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LETTERS TO THE EDITOR

Hydrosilylation of 3,3,4,4-Tetrafluorohexa-1,5-diene and 4-Bromo-3,3,4,4-tetrafluorobut-1-ene

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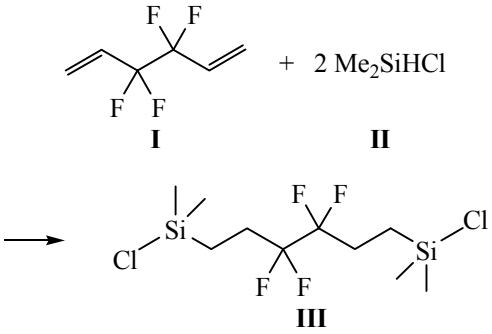
Fluoroalkylchlorosilanes are of interest as starting material for the synthesis of polymeric materials with some unique properties. The most promising method for the synthesis of these compounds is organofluorine hydrosilylation of unsaturated derivatives. However, the literature on studies of such reactions is rather limited. Common Spayer or Karsted catalysts are mentioned in most papers [1–3]. An exception is the work [4], where Ojima et al. describe in detail the hydrosilylation of 3,3,3-trifluoropropene and pentafluorostyrene catalysed by palladium, rhodium, and ruthenium complexes. When using Rh and Ru catalysts,the reaction proceeds non-selectively that excludes their practical application. Addition of chloroosilanes to fluoroalkenes in the presence of catalysts based on Pt complexes proceeds with high regioselectivity in accordance with Farmer rule. The hydrosilylation of 3,3,3-trifluoropropene with methyldichlorosilane forms the basis for the synthesis of the known SKTFt rubber of high oil and fuel resistance. The interaction of 3,3,4,4,4-pentafluorobut-1-ene with methyldichlorosilane was catalysed by Pt complex described in [5].

Recently, we reported on the hydrosilylation of 1-vinyl-2,2,3-trifluoro-3-trifluoromethylcyclobutane with methyldichlorosilane [6].

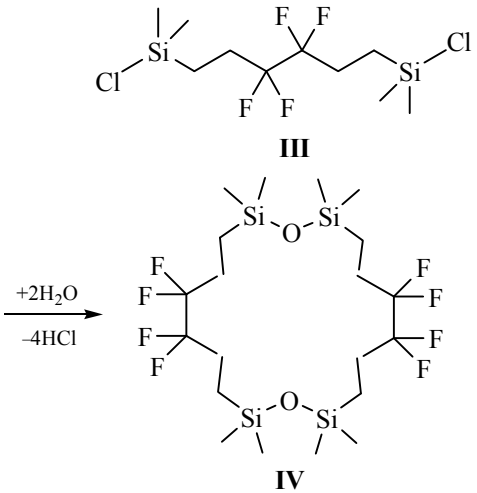
Polyfunctional organofluorosilicon compounds are promising starting materials in the synthesis of block copolymers, as well as self cross-linking polysiloxanes. For the synthesis of these compounds, we used 3,3,4,4-tetrafluorohexa-1,5-diene and 4-bromo-3,3,4,4-tetrafluorobut-1-ene.

It has been established that 3,3,4,4-tetrafluorohexa-1,5-diene **I** reacts with dimethylchlorosilane **II** in the presence of *cis*-bis(dibenzyl sulfide)dichloroplatinum(II) with the formation of 1,6-bis(dimethylchlorosilyl)-3,3,4,4-tetrafluorohexane **III.** The hydrosilylation of compound **I** in this case proceeds in accordance with Farmer rule.

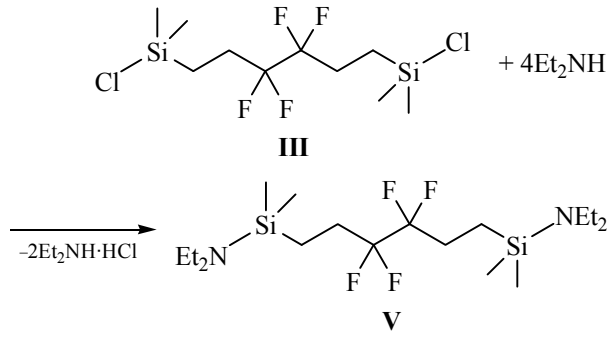


III

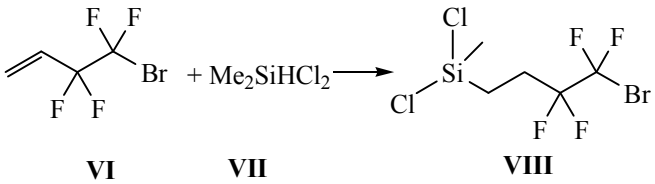
Under controlled hydrolysis bis-chlorosilane **III** undergoes intermolecular cyclization to form siloxane bonds:



The interaction of compound **III** with an excess of diethylamine leads to the corresponding bis(diethylamino) derivative **V:**



Hydrosilylation of 4-bromo-3,3,4,4-tetrafluorobutene **VI** with methyldichlorosilane **VII** proceeds regioselectively in accordance with Farmer rule and leads to compound **VIII:**



3,3,4,4-tetrafluorohexa-1,5-diene was obtained according to [7] by thermolysis of 2,5-diacetoxy-3,3,4,4-tetrafluorohexane in a nitrogen atmosphere at 460–480°C, 4-bromo-3,3,4,4-tetrafluorobut-1-ene was obtained by the procedure [8] by dehydrobromination of 1,4-dibromo-1,1,2,2-tetrafluorobutane.

1,6-Bis(dimethylchlorosilyl)-3,3,4,4-tetrafluorohexane (III). 2.96 g of diene **II** was added dropwise with stirring to 0.04 g of *cis*-bis(dibenzyl sulfide) dichloroplatinum(II) and 6.65 g of dimethylchlorosilane placed in a flask, and the mixture was refluxed for 2 h. The product was isolated by vacuum distillation. Yield: 4.71 g (71.5%). mp 37°C, bp 110°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.46 s (12H, CH_3Si), 1.04 m (4H, CH_2Si), 2.09 m (4H, CH_2CF$_2$). ^{13}C NMR spectrum, δ_C, ppm: –1.46 s (*C*H$_3$Si), 6.24 s (*C*H$_2$Si), 21.32 m (*C*H$_2$CF$_2$). R_T 12.89. MS CI, *m*/*z* (I_{rel}): 328 [*M* – CH$_3$] 205 (5), 151 (5), 121 (40), 99 (75), 93 (100), 79 (72). EI, *m*/*z* (I_{rel}): 39 (10), 54 (15), 59 (32), 65 (17), 77 (45), 90 (25), 93 (100), 95 (32), 103 (30), 121 (5).

2,2,9,9,11,11,18,18-Octamethyl-5,5,6,6,14,14,15,15-oktafluoro-1,10-dioxa-2,9,11,18-tetra-silacyclooctadecane (IV). A solution of 0.12 g of water in 25 ml of ether was added with stirring to 2.26 g of compound **III** in 50 ml of diethyl ether at 0°C. The reaction mixture was stirred for 1 h, the solvent is distilled off, and the residue was recrystallized from petroleum ether. Yield: 0.62 g (32.6%), mp 114°C. ^{1}H NMR spectrum, δ, ppm: 0.11 s (24H, CH_3Si), 0.73 m (8H, CH_2Si), 1.97 m (8H, CH_2CF$_2$). ^{13}C NMR spectrum, δ_C, ppm: –0.36, –0.10 s (*C*H$_3$Si), 7.50 s (*C*H$_2$Si), 22.81–25.36 m (*C*H$_2$CF$_2$). MS CI, *m*/*z* (I_{rel}): 79 (18), 99 (15), 103 (5), 151 (100), 155 (28), 578 (25) [*M* + H]. EI, *m*/*z* (I_{rel}): 59 (10), 73 (8), 77 (20), 79 (35), 99 (5), 103 (12), 118 (5), 151 (100), 155 (15).

1,6-Bis[dimethyl(diethylamino)silyl]-3,3,4,4-tetrafluorohexane (V). To a solution of 2.45 g of compound **III** in 50 ml of diethyl ether a solution of 2.40 g of diethylamine in 25 ml of ether was added with stirring at 0°C. The reaction mixture was stirred for 3 h, the precipitated diethylamine hydrochloride was filtered off. The filtrate was evaporated and the residue was evacuated at 1 mm Hg for 3 h. Yield: 2.41 g (81.0%). ^{1}H NMR spectrum, δ, ppm: 0.05 s (12H, CH_3Si), 0.70 m. (4H, CH_3Si, $^4J_{HF}$ 9.0 Hz), 0.96 t (12H, CH$_3$, $^3J_{HH}$ 7.0 Hz) 1.94 m (4H, CH_2CF$_2$), 2.77 (4H, CH$_2$, J_{HH} 6.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 6.37 s, 7.79 s, 12.72 s, 15.75 s (CH$_3$), 24.14 m., 39.78 s (CH$_2$N), 42.85 s, 119.26 t, 124.36 t (CF$_2$).

(4-Bromo-3,3,4,4-tetrafluorobutyl)methyldichlorosilane (VIII). 9.0 g of the compound **VI** was added dropwise with stirring to 0.04 g of *cis*-bis(dibenzylsulfide)dichloroplatinum(II) and 15.0 g of methyldichlorosilane **VII** placed in a flask equipped with a reflux condenser. The mixture was boiled for 5 h. The product was isolated by vacuum distillation. Yield: 9.69 g (69.2%), bp 78°C (20 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.86 s. (3H, CH$_3$), 1.38 m (2H, CH_2Si, $^3J_{HH}$ 8.4 Hz, $^4J_{HF}$ 4.3 Hz), 2.28 m (2H, CH_2CF$_2$, $^3J_{HH}$ 8.4 Hz, $^3J_{HF}$ 18.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 4.59 s (CH$_3$), 11.92 s (*C*H$_2$Si), 23.97 t (*C*H$_2$CF$_2$, $^2J_{CF}$ 23.8 Hz), 117.16 m, (CF$_2$, $^1J_{CF}$ 311 Hz, $^2J_{CF}$ 31.4 Hz), 123.3 m (CF$_2$Br, $^1J_{CF}$ 311 Hz, $^2J_{CF}$ 31.4 Hz).

NMR spectra were recorded on a Bruker AC200 [200.13 MHz (^{1}H), 50.32 MHz (^{13}C)] instrument in CDCl$_3$, using residual signal of deuterated solvent as reference.

GC–MS analysis of reaction mixtures and isolated products was performed on a Finnigan Trace DCQ instrument using capillary column BPX-5 30×0.32 from SGE. Conditions of electron ionization: 70 eV, ion source temperature 200°C. Conditions of chemical ionization: 120 eV, ion source temperature 200°C, gas-reactant isobutane (flow rate 0.4 ml min^{-1}).

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