related compounds.[7] We have not tested its general applicability, but it gives better results than the direct reaction of the dichloride with MeOH. The general course of the reactions of DMSO with acid chlorides has been discussed extensively.[2-4]

The reaction generates chloromethyl methyl sulfide, which can react further with DMSO, but this reaction is slower than that of DMSO with a phosphonic dichloride, *cf.* ref 8, and causes no problems.

Registry No.—I, 824-72-6; III, 38555-73-6; DMSO, 67-68-5.

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Isomeric 2,4,6-Tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxanes

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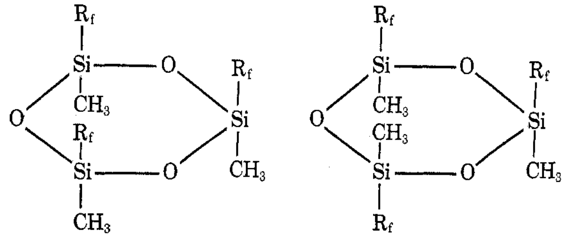
Diorganocyclosiloxanes are an important segment of silicone chemistry and have been studied extensively;[1] however, fluorine-containing diorganocyclosiloxanes are a relatively new class of compounds.[2] Although numerous studies involving diorganocyclosiloxanes have been described in the literature,[1] the isolation and characterization of the stereoisomeric diorganocyclosiloxanes are limited to methylphenylsiloxane[3] and methyl-(3,3,3-trifluoropropyl)siloxane[4] systems. We now wish to report the synthesis and characterization of the *cis*- and *trans*-2,4,6-tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxanes (1 and 2).

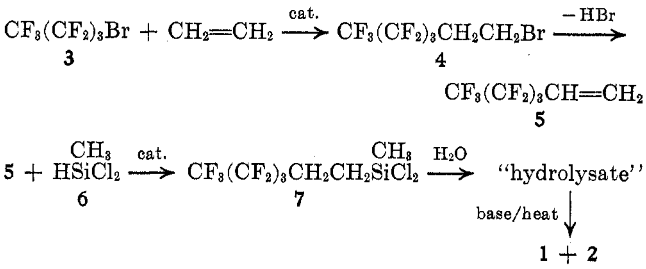


1, cis **2**, trans

$R_f = CF_3CF_2CF_2CF_2CH_2CH_2$

The synthetic route for the preparation of the cyclotrisiloxanes **1** and **2** is shown in Scheme I. The free radical catalyzed addition of ethylene to the bromide **3**[5] followed by dehydrobromination of the resulting adduct **4** gave the olefin **5** in high yield. In the ethylene addition, some of the higher telomers and a small amount of 1,1,1,2,2,3,3,4,4-nonafluorohexane (**8**) were formed in addition to the adduct **4**. The silane **7** was prepared in 86% yield by the addition of silane **6** to olefin **5** using chloroplatinic acid as a catalyst at reflux temperature. The base-induced "cracking" of the hydrolysate of silane **7** at 225–250° yielded a mixture of two stereoisomeric cyclotrisiloxanes (**1** and **2**), a high-melting crystalline solid (mp 36–37°), and a low-melting liquid [mp 22–23°, bp 96° (0.17 mm)], in a ratio (glc) of approximately 1:2, respectively. The stereoisomers were both isolated in gas chromatographically pure form by crystallization from pentane and by fractional distillation, respectively. Both isomers gave a satisfactory elemental analysis and molecular weight for 2,4,6-tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxane. The characteristic cyclotrisiloxane band (Si–O, 9.8 μ)[6] was observed in the infrared absorption spectra of the isomers.

SCHEME I



$$\underset{3}{CF_3(CF_2)_3Br} + CH_2{=}CH_2 \xrightarrow{\text{cat.}} \underset{4}{CF_3(CF_2)_3CH_2CH_2Br} \xrightarrow{-HBr} \underset{5}{CF_3(CF_2)_3CH{=}CH_2}$$

$$5 + \underset{6}{\overset{CH_3}{HSiCl_2}} \xrightarrow{\text{cat.}} \underset{7}{CF_3(CF_2)_3CH_2CH_2\overset{CH_3}{Si}Cl_2} \xrightarrow{H_2O} \text{"hydrolysate"} \xrightarrow{\text{base/heat}} 1 + 2$$

On the basis of thermodynamic considerations[7] and the measurement of the dipole moments (high-melting form, 5.67 D, and low-melting form, 2.75 D),[8] the high-melting form was assigned the cis configuration (**1**) while the low-melting isomer was assigned the trans configuration (**2**). In the infrared absorption spectra, bands at 12.7 and 12.4 μ have been observed for the cis and trans isomers **1** and **2**, respectively. Bands at 12.7 and 12.4 μ were also observed for the *cis*- and *trans*-2,4,6-tris(3,3,3-trifluoropropyl)-2,4,6-trimethylcyclotrisiloxanes, respectively, and appear to be characteristic bands for the respective stereoisomers.[9] It may be of interest to note that the trans isomer was found to be the high-melting solid in the case of 2,4,6-tris(3,3,3-trifluoropropyl)-2,4,6-trimethylcyclotrisiloxanes.[4a]

Experimental Section

All melting points and boiling points are uncorrected. All melting points were measured by placing a sample in a cooling device and the observations were made using a Lietz hot stage microscope. Infrared absorption spectra were determined on a Perkin-Elmer Model 521 grating infrared spectrophotometer. The ^{19}F resonance spectra were measured on a Varian high-

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(7) The stronger reciprocal repulsions of the bulky and electronegative nonafluorohexyl groups would tend to make the formation of the cis isomer less favorable than that of the trans isomer. The trans/cis ratio observed is approximately two.

(8) Since all electronegative nonafluorohexyl groups in the cis isomer are on the one side of the plane of the siloxane ring, a greater dipole moment should be expected for the cis isomer than for the trans isomer.

(9) H. M. Klimisch and R. R. Buch, unpublished results.

resolution nmr spectrometer operating at 56.4 MHz. Chemical shifts are determined in parts per million using CCl_3F as an internal standard (δ 0 ppm). The proton resonance spectra were obtained on a Varian A-60 nmr spectrometer using tetramethylsilane as an internal standard (δ 0 ppm). Gas chromatography was carried out on a Hewlett-Packard Model 5750 using a 10 ft × 0.25 in. column containing 20% Dow Corning FS 1265 Fluid (10,000 cSt) on Anakron 90–100 mesh ABS. The dipole moments were determined by the infinite dilution method at 25° (benzene as solvent).

Addition of Ethylene to 1-Bromononafluorobutane (3).—Into a 2-l. stainless steel stirred pressure reactor were placed 990 g (3.31 mol) of **3** and 33.8 g (0.232 mol) of di-*tert*-butyl peroxide, and the system was flushed with ethylene. The reaction mixture was heated to about 100°, after which ethylene was introduced to a total pressure of about 190 psi. The reaction was then continuously heated to 130–135° and maintained at that temperature throughout the reaction. As the reaction proceeded, the ethylene pressure decreased to about 150 psi; then, additional ethylene was again added to a total pressure of 190 psi. This process was repeated for 2 hr, after which a constant ethylene pressure of about 110 psi was maintained for 16 hr. Distillation of the crude product (1030 g) gave, in addition to intercuts, 350 g (35% recovery) of starting material **3**, bp 44–46°, 363 g (51% yield) of 1-bromo-3,3,4,4,5,5,6,6,6-nonafluorohexane (**4**), bp 42° (35 mm), $n^{25}\mathrm{D}$ 1.3330, 55 g (7% yield) of 1-bromo-5,5,6,6,7,7,-8,8,8-nonafluorooctane (**9**), bp 86° (28 mm), $n^{25}\mathrm{D}$ 1.3580, and 46 g of still residue.

Anal. Calcd for $C_6H_4F_9Br$: C, 22.04; H, 1.23. Found: C, 22.2; H, 1.37.

Anal. Calcd for $C_8H_8F_9Br$: C, 27.06; H, 2.27. Found: C, 27.2; H, 2.39.

The ^{19}F and ^{1}H nmr spectra of **4** and **9** are consistent with the assigned structures, respectively. In making several runs of this reaction, a third component was isolated and identified as 1,1,1,2,2,3,3,4,4-nonafluorohexane (**8**), bp 67°, $n^{25}\mathrm{D}$ *ca.* 1.28.

Anal. Calcd for $C_6H_5F_9$: C, 29.04; H, 2.03; F, 68.93. Found: C, 28.8; H, 2.20; F, 68.6.

The ^{19}F nmr spectrum of **8** shows signals centered at δ 81.6 (3 F), 117.1 (2 F), 124.3 (2 F), and 126.2 (2 F). The ^{1}H nmr spectrum is comprised of signals centered at δ 1.6–2.6 ($-CF_2CH_2-$, 2 H) and 1.12 (CCH_3, 3 H).

Dehydrobromination of 1-Bromo-3,3,4,4,5,5,6,6,6-nonafluorohexane (4).—Into a stirred solution of 220 g of potassium hydroxide in 800 ml of ethanol was added slowly 668 g (2.04 mol) of **4** at room temperature (<45°). After completion of the addition, the mixture was stirred at room temperature overnight. Then, about 700 ml of water was added to the mixture, and the organic layer was separated, washed with water, and dried over Drierite to yield 470 g (93% yield) of crude product. Distillation gave 425 g (85% yield) of analytically pure 3,3,4,4,5,5,-6,6,6-nonafluorohexene-1 (**5**), bp 59–59.5°, $n^{26}\mathrm{D}$ *ca.* 1.28.

Anal. Calcd for $C_6H_3F_9$: C, 29.28; H, 1.23; F, 69.49 Found: C, 29.2; H, 1.40; F, 70.2.

The spectral properties are in agreement with the olefin **5**.

Addition of Methyldichlorosilane (6) to 3,3,4,4,5,5,6,6,6-Nonafluorohexene-1 (5).—Into a stirred and refluxing mixture of 383 g (1.56 mol) of olefin **5** and 1.5 ml of a 0.1 *M* solution of chloroplatinic acid hexahydrate in isopropyl alcohol was added slowly 280 g (2.44 mol) of methyldichlorosilane. After the addition was complete, the mixture was continuously heated under reflux (about 43°) while stirring slowly. At the end of 20 hr, an additional 1 ml of the catalyst was introduced into the mixture, and heating was continued for an additional 48 hr. The resulting mixture, deep yellow in color, was distilled to give 475 g (84% yield) of (3,3,4,4,5,5,6,6,6-nonafluorohexyl)methyldichlorosilane (**7**), bp 78.5° (31 mm), $n^{26}\mathrm{D}$ 1.3540.

Anal. Calcd for $C_7H_7F_9SiCl_2$: C, 23.28; H, 1.95; F, 47.35; Si, 7.78; Cl, 19.64. Found: C, 23.5; H, 1.96; F, 48.2; Si, 7.90; Cl, 19.0.

The ^{19}F nmr spectrum shows signals centered at δ 82.3 (3 F), 116.3 (2 F), 124.3 (2 F), and 126.4 (2 F), indicating the presence of nonafluorobutyl group.

Preparation of a Mixture of the *cis*- and *trans*-2,4,6-Tris-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxanes (1 and 2).—Into a flask containing stirred water (1 l.) was added a solution of 927 g (2.6 mol) of the silane **7** in about 700 ml of ether at room temperature. After the addition was complete, the mixture was stirred at room temperature for several hours, and then the organic layer was separated, washed with aqueous sodium bicarbonate (5%), and dried over Drierite. After removal of ether *in vacuo*, the resulting liquid hydrolysate (790 g) was mixed with 30 g of powdered potassium hydroxide. The mixture was distilled *in vacuo* using a 1 ft vacuum-jacketed bubble-cap column at a pot temperature of 225–250°. Under a heavy reflux, the distillate boiling between 138 and 149° (3 mm) was collected to yield 559 g of a mixture of the cis and trans isomers **1** and **2**. Gas chromatographic analysis indicates that the isomeric mixture (cis:trans = ~1:2) is fairly pure.

Redistillation of the isomer mixture through a bubble-cap column (1 ft × 0.75 in.) with a reflux ratio of 1:50 gave the following fractions (Table I).

TABLE I

Fraction	Bp, °C (1–2 mm)	wt, g	Approx cis:trans (glc)
1	93–136	40	Forecut
2	139–140	23	3:1
3	139–144	25	2:1
4	141	80	1:1
5	141	46	1:1
6	143–144	24	1:2
7	142	38	1:2
8	142–144	40	1:3
9	142	44	1:4
10	142–143	22	1:10
11	Still residue	51	Mostly trans

Isolation of *cis*-2,4,6-Tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxane (1).—A mixture of cis and trans isomers **1** and **2** (175 g, cis:trans *ca.* 1) was cooled briefly (−20°), and the solid was quickly collected by filtration to yield 68 g of an isomeric mixture of **1** and **2** (cis:trans *ca.* 2). This isomeric mixture was dissolved in warm pentane (50 ml), filtered while warm, and then cooled. A white solid was collected by filtration and dried *in vacuo* to yield gas chromatographically pure cis isomer **1**, mp 36–37°, $n^{42}\mathrm{D}$ 1.3348.

Anal. Calcd for $C_{21}H_{21}F_{27}O_3Si_3$: C, 27.45; H, 2.30; Si, 9.17; mol wt, 919. Found: C, 27.80; H, 2.42; Si, 9.17; mol wt, 880 (vpo).

The ^{19}F nmr spectrum shows signals centered at δ 82.1 (CF_3), 117.1 (CF_2CH_2), 125.1 (CF_2), and 126.8 (CF_2). The ^{1}H nmr spectrum is comprised of signals centered at δ 0.24 ($SiCH_3$), 0.65–1.1 ($SiCH_2$), and 1.6–2.6 (CH_2CF_2). The infrared spectrum shows bands at 8.1 and 8.2 (CF), 9.8 (SiOSi), and ~12.7 μ.

Isolation of *trans*-2,4,6-Tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxane (2).—A mixture of cis and trans isomers **1** and **2** (mostly trans isomer) was distilled *in vacuo* using a spinning band column (36 × 0.75 in.; *ca.* 35 theoretical plates) to yield a greater than 98% stereochemically pure trans isomer **2**: bp 96° (0.17 mm); mp 22–23°; $n^{25}\mathrm{D}$ 1.3403; $d^{25}{}_4$ 1.495.

Anal. Calcd for $C_{21}H_{21}F_{27}O_3Si_3$: C, 27.45; H, 2.30; F, 55.84; Si, 9.17; mol wt, 919. Found: C, 27.30; H, 2.52; F, 55.9; Si, 9.15; mol wt, 907 (vpo).

The ^{19}F nmr spectrum is comprised of signals centered at δ 81.0 (CF_3), 116.5 (CF_2CH_2), 124.5 (CF_2), and 126.0 (CF_2). The ^{1}H nmr spectrum is identical with that of the cis isomer. The infrared spectrum shows bands at 8.1 and 8.2 (CF), 9.8 (SiOSi), and ~12.4 μ.

Registry No.—**1**, 38521-58-3; **2**, 38521-59-4; **3**, 375-48-4; **4**, 38436-14-5; **5**, 19430-93-4; **6**, 75-54-7; **7**, 38436-16-7; **8**, 38436-17-8; **9**, 38436-18-9; ethylene, 74-85-1.