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1,3,5-Trimethyl-1,3,5-tris(hexafluoroalkyl)cyclotrisiloxanes. Basicity of Ethoxysilanes and Cyclosiloxanes

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Abstract—1,3,5-Trimethyl-1,3,5-tris(hexafluoroalkyl)cyclotrisiloxanes were synthesized by hydrolytic polycondensation of methyl(hexafluoroalkyl)dichlorosilanes, and 1,1,3,3,5-pentamethyl-5-(trifluoromethyltrifluorobicyclo[2.2.1]heptyl)cyclotrisiloxane was synthesized by heterofunctional condensation. The effect of hexafluoroalkyl substituents at the silicon atom on the reactivity of the siloxane bonds has been studied.

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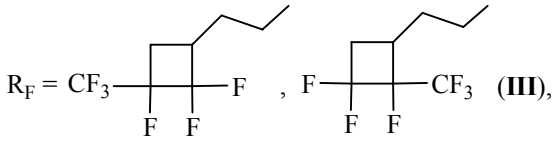
1,3,5-Trimethyl-1,3,5-tris(hexafluoroalkyl)cyclotrisiloxanes are monomers for preparation of the polymethyl(hexafluoroalkyl)siloxane based hermetics and rubbers working in a wide temperature range and possessing high resistance to oils, fuels, greases, aliphatic, aromatic and chlorinated hydrocarbons. Polymethyl(hexafluoroalkyl)siloxane rubbers [1–3] should replace the missing in the domestic market polymethyl (3,3,3-trifluoropropyl)siloxane rubbers.

In the present work by the method of hydrolytic polycondensation (HPC) of the earlier prepared [4] mixtures of 2-(2-trifluoromethyl-2,3,3-trifluorocyclobutyl)ethylmethyldichlorosilane and 2-(3-trifluoromethyl-2,2,3-trifluorocyclobutyl)ethylmethyldichlorosilane (**I**), and 2,2,3-trifluoro-3-trifluoromethyl-5-methyldichlorosilylbicyclo[2.2.1]heptane and 2,3,3-trifluoro-2-trifluoromethyl-5-methyldichlorosilylbicyclo[2.2.1]-heptane (**II**) followed by thermocatalytic rearrangement of the hydrolyzate and vacuum rectification were obtained the corresponding cyclotrisiloxanes **III** and **IV** of the general formula $(R_FSiMeO)_3$.

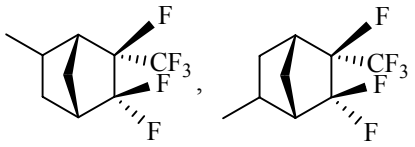
The conditions of HPC were investigated in order to maximize the yield of the trimer. The amount of the formed trimer was determined by the methods of GLC and ^{29}Si NMR spectroscopy.

The most widely used method of hydrolysis with water [5] taken as calculated on 25% liberated hydrochloric acid, gives 25–28% of the trimer, 15% of tetramer, and 64% of linear oligomers. Similar results

$$R_F(CH_3)SiCl_2 + H_2O$$
$$\rightarrow HO[SiR_F(CH_3)O]_nH + [SiR_F(CH_3)O]_m,$$
$$HO[SiR_F(CH_3)O]_nH \rightleftarrows [SiR_F(CH_3)O]_3,$$
$$m = 3–6,\ n = 1–10;$$



(**III**),



(**IV**).

were obtained in the hydrolysis with water–tetrahydrofuran mixtures [5] or with *tert*-butyl alcohol (24–28 and 25–26%, respectively) [6].

The saturated aqueous solutions of sodium, magnesium, and aluminum sulfates were inefficient as hydrolytic agents; the yield of cyclotrisiloxanes did not exceed 5–8% [7].

We have also used the mixture of sodium carbonate with urea, which afforded a "standard" yield of the trimer, 30%. The mixture of sodium carbonate with pyridine [8] gave somewhat higher yield, 33–35%.

The most efficient was the hydrolysis of methyl(hexafluoroalkyl)dichlorosilanes with urea in acetone, where the yield of the trimer reached 50–55%.

The ^{29}Si NMR spectrum of trimers **III** and **IV** contains two signals, due to the difference in the chemical shifts of the silicon atoms bearing isomeric radicals R_F, rather than the *cis*-*trans* isomerism with respect to the ring plane. This is proved by the fact that the mixture of the starting chlorosilanes gives two different signals in the ^{29}Si NMR spectra with the ratio of intensities corresponding to the ratio of the isomers in the mixture, and that the *cis*- and *trans*-1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxanes F_3 give one signal at –9.41 ppm. The ^{19}F and ^{1}H NMR spectra prove the retention of the hexafluoroalkyl radical in both trimers.

The thermocatalytic decomposition of the stillage residues gives depolymerizate containing up to 50% of trimers **III** and **IV**, respectively, which were isolated by the subsequent vacuum rectification. All their characteristics were identical to those obtained earlier. Besides, from the depolymerizate, cyclotetrasiloxanes and α,ω-oligosiloxanediols were isolated and characterized.

The necessity to prepare the copolymer with dimethylsiloxane links is due to the fact that poly [methyl(5-trifluoromethyl-5,6,6-trifluorobicyclo[2.2.1] heptyl)]siloxane is not an elastomer.[1] For this, we have synthesized 1,1,3,3,5-pentamethyl-5-(5-trifluoromethyl-5,6,6-trifluorobicyclo[2.2.1.]heptyl)cyclotrisiloxane (**V**) by the method of heterofunctional condensation of chlorosilane **II** with tetramethyldisiloxanediols in the presence of amine for binding the liberated HCl. Apart from the main product formed in 80% yield, up to 15% of 1,1,3,3,5,7,7,9,9,11-decamethyl-5,11-di(5-trifluoromethyl-5,6,6-trifluorobicyclo[2.2.1]heptyl)-hexatrisiloxane was obtained.

We have studied the effect of the hexafluoroalkyl groups on the basicity and, hence, the reactivity of the siloxane bonds [9–13]. For this, methyl(hexafluoroalkyl)diethoxysilanes were synthesized using the hydrosilylation reaction [4]. The vacuum rectification gave the mixture of the isomers of 2-(2-trifluoromethyl-2,3,3-trifluorocyclobutyl)ethylmethyldiethoxysilane and 2-(3-trifluoromethyl-2,2,3-trifluorobicyclobutyl)ethylmethyldiethoxysilane (**VI**), and the mixture of the isomers of 2- trifluoromethyl-2,3,3-trifluoro-5-(diethoxymethylsilyl)bicyclo[2.2.1]-heptane and 3-trifluoromethyl-2,2,3-trifluoro-5-(diethoxymethylsilyl)bicyclo[2.2.1]heptane (**VII**).

Values of Δν of diethoxysilanes and cyclotrisiloxanes

Compound	Δν
$(CH_3)_2Si(OC_2H_5)_2$	257 [9]
$(CF_3CH_2CH_2)_2Si(OC_2H_5)_2$	217 [10]
$(CH_3)_3Si(OC_2H_5)$	275 [9, 12]
$(CF_3CH_2CH_2)(CH_3)_2Si(OC_2H_5)$	255 [10]
$(CF_3CH_2CH_2)_2(CH_3)Si(OC_2H_5)$	235 [10]
$(CF_3CH_2CH_2)(CH_3)Si(OC_2H_5)_2$	237
VI	250
VII	240
1,1,3,3,5,5-Hexamethylcyclotrisiloxane	166 [11]
cis-F_3	131 [11]
trans-F_3	129 [11]
III	150
IV	130

We have studied the basicity of a series of diethoxysilanes by the method of IR spectroscopy using the shift of the Δν(OH) band of phenol in carbon tetrachloride solutions. The obtained data are shown in the table.

It can be seen from these data that the replacement of one methyl group in ethoxysilanes by trifluoropropyl causes the shift of the stretching vibrations frequency by 20 cm^{-1}, which is related to the negative inductive effect of the fluorine atom decreasing the basicity of ethoxysilane [13].

The value of this shift for ethoxysilanes **VI** is close to that for dimethyldiethoxysilane: 250 and 260 cm^{-1}, respectively. A small difference in the shifts is due to the steric effect of a bulky ethylcyclobutyl substituent rather than the inductive effect of the fluorine atom, which is separated from the silicon atom by five σ-bonds [14].

The value of the shift for ethoxysilanes **VII** is strongly different from that for dimethyldiethoxysilane due to closer location of the fluorine atoms to silicon (4 σ-bonds), and it is practically identical to that for methyl(3,3,3-trifluoropropyl)diethoxysilane, in spite of the doubled number of the fluorine atoms. Apparently

[1] Preparation of polymethyl(hexafluoroalkyl)siloxane rubbers will be reported elsewhere.

at the same number of the σ-bonds, the presence of two branches of the carbon chain decreases the inductive effect of fluorine much stronger than in the direct carbon chain.

Cyclotrisiloxanes **III** and **IV** are characterized by a clearly exhibited influence of the steric effect of the substituent on the basicity, which is proved by very low intensity of the band of associated hydroxy group that becomes hardly distinguishable from the band of homoassociates of the phenol molecules.

The value of the shift for **III** is close to that for 1,1,3,3,5,5-hexamethylcyclotrisiloxane (D_3) and much higher than for F_3, that proves manifestation of the steric effect of the substituent. The value of the shift for **IV** is equal to the value for F_3 because of manifestation of the combined effect of the inductive and steric effects of the bicycloheptyl radical.

Therefore, cyclotrisiloxanes and cyclotetrasiloxanes possessing hexafluorinated cyclic and bicyclic substituents are described. The effect of the hexafluoroalkyl substituent on the basicity and reactivity of the siloxane bonds is studied. The reactivity of 1,3,5-trimethyl-1,3,5-tris(2-trifluoromethyl-2,3,3-trifluorocyclobutyl)ethylcyclotrisiloxane in the reactions of anionic and cationic polymerization is found to be lower than that of dimethylcyclosiloxanes due to the steric effect of the (hexafluorobutyl)ethyl radical; the reactivity of 1,3,5-trimethyl-1,3,5-tris(5-trifluoromethyl-5,6,6-trifluorobicyclo[2.2.1]heptyl)cyclotrisiloxane in the reactions of anionic polymerization is higher than in cationic polymerization because of the (*–I*)-effect of the fluorine atom, but in both cases is low due to steric hindrances.

EXPERIMENTAL

^1H, ^{19}F, ^{29}Si NMR spectra were registered on a Bruker Spectrospin AM-500 spectrometer at working frequencies of 500.13, 470.6, and 99.36 MHz, respectively. For the ^{19}F NMR spectra the chemical shifts are reported relative to the external reference hexafluorobenzene, for the ^1H and ^{29}Si NMR spectra, relative to the internal reference tetramethylsilane, solvents $CDCl_3$ and $(CD_3)_2CO$. IR spectra were taken on a Beckman spectrometer.

The analysis of the reaction mixture, intermediate fractions, and the target products was performed by the GLC method on LKhM-8MD chromatograph, diameter of column 4 mm, length 1m, stationary phase SKTFT-50 on Celite-545 0.25–0.5, detector catharometer, carrier gas helium.

Preparation of 1,3,5-trimethyl-1,3,5-tris(hexafluoroalkyl)cyclotrisiloxanes *(general procedure).* A three-neck flask of 1 l capacity equipped with a mechanical stirrer and a dropping funnel was charged with urea taken in 1.1 mol per 1 g-atom of chlorine and mixed with the five-fold volume of acetone (relative to chlorosilane). The stirrer was switched on and chlorosilane was supplied with such a speed that the temperature of the mixture would not exceed 40°C. After the addition was completed the mixture was refluxed for 3 h, cooled to room temperature, 250 ml of ethyl acetate was added, the organic layer was separated, washed with water, with 3% aqueous sodium carbonate and again with water. The cyclotrisiloxane was isolated by the vacuum rectification.

Stillage residues were subjected to thermocatalytic decomposition by treatment with KOH taken in the amount of 0.5 mol % from the mass of the residue, and cyclotrisiloxane and cyclotetrasiloxane were isolated by rectification.

1,3,5-Trimethyl-1,3,5-tris(2-trifluoromethyl-2,3,3-trifluorocyclobutyl)ethylcyclotrisiloxane (III). By the hydrolysis with the mixture of 400 ml of acetone and 43 g (0.68 mol) of urea, from 80 ml (0.323 mol) of chlorosilanes **I** 45.2 g of 1,3,5-trimethyl-1,3,5-tris(2-trifluoromethyltri-fluorocyclobutyl)ethylcyclotrisiloxane **III** was obtained, bp 185°C (2 mm Hg); n_D^{20} 1.3950; d_{20}^{20} 1.3630. Found, %: C 36.45; H 3.41; F 43.31; Si 10.95. *M* 798, 795. Calculated, %: C 36.50; H 3.10; F 43.40; Si 10.90. *M* 792. ^1H NMR spectrum: 0.45 (3H, Si–CH_3); 0.64 (2H, 1-CH_2); 1.4 (2H, 2-CH_2); 1.65 (1H, 1'-CH); 2.2 (2H, 4'-CH_2). ^{19}F NMR spectrum: –78.58 (3F, 2-CF_3); –73.88 (3F, 3-CF_3); AB quartet δ_A –103.66, δ_B –106.52, J_{AB} = 229 Hz, (2F, 3-CF_2); AB quartet δ_A –100.12, δ_B –116.58, J_{AB} = 225 Hz, (2F, 2-CF_2) –193.53 (1F, 2-CF), –170.47 (1F, 3-CF). ^{29}Si NMR spectrum: –9.51, –9.61.

The residue of 40 g (0.39 mol) was depolymerized by the action of 0.035 g KOH, and vacuum rectification gave 17 g of **III**. The total yield of **III** 73%.

1,3,5,7-Tetramethyl-1,3,5,7-tetra(2-trifluoromethyl-2,3,3-trifluorocyclobutyl)ethylcyclotetrasiloxane. bp 200°C (1 mm Hg); n_D^{20} 1.3971; d_{20}^{20} 1.3644. ^{29}Si NMR spectrum: –20.08, –20.31.

1,3,5-Trimethyl-1,3,5-tris-(5-trifluoromethyl-5,6,6-trifluorobicyclo[2.2.1]heptyl)cyclotrisiloxane

(IV). By the hydrolysis with the mixture of 365 ml of acetone and 43 g (0.68 mol) of urea, from 73.6 ml (0.323 mol) of chlorosilanes **II** 44.5 g of 1,3,5-trimethyl-1,3,5-tris(trifluoromethyltrifluorobicyclo-[2.2.1]heptyl)cyclotrisiloxane (**IV**) was obtained, bp 240°C (1 mm Hg); mp 130°C. Found, %: C 39.41; H 3.21; F 41.45; Si 10.59. *M* 834, 835. Calculated, %: C 39.30; H 3.01; F 41.52; Si 10.62. *M* 792. ^{1}H NMR spectrum: 0.36 (3H, Si–CH_3); 1.34 (1H, 5-CH); 1.86 (2H, 6-CH_2); 1.98 (2H, 7-CH_2), 2.78–2.97 (2H, 1-CH and 4-CH). ^{19}F NMR spectrum: –68.17, –70.44, –71.77, –72.77 (–F_3); 3AB quartets δ_A –108.18, δ_B –118.14, J_{AB} = 235.5 Hz, δ_A –107.26, δ_B –113.26, J_{AB} = 260 Hz, δ_A –108.61, δ_B –117.65, J_{AB} = 250 Hz, (–CF_2); –165.3, –170.06, –175.2, –176.9, (–CF). ^{29}Si NMR spectrum: –10.29, –10.80.

The residue of 37 g was depolymerized by the action of 0.04 g KOH, and vacuum rectification gave 18 g of **IV**. The total yield of **IV** 70%.

1,3,5,7-Tetramethyl-1,3,5,7-tetra(5-trifluoromethyl-5,6,6-trifluorobicyclo[2.2.1]heptyl)cyclotetrasiloxane. bp 250°C (1 mm Hg). ^{29}Si NMR spectrum: –20.72 and –20.74.

1,1,3,3,5-Pentamethyl-5-(trifluoromethyltrifluorobicyclo[2.2.1]heptyltricyclotrisiloxane (V). *General procedure of heterofunctional condensation*. To a three-neck flask of 1 l capacity equipped with a mechanical stirrer and two dropping funnels a half of the required volume of dibutyl ether was added and at vigorous stirring simultaneously from one dropping funnel the solution of methyl(hexafluoroalkyl)dichlorosilane in 1/4 of volume of the solvent, and from the other dropping funnel the solution of tetramethyldisiloxanediol (TMD) with pyridine in 1/4 of volume of the solvent was added. The molar ratio dichlorosilane/TMD/pyridine was 1:1:2. During the reaction the precipitate of pyridinium hydrochloride was formed. When the addition was completed the mixture was reflluxed for 3 h, the organic layer was separated, washed with water, with 3% HCl, with water, with 3% solution of sodium carbonate, with water, and dried over $CaCl_2$. The solvent was removed at atmospheric pressure, the residue was distilled in a vacuum. From 91.2 g (86.4 ml, 0.4 mol) of chlorosilane **II**, 66.4 g (0.4 mol) of TMD and 111 ml (0.8 mol) of pyridine and 400 ml of dibutyl ether, 45 g (80%) of product **VII** was obtained, bp 62°C (1 mm Hg); n_D^{20} 1.4085, d_{20}^{20} 1.2656. Found, %: C 36.99; H 4.91; F 26.65; Si 20.59. *M* 418, 422. Calculated, %: C 36.93; H 4.68; F 26.54; Si 20.68. *M* 424. ^{1}H NMR spectrum: 0.36 (3H, Si–CH_3); 1.34 (1H, 5-CH); 1.86 (2H, 6-CH_2); 1.98 (2H, 7-CH_2), 2.78–2.97 (2H, 1-CH and 4-CH). ^{19}F NMR spectrum: –68.17, –70.44, –71.77, –72.77 (–CF_3); 3AB quartets δ_A –108.18, δ_B –118.14, J_{AB} = 235.5 Hz, δ_A –107.26, δ_B –113.26, J_{AB} = 260 Hz, δ_A –108.61, δ_B –117.65, J_{AB} = 250 Hz, (–CF_2); –165.3, –170.06, –175.2, –176.9, (–CF). ^{29}Si NMR spectrum: –8.14, –11.89, and –12.41.

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