Synthesis of 3-[tris(γ-trifluoropropyl)silyl]propyldimethylsilane

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Monofunctional silane containing a tris(γ-trifluoropropyl) fragment was synthesized in high yield by a series of successive reactions including the Grignard reaction, hydrosilylation, and reduction.

Key words: fluorine-containing organosilicon compounds, physicochemical properties, hydrosilylation, ^{1}H NMR spectra.

Organosilicon compounds having fluorine-containing organic substituents at the silicon atom are widely used in organosilicon chemistry because of their specific surface properties. Incorporation of these molecular fragments in polymers decreases their surface energy. Versatile modifiers of polymers are monofunctional fluorine-containing compounds such as chloro[tris(γ-trifluoropropyl)]silane.[1] Their modifying properties are the most pronounced in highly functional polymeric systems, in particular, in dendrimers.[2] It has been shown that the chemical structure of organosilicon dendrimers and hyperbranched polymers with high concentration of double bonds[3] can be effectively modified by hydrosilylation of the double bonds with substituted silane hydrides.[4—6]

Tris(γ-trifluoropropyl)silane could be considered as an ideal reagent for solving such problems, but the Si—H functional group is strongly shielded and hence has low reactivity, especially in reactions with sterically hindered reagents. In connection with this, the synthesis of compounds containing both a nonshielded Si—H functional group and a tris(γ-trifluoropropyl)silyl group is a topical problem.

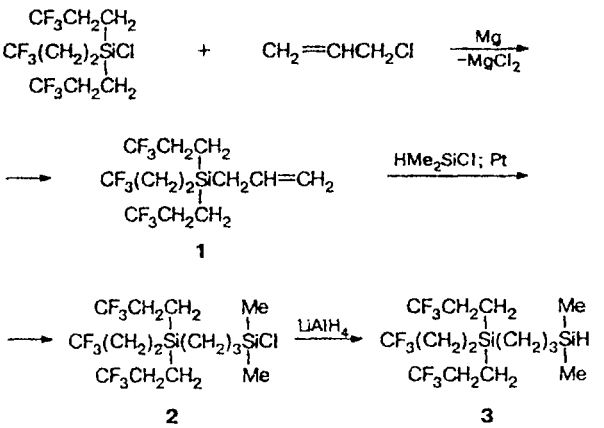
In the present work, the synthesis of a monofunctional silane hydride bearing a tris(γ-trifluoropropyl) fragment is described (Scheme 1).

The reaction of allylmagnesium chloride with chloro-[tris(γ-trifluoropropyl)]silane was carried out in one step (according to the recommendations given in a paper devoted to the synthesis of allylsilanes),[7] to give compound **1** in 93% yield. The high yield of the target product suggests that the C—F bond is not involved in the reaction with allylmagnesium chloride, which is also consistent with the literature data.

The second process of the synthetic scheme is hydrosilylation. It is known that the presence of electronegative groups at the double bond lowers its reactivity in reactions of polyaddition.[8] To avoid such a decrease in reactivity, we used allyl[tris(γ-trifluoropropyl)]silane, where the double bond is remote from the electronegative trifluoromethyl groups. Two different catalysts were tested, namely, a Pt^0 complex (the Karsted catalyst) and octacarbonyldicobalt. In the former case, chloro{3-[tris(γ-trifluoropropyl)silyl]propyl}dimethylsilane **2** was obtained in 87% yield. In the latter case, the reaction was more complex, and the content of the main product in the reaction mixture did not exceed 25—30% (GLC).

Reduction of compound **2** with $LiAlH_4$ gave the corresponding silane hydride **3** in 70% yield. The presence of the sterically nonhindered Si—H group in structure **3** as well as its high boiling point and good solubility in both polar and nonpolar solvents enable one to consider this compound as a promising reagent for modification of polymers.

Scheme 1



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Experimental

^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250.13 MHz) in $CDCl_3$ with $CHCl_3$ (δ 7.25) as the standard. GLC analysis was carried out on a 3700 chromatograph (katharometer as a detector, columns 2×2000 mm with 5% SE-30 on Chromaton-N-AW-HMDS, helium as the carrier gas, flow rate 60 mL min^{-1}) either isothermally or with the temperature programmed from 140 to 260 °C at a rate of 20 deg min^{-1}.

Allyl[tris(γ-trifluoropropyl)]silane (1). Allyl chloride (1 mL) was added in the atmosphere of an inert gas to a mixture of Mg cuttings (10.5 g, 0.43 mol) and anhydrous THF (50 mL). After the reaction was initiated, a solution of chloro[tris(γ-trifluoropropyl)]silane (106.4 g, 0.3 mol) and allyl chloride (27.5 g, 0.36 mol) in 250 mL of anhydrous THF was added dropwise with stirring. The reaction mixture was refluxed with stirring for 5 h. The precipitate that formed was filtered off and washed with *n*-hexane. The filtrate was concentrated, and the residue was distilled *in vacuo* (1 Torr) to give compound **1** (100.7 g, 93.2%), b.p. 62—63 °C (1 Torr). Purity 99% (GLC), d_4^{25} 1.2635, n_D^{20} 1.3833. Found (%): Si, 7.78; C, 40.05; H, 4.73; F, 47.51. $C_{12}H_{17}F_9Si$. Calculated (%): Si, 7.80; C, 39.99; H, 4.76; F, 47.45. ^{1}H NMR, δ: 0.37 (m, 6 H, $CF_3CH_2CH_2$); 1.00 (d, 2 H, $SiCH_2$); 1.55 (m, 6 H, $CF_3CH_2CH_2$); 4.81 (t, 2 H, CH_2=CH); 5.35 (m, 1 H, CH_2=CH).

Chloro{3-[tris(γ-trifluoropropyl)silyl]propyl}dimethylsilane (2). The PC072 platinum catalyst (100 μL) was added in the atmosphere of an inert gas to a solution of compound **1** (36 g, 0.1 mol) in 50 mL of anhydrous *n*-hexane. An excess of chlorodimethylsilane (18.9 g, 0.2 mol) was added with stirring. Then the reaction mixture was stirred at −20 °C for 7 h (monitored by ^{1}H NMR). The volatile components were removed at atmospheric pressure, and the residue was distilled *in vacuo* to give compound **2** (44.5 g, 87%), b.p. 120—121 °C (1 Torr). Purity 98% (GLC), d_4^{25} 1.2325, n_D^{20} 1.4022. Found (%): Si, 12.29; C, 37.10; H, 5.30; F, 37.61; Cl, 7.80. $C_{14}H_{24}F_9ClSi_2$. Calculated (%): Si, 12.35; C, 36.96; H, 5.32; F, 37.58; Cl, 7.79. ^{1}H NMR, δ: 0.42 (d, 6 H, Me); 0.80 (d, 2 H, $SiCH_2$ and m, 2 H, CH_2Si); 0.88 (m, 6 H, $CF_3CH_2CH_2$); 1.45 (m, 2 H, CH_2); 2.00 (m, 6 H, $CF_3CH_2CH_2$).

3-[Tris(γ-trifluoropropyl)silyl]propyldimethylsilane (3). A solution of compound **2** (42.4 g, 0.10 mol) in 130 mL of anhydrous diethyl ether was added dropwise with stirring in the atmosphere of an inert gas to a suspension of $LiAlH_4$ (1.0 g, 0.02 mol) in 100 mL of anhydrous diethyl ether. The reaction mixture was refluxed for 8 h, the precipitate that formed was filtered off, and the filtrate was washed with water and dried with Na_2SO_4. The diethyl ether was removed, and the residue was distilled *in vacuo* to give compound **3** (24.5 g, 68.5%), b.p. 112—113 °C (1 Torr). Purity 98% (GLC), d_4^{25} 1.1617, n_D^{20} 1.3939. Found (%): Si, 13.33; C, 40.01; H, 5.98; F, 40.53. $C_{14}H_{25}F_9Si_2$. Calculated (%): Si, 13.36; C, 39.98; H, 5.99; F, 40.67. ^{1}H NMR, δ: 0.06 (d, 6 H, Me); 0.68 (d, 2 H, $SiCH_2$ and m, 2 H, CH_2Si); 0.79 (m, 6 H, $CF_3CH_2CH_2$); 1.38 (m, 2 H, CH_2); 2.00 (m, 6 H, $CF_3CH_2CH_2$); 3.85 (m, 1 H, SiH).

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