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Abstract

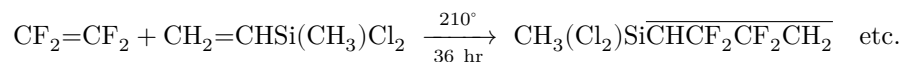
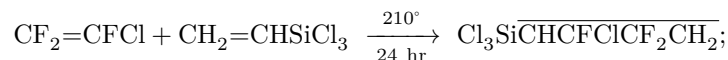
Full Text

Chemistry

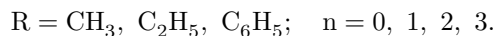
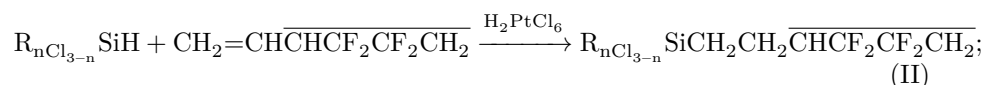
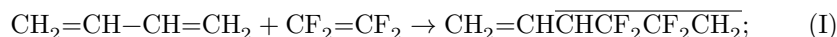
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Organosilicon Monomers with Fluorine-Containing Cyclobutyl Rings

Organosilicon polymers containing fluorinated cyclobutyl rings, according to literature data (¹⁻³), possess a number of valuable properties. The method for synthesizing the monomers from which the indicated polymers are obtained consists in the condensation of tetra- and trifluorochloroethylenes with alkenylsilanes, proceeding under pressure for 24-36 hours (¹⁻⁴). The reactions proceed according to the schemes:



In the present work another route was studied for the synthesis of organosilicon monomers containing fluorinated cyclobutyl rings, namely synthesis according to the schemes:



The condensation of butadiene with tetrafluoroethylene (scheme I) proceeds fairly readily. The yield of $\text{CH}_2=\text{CH}\overline{\text{CHCF}_2\text{CF}_2\text{CH}_2}$ in this case reaches 90% (⁵). As can be seen from Table 1, all the silicon hydrides taken by us, in the presence of platino-

Table 1

No.	Silicon hydride	Amount, g (mol)	Vinyl tetrafluorocyclobutane, g (mol)	Amount of 0.1 M solution of H ₂ PtCl ₆ , ml	Weight of reaction products, g	Reaction products	Yield, g	Yield, %
1	Cl ₃ SiH	13.6 (0.1)	15.4 (0.1)	0.1	27.5	Cl ₃ SiCH ₂ CH ₂ CHCF ₂ CF ₂ CH ₂	27.5	46%
2	CH ₃ SiCl ₂ H	4.0 (0.12)	16.5 (0.11)	0.2	29.5	CH ₃ (Cl ₂)SiCH ₂ CH ₂ CHCF ₂ CF ₂ CH ₂	29.5	46%
3	C ₂ H ₅ SiCl ₂ H	8.0 (0.06)	9.0 (0.06)	0.1	16.0	C ₂ H ₅ (Cl ₂)SiCH ₂ CH ₂ CHCF ₂ CF ₂ CH ₂	16.0	46%
4	CH ₃ (C ₂ H ₅) ₂ SiH	16.0 (0.1)	15.4 (0.1)	0.1	25.7	CH ₃ (C ₂ H ₅) ₂ SiCH ₂ CH ₂ CHCF ₂ CF ₂ CH ₂	25.7	46%
5	CH ₃ (C ₂ H ₅) ₂ SiH	16.0 (0.1)	15.4 (0.1)	0.1	24.5	CH ₃ (C ₂ H ₅) ₂ SiCH ₂ CH ₂ CHCF ₂ CF ₂ CH ₂	24.5	46%
6	C ₆ H ₅ SiCl ₂ H	8.8 (0.04)	6.0 (0.04)	0.05	11.3	C ₆ H ₅ (Cl ₂)SiCH ₂ CH ₂ CHCF ₂ CF ₂ CH ₂	11.3	46%
7	Cl ₂ SiH ₂	7.5 (0.075)	23.2 (0.15)	0.3	25.6	Cl ₂ Si(CH ₂ CH ₂ CHCF ₂ CF ₂ CH ₂) ₂	25.6	46%

hydrochloric acid add to vinyltetrafluorocyclobutane in high yields. We also succeeded, under relatively more severe conditions (in an autoclave at 130°), in adding dichlorosilane in the presence of chloroplatinic acid to two molecules of vinyltetrafluorocyclobutane and obtaining, as is seen from Table 1, the corresponding monomer in 46% yield.

Experimental Part

1. β -(2,2,3,3-Tetrafluorocyclobutylethyl)trichlorosilane

Cl₃SiCH₂CH₂CHCF₂CF₂CH₂. Into a three-necked round-bottom flask of 250 ml capacity, equipped with a mechanical stirrer, reflux condenser, and dropping funnel, were placed 4 ml of vinyltetrafluorocyclobutane, 0.1 ml of a 0.1 M solution of H₂PtCl₆ · 6H₂O in isopropyl alcohol, and 1 ml of HSiCl₃. The reaction mixture was heated on a water bath until the reaction began (~80°), then a mixture of CH₂ = CHCHCF₂CF₂CH₂ with HSiCl₃ was gradually added (in all, 15.4 g (0.1 mole) of CH₂ = CHCHCF₂CF₂CH₂ and 13.6 g (0.1 mole) of HSiCl₃ were taken for the reaction) at such a rate as to maintain the temperature at this level. After the addition of the reagents was complete, the reaction mixture was heated for a further 15 min on the water bath

with vigorous stirring. From 27.5 g of the crude reaction-product mixture, distillation in vacuo gave 26.5 g (91%) of $\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$, b.p. 103.5–104.0° (31 mm); d_4^{20} 1.4395; n_D^{20} 1.4160; found MR_D 50.48; calculated 50.31.

Found, %: C 25.11; 25.21; H 2.89; 3.02; Cl 36.56; 36.50
 $\text{C}_6\text{H}_7\text{SiCl}_3\text{F}_4$. Calculated, %: C 24.89; H 2.44; Cl 36.76

2. **β -(2,2,3,3-Tetrafluorocyclobutylethyl)methyldichlorosilane**

$\text{CH}_3(\text{Cl}_2)\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$. From 29.5 g of the crude reaction-product mixture obtained under the conditions of experiment 1, distillation in vacuo gave 25.8 g (91%) of $\text{CH}_3(\text{Cl}_2)\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$, b.p. 105–105.5° (28.5 mm), d_4^{20} 1.3151; n_D^{20} 1.4120; found MR_D 50.93; calculated 50.68.

Found, %: C 31.38; 31.45; H 3.94; 3.86; Cl 26.07; 26.06
 $\text{C}_7\text{H}_{10}\text{SiCl}_2\text{F}_4$. Calculated, %: C 31.30; H 3.72; Cl 26.05

3. **β -(2,2,3,3-Tetrafluorocyclobutylethyl)ethyldichlorosilane**

$\text{C}_2\text{H}_5(\text{Cl}_2)\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$. From 16 g of the crude reaction-product mixture obtained under the conditions of experiment 1, distillation in vacuo gave 13.9 g (82%) of $\text{C}_2\text{H}_5(\text{Cl}_2)\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$, b.p. 99° (11 mm), d_4^{20} 1.2834; n_D^{20} 1.4180; found MR_D 55.61; calculated 55.19.

Found, %: C 34.54; 34.44; H 4.79; 4.69; Cl 24.87; 24.68
 $\text{C}_8\text{H}_{12}\text{SiCl}_2\text{F}_4$. Calculated, %: C 33.92; H 4.26; Cl 25.00

4. **β -(2,2,3,3-Tetrafluorocyclobutylethyl)methylethylchlorosilane**

$\text{CH}_3(\text{C}_2\text{H}_5)(\text{Cl})\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$. From 25.7 g of the crude reaction-product mixture obtained under the conditions of experiment 1, distillation in vacuo gave 20.6 g (79%) of $\text{CH}_3(\text{C}_2\text{H}_5)(\text{Cl})\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$

b.p. 96–96.5° (13.5 mm), d_4^{20} 1.1663; n_D^{20} 1.4102; found MR_D 55.84; calculated 55.56.

$\text{C}_9\text{H}_{15}\text{SiClF}_4$. Found, %: C 41.03; 41.05; H 5.68; 5.81; Cl 13.33; 12.79
 Calculated, %: C 41.10; H 5.75; Cl 13.47

5. **β -(2,2,3,3-tetrafluorocyclobutylethyl)methyldiethylsilane**

$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$. From 24.5 g of the crude mixture of reaction products obtained under the conditions of

experiment 1, distillation under vacuum gave 18.3 g (72%) of $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$, b.p. $86-86.5^\circ$ (11 mm), d_4^{20} 1.0373; n_D^{20} 1.4070; found MR_D 60.84; calculated 60.94.

$\text{C}_{11}\text{H}_{20}\text{SiF}_4$. Found, %: C 52.01; 52.24; H 7.92; 7.79; F 29.69; 29.69
Calculated, %: C 51.79; H 7.83; F 29.66

6. **β -(2,2,3,3-tetrafluorocyclobutylethyl)phenyldichlorosilane**

$\text{C}_6\text{H}_5(\text{Cl})_2\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$. From 11.3 g of the crude mixture of reaction products obtained under the conditions of experiment 1, distillation under vacuum gave 8.9 g (70%) of $\text{C}_6\text{H}_5(\text{Cl})_2\text{SiCH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2$, b.p. $119.5-120^\circ$ (3.5 mm), d_4^{20} 1.3223; n_D^{20} 1.4836; found MR_D 70.90; calculated 70.35.

$\text{C}_{12}\text{H}_{12}\text{SiCl}_2\text{F}_4$. Found, %: C 44.55; 44.27; H 3.69; 3.92; Cl 21.90; 21.68
Calculated, %: C 43.80; H 3.64; Cl 21.26

7. **Bis-(β -2,2,3,3-tetrafluorocyclobutylethyl)dichlorosilane** $\text{Cl}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2)_2$.

Into a sampling autoclave of stainless steel with a capacity of 200 ml, in a glass tube, was placed a mixture of 23.2 g (0.15 mole) of $\text{CH}_2=\text{CHCHCF}_2\text{CF}_2\text{CH}_2$, 7.5 g (0.075 mole) of H_2SiCl_2 , and 0.3 ml of a 0.1 M solution of $\text{H}_2\text{PtCl}_2 \cdot 6\text{H}_2\text{O}$ in isopropyl alcohol. The mixture was heated to 120° , at which a sharp temperature rise to 158° was observed. The pressure meanwhile remained unchanged, 5.5 atm. The reaction time was 2 hours. On unloading the autoclave, the residual pressure was 1 atm. From 25.6 g of the crude mixture of reaction products, distillation under vacuum gave 14.2 g (46%) of crystalline $\text{Cl}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CHCF}_2\text{CF}_2\text{CH}_2)_2$, b.p. $125-126^\circ$ (2.5 mm).

$\text{C}_{12}\text{H}_{14}\text{SiCl}_2\text{F}_8$. Found, %: C 35.17; 35.55; H 3.48; 3.57; Cl 17.10; 17.35
Calculated, %: C 35.18; H 3.48; Cl 17.32

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CITED LITERATURE

1. L. W. Frost, U.S. pat. 2596967 (1952); *Chem. Abstr.*, **47**, 4365 (1953).

2. Brit. pat. 760201 (1956); *Chem. Abstr.*, **51**, 14796 (1957).
3. Brit. pat. 802358 (1958); *Chem. Abstr.*, **52**, 9100 (1959).
4. J. D. Park, J. D. Groves, J. R. Lacher, *J. Org. Chem.*, **25**, No. 9, 1628 (1960).
5. D. D. Goffman, P. L. Barrick et al., *J. Am. Chem. Soc.*, **71**, 490 (1948).

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