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Abstract

Full Text

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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:

$$CF_2{=}CFCl + CH_2{=}CHSiCl_3 \xrightarrow[24\ hr]{210^\circ} Cl_3Si\overline{CHCFClCF_2CH_2};$$

$$CF_2{=}CF_2 + CH_2{=}CHSi(CH_3)Cl_2 \xrightarrow[36\ hr]{210^\circ} CH_3(Cl_2)Si\overline{CHCF_2CF_2CH_2} \quad \text{etc.}$$

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

$$CH_2{=}CH{-}CH{=}CH_2 + CF_2{=}CF_2 \rightarrow CH_2{=}CH\overline{CHCF_2CF_2CH_2}; \qquad \text{(I)}$$

$$R_{nCl_{3-n}}SiH + CH_2{=}CH\overline{CHCF_2CF_2CH_2} \xrightarrow{H_2PtCl_6} R_{nCl_{3-n}}SiCH_2CH_2\overline{CHCF_2CF_2CH_2}; \qquad \text{(II)}$$

$$R = CH_3,\ C_2H_5,\ C_6H_5; \quad n = 0,\ 1,\ 2,\ 3.$$

The condensation of butadiene with tetrafluoroethylene (scheme I) proceeds fairly readily. The yield of $CH_2{=}CH\overline{CHCF_2CF_2CH_2}$ 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)	Vinyltetrafluorocyclobutane, g (mol)	Amount of 0.1 M solution of H_2PtCl_6, ml	Weight of reaction products, g	Reaction products	Yield, g	Yield, %
1	Cl_3SiH	13.6 (0.1)	15.4 (0.1)	0.1	27.5	$Cl_3SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	25.5	91.0
2	CH_3SiCl_2H	14.0 (0.12)	16.5 (0.11)	0.2	29.5	$CH_3(Cl_2)SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	26.8	90.0
3	$C_2H_5SiCl_2H$	8.0 (0.06)	9.0 (0.06)	0.1	16.0	$C_2H_5(Cl_2)SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	13.9	82.0
4	$CH_3(C_2H_5)SiClH$	9.9 (0.1)	15.4 (0.1)	0.1	25.7	$CH_3(C_2H_5)(Cl)SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	20.6	79.0
5	$CH_3(C_2H_5)_2SiH$	10.5 (0.1)	15.4 (0.1)	0.1	24.5	$CH_3(C_2H_5)_2SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	18.3	71.0
6	$C_6H_5SiCl_2H$	6.8 (0.04)	6.0 (0.04)	0.05	11.3	$C_6H_5(Cl_2)SiCH_2CH_2\overline{CHCF_2CF_2CH_2}$	8.9	77.0
7	Cl_2SiH_2	7.5 (0.075)	23.2 (0.15)	0.3	25.6	$Cl_2Si(CH_2CH_2\overline{CHCF_2CF_2CH_2})_2$	16.0	46.0

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** $Cl_3SiCH_2CH_2\,CHCF_2CF_2CH_2$. 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 $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol, and 1 ml of $HSiCl_3$. The reaction mixture was heated on a water bath until the reaction began (~80°), then a mixture of $CH_2 = CH\,CHCF_2CF_2CH_2$ with $HSiCl_3$ was gradually added (in all, 15.4 g (0.1 mole) of $CH_2 = CH\,CHCF_2CF_2CH_2$ and 13.6 g (0.1 mole) of $HSiCl_3$ 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 $Cl_3SiCH_2CH_2\,CHCF_2CF_2CH_2$, 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
$C_6H_7SiCl_3F_4$. Calculated, %:	C 24.89;	H 2.44;	Cl 36.76

2. **β-(2,2,3,3-Tetrafluorocyclobutylethyl)methyldichlorosilane** $CH_3(Cl_2)SiCH_2CH_2\,CHCF_2CF_2CH_2$. 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 $CH_3(Cl_2)SiCH_2CH_2\,CHCF_2CF_2CH_2$, 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
$C_7H_{10}SiCl_2F_4$. Calculated, %:	C 31.30;	H 3.72;	Cl 26.05

3. **β-(2,2,3,3-Tetrafluorocyclobutylethyl)ethyldichlorosilane** $C_2H_5(Cl_2)SiCH_2CH_2\,CHCF_2CF_2CH_2$. 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 $C_2H_5(Cl_2)SiCH_2CH_2\,CHCF_2CF_2CH_2$, 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
$C_8H_{12}SiCl_2F_4$. Calculated, %:	C 33.92;	H 4.26;	Cl 25.00

4. **β-(2,2,3,3-Tetrafluorocyclobutylethyl)methylethylchlorosilane** $CH_3(C_2H_5)(Cl)SiCH_2CH_2\,CHCF_2CF_2CH_2$. 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 $CH_3(C_2H_5)(Cl)SiCH_2CH_2\,CHCF_2CF_2CH_2$

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.

$C_9H_{15}SiClF_4$.	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** $CH_3(C_2H_5)_2SiCH_2CH_2CHCF_2CF_2CH_2$. 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 $CH_3(C_2H_5)_2SiCH_2CH_2CHCF_2CF_2CH_2$, b.p. 86–86.5° (11 mm), d_4^{20} 1.0373; n_D^{20} 1.4070; found MR_D 60.84; calculated 60.94.

$C_{11}H_{20}SiF_4$.	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** $C_6H_5(Cl)_2SiCH_2CH_2CHCF_2CF_2CH_2$. 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 $C_6H_5(Cl)_2SiCH_2CH_2CHCF_2CF_2CH_2$, b.p. 119.5–120° (3.5 mm), d_4^{20} 1.3223; n_D^{20} 1.4836; found MR_D 70.90; calculated 70.35.

$C_{12}H_{12}SiCl_2F_4$.	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** $Cl_2Si(CH_2CH_2CHCF_2CF_2CH_2)_2$. 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 CH_2=CHCHCF$_2$CF$_2$CH$_2$, 7.5 g (0.075 mole) of H_2SiCl_2, and 0.3 ml of a 0.1 M solution of $H_2PtCl_2 \cdot 6H_2O$ 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 $Cl_2Si(CH_2CH_2CHCF_2CF_2CH_2)_2$, b.p. 125–126° (2.5 mm).

$C_{12}H_{14}SiCl_2F_8$.	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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Note: Figure translations are in progress. See original paper for figures.