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Syntheses of branched-polyfluoroalkylsilanes

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Abstract

Three types of branched-type polyfluoroalkylsilanes, trichloro[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl] silane (D3CL3), monochlorodimethyl[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl]silane (D3CL), triethoxy[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl]silane (D3Et3), could be synthesized using the hydrosilylation reaction of the branched-type polyfluoroalkene and corresponding silanes in the presence of hydrogen hexachloroplatinate (IV) as a catalyst. The hydrosilylation reaction of 4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoro-1-heptene with silanes produced only β -addition compounds highly regioselectively. From the MM2 calculation, it was found that the branched-polyfluoroalkylsilane has a bent structure at quaternary carbon. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Branched-polyfluoroalkylsilane; Fluorinated compounds; MM2 calculation

1. Introduction

Linear-type polyfluoroalkylsilanes have been synthesized by the hydrosilylation of fluorinated alkenes with various silanes for modification of surface of various materials [1– 10]. The molecular structure is shown in Scheme 1. Although these compounds are very useful for modification of the surface, there are some synthetic and technical problems. CF_2 -Si bonds are not difficult to form but perfluoroalkylsilanes can be relatively unstable thermally because of facile β - or α -F-silane elimination [11].

In this paper, the synthesis of three types of branchedpolyfluoroalkylsilanes have been studied using the hydrosilylation reaction of the readily available hexafluoropropylene dimer, perfluoro(2-methyl-2-pentene) [12–17].

2. Experimental

Special precautions were adopted in order to avoid hydrolysis of the starting materials and products; all experiments CF₃--(CF₂)_n--CH₂CH₂--Sin=3,5,7,9 Scheme 1

were carried out in an ampule or under an atmosphere of

purified nitrogen or argon to preclude oxygen and moisture.

2.1. Materials

Trichlorosilane, dimethylmonochlorosilane and triethoxysilane were purchased from Tokyo Kasei Kogyo and were used without further purification. Hydrogen hexachloroplatinate (IV) was purchased from Kojima Chemicals. Dimethylacetamid (DMA), potassium fluoride, potassium iodide, allylbromide, sodium sulfate and sodium hydrogensulfate (Kanto Chemical) were of reagent grade and used without further purification. Perfluoro(2-methyl-2-pentene) (D-2) was obtained from NEOS.

2.2. Measurements

IR spectra were measured in liquid film with a Hitachi 260-50 type spectrophotometer. ¹H-NMR was run in CCl₄

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with tetramethylsilane (TMS) as an internal standard using a JEOL PMX-60 Si (60 MHz) spectrometer at room temperature. ¹⁹F-NMR was recorded on a JEOL JNM-FX-90Q with CFCl₃ as an internal standard at room temperature. Mass spectra (MS) were measured (at 70 eV) with a Hitachi M-80A GC-MS spectrometer and data were evaluated using a Hitachi M-003 data processing system. Elemental analysis was performed at Institute of Physical and Chemical Research (Wako, Japan). Gas chromatography was performed with a Hitachi 663-30 (G-100 40 m column, film thickness 2.0×10^{-6} m, i.d. 1.2 mm, FID) and intensities were measured with a Hitachi D-2500 chromato integrator.

2.3. Synthesis of 4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7heptafluoro-1-heptene (DAL), $C_3F_7C(CF_3)_2CH_2CH=CH$

DMA (315 g) as a solvent and potassium fluoride (122 g, 2.1 mol) were stirred slowly throughout in a four-necked 1000 ml flask connected with a reflux condenser and dropping funnel at 110–120°C for 4 h under nitrogen atmosphere. After adding potassium iodide (9.8 g, 0.06 mol), the mixture was further heated for 6 h. After cooling down to room temperature perfluoro(2-methyl-2-pentene) (D-2, 450 g, 1.50 mol) and allylbromide (163.3 g, 1.35 mol) were added to the mixture, which was then subjected to stepwise heating, 40–45°C, 11 h, 50–55°C, 10 h and 55–65°C, 11 h. The resultant mixture was filtered and dried with sodium sulfate and sodium hydrogensulfate. The final product, 4, 4-bis(trifluoromethyl)-5, 5, 6, 6, 7, 7, 7-heptafluoro-1-heptene (187 g), was obtained as a colorless liquid by fractional distillation [16].

Bp 119.5°C; IR (Neat) 1645 (C=C), 1340–1150 (CF₃) cm⁻¹; ¹H-NMR δ = 2.95 (1H, m, *J* = 7 Hz), 4.9–5.3 (2H, m), 5.4–6.1 (1H, m); ¹⁹F-NMR δ = 69.2 (6F, se, C(CF₃)₂, *J* = 10 Hz), 80.9 (3F, t, CF₃, *J* = 10 Hz), 107.5 (2F, m, CCF₂), 123.2 (2F, m, CF₂).

2.4. Synthesis of trichloro[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl] silane (D3CL3), C₃F₇C(CF₃)₂CH₂CH₂CH₂SiCl₃

2.4.1. Method A (open)

4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoro-1-heptene (19.1 g, 53.2 mmol) and hydrogen hexachloroplatinate (IV) (5.6×10^{-2} g, 1.37×10^{-4} mol) were blended slowly throughout at 60°C in a three-necked 100 ml flask connected with a reflux condenser and dropping funnel. Trichlorosilane (10.1 g, 75.2 mmol) was dropped slowly to the mixture. Heating at 100°C for 3 h gave the orange transparent mixture. The product, trichloro[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl] silane (19.4 g), was obtained as a colorless liquid by fractional distillation under reduced pressure.

2.4.2. Method B (ampule)

4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoro-1-heptene (11.6 g, 32.2 mmol) and trichlorosilane (6.77 g, 50.1 mmol) were blended in a glass ampule to the rigorous exclusion of moisture and frozen under argon atmosphere. After adding hydrogen hexachloroplatinate (IV) (9.4×10^{-2} g, 2.30×10^{-4} mol) the mixture was sealed under reduced pressure and then was allowed to react at 100°C for 3 h. The product, trichloro[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl] silane (14.3 g), was obtained as a colorless liquid by fractional distillation under reduced pressure.

Bp 111°C/6916 Pa; IR (Neat) 1480 (SiCH₂), 815 (SiCl), 1340–1150 (CF₃) cm⁻¹; ¹H-NMR δ = 1.4 (2H, m, SiCH₂), 1.6–2.5 (4H, m, CH₂CH₂); ¹⁹F-NMR δ = 69.2 (6F, se, C(CF₃)₂, *J* = 10 Hz), 80.9 (3F, t, CF₃, *J* = 10 Hz), 107.5 (2F, m, CCF₂), 123.2 (2F, m, CF₂).

2.5. Synthesis of monochlorodimethyl[4,4bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl]silane (D3CL), triethoxy[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7heptafluoroheptyl]silane (D3Et3), $C_3F_7C(CF_3)_2CH_2CH_2CH_2Si(CH_3)_2Cl,$ $C_3F_7C(CF_3)_2CH_2CH_2CH_2Si(OC_2H_5)_3$

The preparation procedures and purification techniques were almost the same as those for trichloro[4,4-bis(trifluoro-methyl)-5,5,6,6,7,7,7-heptafluoroheptyl]silane.

Monochlorodimethyl[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl]silane was a colorless liquid: Bp 59°C/266 Pa; IR (Neat) 1470 (SiCH₂), 850– 800 (SiCH₃), 1340–1110 (CF₃) cm⁻¹; ¹H-NMR δ = 0.4 (6H, s, CH₃), 0.8 (2H, m, SiCH₂), 1.4–2.4 (4H, m, CH₂CH₂); ¹⁹F-NMR δ = 64.0 (6F, se, C(CF₃)₂, *J* = 10 Hz), 80.9 (3F, t, CF₃, *J* = 10 Hz), 107.4 (2F, m, CCF₂), 123.2 (2F, m, CF₂).

Triethoxy[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl]silane was a colorless liquid: Bp 87.5°C/ 266 Pa; IR (Neat) 1110–1080 (SiO), 1340–1120 (CF) cm⁻¹; ¹H-NMR $\delta = 0.58$ (2H, t, SiCH₂, J = 6.8 Hz), 1.16 (9H, t, CH₃, J = 7.0 Hz), 1.4–2.5 (4H, m, CH₂CH₂), 3.70 (6H, q, CH₂, J = 7.0 Hz); ¹⁹F-NMR $\delta = 63.9$ (6F, se, C(CF₃)₂, J = 10 Hz), 80.8 (3F, t, CF₃, J = 10 Hz), 107.3 (2F, m, CCF₂), 123.1 (2F, m, CF₂); MS (EI, 70 eV) *m*/*z* 524(M + 1, 1%), 523 (M+, 4), 163 (Si(OEt)₃+, 100); elemental analysis: calculated for C₁₅H₂₁F₁₃SiO₃(C 33.36%, H 4.04%, F 47.10%), found (C 33.98%, H 4.01%, F 47.22%).

2.6. MM2 calculation

The molecular force field calculations of various types of trimethylalkylsilanes which were linear-type fluoroalkylsilane, branched-type fluoroalkylsilane and branched-type hydrocarbonaceous silane were performed by MM2 force field (Allinger) method and Augmented MM2 method included in CAChe system (SONY Tektoronix, Tokyo, Japan) using Macintosh computer.

3. Results and discussion

The synthetic procedures are shown in Fig. 1. Hydrosilylation of alkenes is conducted using various complexes of transition metals as a catalyst [18]. In this study, hydrogen hexachloroplatinate (IV) having high activity was used to react branched-type polyfluoroalkene with various silanes under atmospheric pressure or in a sealed tube. Reaction condition and products are shown in Table 1. In the case of trichlorosilane the yield at atmospheric pressure was 74% while the reaction in a sealed tube proceeded almost quantitatively in a 90% yield. In triethoxysilane also the yield increased from 55% to 71% under pressure condition.

The structure of synthesized polyfluoroalkylsilane (D3CL3, D3CL, D3Et3) were determined based on the data of various spectra and elemental analysis. In the case of D3CL3, the signals attributed to methylene chain appeared at $\delta = 1.4$ and 1.6–2.5 in ¹H-NMR spectrum. In ¹⁹F-NMR spectrum the signals appeared at $\delta = 63.9$ (CF₃ bonded to quaternary carbon), 80.8 (CF₃ the end of the molecule), 107.3 and 123.1 (CF₂). These signals slightly shifted to high magnetic fields compared with the alkene as a starting material and the integral ratio of the signals is 6:3:2 in the decreasing order of magnetic filed. D3CL3 and D3CL were very sensitive against moisture in atmosphere and decomposed immediately to produce hydrogen chloride. As D3Et3 was relatively stable against hydrolysis, the mass spectrum and elemental analysis supported its molecular structure.

Substitution



Fig. 1. Synthetic procedure of branched-polyfluoroalkylsilanes.

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The preparation conditions of hydrosilylation of 4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoro-1-heptene with various silanes in the presence of H₂PtCl₆

Silane	Molar ratio		Condition		Yield (%)	Method	
	D-2	Silane	H ₂ PtCl ₆	Temperature (°C)	Time (h)		
HSiCl ₃	1.0	1.4	2.6×10^{-3}	100	3	74	Open
HSiCl ₃	1.0	1.6	7.2×10^{-3}	100	3	90	Ampule
HSi(CH ₃) ₂ Cl	1.0	1.1	7.1×10^{-3}	80	3	81	Open
HSi(OEt) ₃	1.0	1.3	1.3×10^{-3}	120	3	55	Open
HSi(OEt) ₃	1.0	1.3	4.3×10^{-3}	120	3	71	Ampule



Fig. 2. Molecular structures calculated by MM2. Linear-type fluoroalkylsilane (A), hydrocarbonaceous branched-type alkylsilane (B), branched-type fluoroalkylsilane (C).

In general, mixed products of the Si–CHX–CH₃-type (the α -addition product) and Si–CH₂–CH₂–X-type (the β -addition product) are formed by the platinum-catalyzed addition reaction of the compounds containing Si–H bonding with the compounds having a general formula CH₂=CH–X, where the X group is not conjugated with C=C [19–21]. From ¹H-NMR spectra of the trichloro[4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl]silane, only three kinds of proton signals such as Si–CH₂, Si–CH₂–CH₂ and Si–CH₂–CH₂–CH₂ were observed and other proton signals such as Si–CH₃ were not observed at least. These results indicated that the hydrosilylation reaction of trichlorosilane with 4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoro-1-heptene produced only β -addition compound highly regioselectively.

Molecular structures of the trimethylalkylsilanes obtained by MM2 calculation are shown in Fig. 2. Lineartype fluoroalkylsilane (A), $CF_3(CF_2)_5CH_2CH_2Si(CH_3)_3$ and branched-type hydrocarbonaceous silane (B), $CH_3CH_2CH_2$ - $C(CH_3)_2(CH_2)_3Si(CH_3)_3$ have a zigzag structure without bending at the connection of CH₂ and CF₂ or CH₂ and quaternary carbon. On the contrary, branched-type fluoroalkylsilane, $CF_3CF_2CF_2C(CF_3)_2(CH_2)_3Si(CH_3)_3$ has the bent structure at quaternary carbon. It seems that this structure is caused by the steric repulsion between CF_2 or CH_2 and CF_3 group having larger molecular volume than CH_3 group.

4. Conclusions

Three kinds of branched-type polyfluoroalkylsilanes were synthesized by the hydrosilylation of the branchedtype polyfluoroalkene with silanes and their molecular structures were calculated by MM2 method. Three types of branched-type polyfluoroalkylsilanes, trichloro[4,4-bis-(trifluoromethyl)-5, 5, 6, 6, 7, 7, 7-heptafluoroheptyl] silane (D3CL3), monochlorodimethyl[4,4-bis(trifluoromethyl)-5, 5,6,6,7,7,7-heptafluoroheptyl]silane (D3CL), triethoxy[4,4bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoroheptyl]silane (D3Et3), could be synthesized using the hydrosilylation reaction of the branched-type polyfluoroalkene and corresponding silanes in the presence of hydrogen hexachloroplatinate (IV) as a catalyst. The hydrosilylation reaction of 4,4-bis(trifluoromethyl)-5, 5, 6, 6, 7, 7, 7-heptafluoro-1-heptene with silanes produced only β -addition compounds highly regioselectively. From the MM2 calculation, it was found that the branched-polyfluoroalkylsilane has a bent structure at quaternary carbon. It seems that this structure is caused by the repulsion between CF_3 group and CF_2 or CH_2 group differing from hydrocarbonaceous branched-type alkylsilane.

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