure 2 depicts the molecular structure of **6a**. The established geometry shows once again that the endocyclic siloxane bond angle does not differ significantly from those in acyclic and six-membered cyclic silanes. Thus, the predominant retention stereochemistry in nucleophilic substitution at chlorocyclotrisiloxanes seems to be the result of the overall ring strain in the molecule, rather than of a lower endocyclic bond angle at the reacting silicon atom.

The agreement between the structure established by X-ray diffraction and the NMR assignments based on

TABLE 3. Bond angles (°) for compound **6a**

O(1)–Si(1)–O(3)	106.4(1)	O(4)–C(2)–C(3)	105.3(2)
O(1)–Si(1)–O(4)	111.4(1)	O(4)–C(2)–C(4)	108.1(2)
O(1)–Si(1)–C(1)	111.5(2)	O(4)–C(2)–C(5)	110.6(3)
O(3)–Si(1)–O(4)	111.4(1)	C(3)–C(2)–C(4)	111.3(3)
O(3)–Si(1)–C(1)	108.9(2)	C(3)–C(2)–C(5)	110.2(3)
O(4)–Si(1)–C(1)	107.2(2)	C(4)–C(2)–C(5)	111.1(3)
O(1)–Si(2)–O(2)	106.8(1)	Si(2)–C(7)–C(8)	121.5(3)
O(1)–Si(2)–C(6)	108.3(2)	Si(2)–C(7)–C(12)	122.1(3)
O(1)–Si(2)–C(7)	110.5(1)	C(8)–C(7)–C(12)	116.4(3)
O(2)–Si(2)–C(6)	111.2(2)	C(7)–C(8)–C(9)	121.1(4)
O(2)–Si(2)–C(7)	108.2(1)	C(8)–C(9)–C(10)	120.2(5)
C(6)–Si(2)–C(7)	111.6(2)	C(9)–C(10)–C(11)	120.3(5)
O(2)–Si(3)–O(3)	107.2(1)	C(10)–C(11)–C(12)	119.4(5)
O(2)–Si(3)–C(13)	109.7(2)	C(7)–C(12)–C(11)	122.6(4)
O(2)–Si(3)–C(14)	109.1(1)	Si(3)–C(14)–C(15)	121.7(2)
O(3)–Si(3)–C(13)	109.5(2)	Si(3)–C(14)–C(19)	121.3(2)
O(3)–Si(3)–C(14)	107.7(1)	C(15)–C(14)–C(19)	117.0(3)
C(13)–Si(3)–C(14)	113.5(2)	C(14)–C(15)–C(16)	121.1(3)
Si(1)–O(1)–Si(2)	133.4(1)	C(15)–C(16)–C(17)	120.5(4)
Si(2)–O(2)–Si(3)	132.3(1)	C(16)–C(17)–C(18)	120.1(4)
Si(1)–O(3)–Si(3)	132.5(1)	C(17)–C(18)–C(19)	119.1(4)
Si(1)–O(4)–C(2)	132.5(2)	C(14)–C(19)–C(18)	122.2(3)

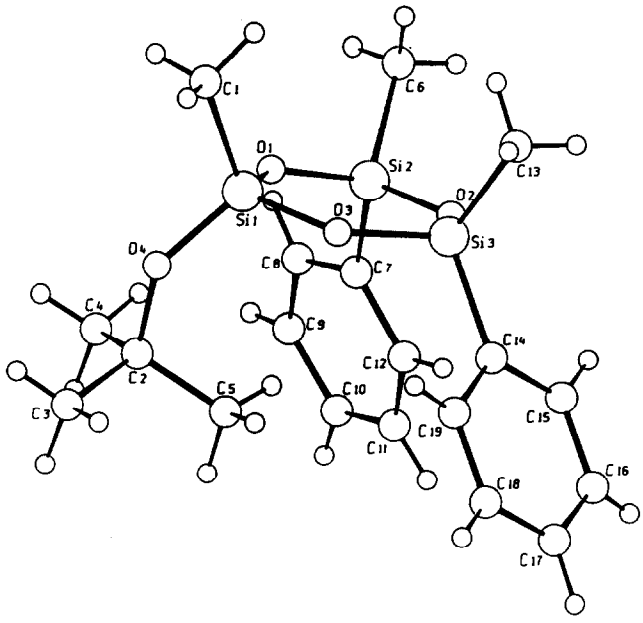


Fig. 2. Structure of 2-t-butoxy-2,4,6-trimethyl-4,6-diphenyl-(2α,4α,6α)-cyclotrisiloxane (**6a**).

isomeric distribution confirms that steric hindrance due to bulky substituents, acting via the planar geometry of the cyclotrisiloxane molecule, results in considerable deviations of the isomeric proportions from the statistical values. This will facilitate extension of our stereochemical studies on functional cyclotrisiloxanes to include new model compounds and previously uninvestigated substitution reactions such as the replacement of a chloride substituent by alkoxy groups by use of orthoformates.

Acknowledgment

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References

1 K. Käppler, U. Scheim, K. Rühlmann and A. Porzel, *J. Organomet. Chem., 441* (1992) 15.
2 R. Gewald, U. Scheim, R. Lang, K. Rühlmann and R. Lehnert, *J. Organomet. Chem., 446* (1993) 79.
3 R. Gewald, K. Rühlmann, U. Scheim and A. Porzel, *J. Organomet. Chem., 377* (1989) 9.
4 U. Scheim, K. Rühlmann, H. Große-Ruyken and A. Porzel, *J. Organomet. Chem., 314* (1986) 39.
5 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.
6 J. Hickton, A. Holt, J. Homer and A. W. Jarvie, *J. Chem. Soc. C*, (1966) 149.
7 U. Wannagat and P. Geymayer, *Mh. Chem., 95* (1964) 1095.

8 E. Pelletier and J. F. Harrod, *Organometallics, 3* (1984) 1070.
9 M. G. Karchkhadse, P. Sh. Tkeshelashvili, L. M. Khananashvili and M. O. Labartkava, *Zh. Obshch. Khim., 60* (1990) 1567.
10 N. R. Belyakova and V. P. Mileshkevich, *Zh. Obshch. Khim., 60* (1990) 2287.
11 G. Sheldrick, SHELXS-76, *Program for Crystal Structure Determination*, Cambridge, 1976.
12 G. Sheldrick, SHELXS-86, *Program for Crystal Structure Solution*, Göttingen, 1986.