Hydrosilylation of fullerene C_{60}

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The hydrosilylation of C_{60} by diphenylsilane was studied. Silicon-containing derivatives $C_{60}H_n(HSiPh_2)_n$ (n = 2, 4, 6) were obtained.

Key words: fullerene C_{60}, hydrosilylation by diphenylsilane.

It is known that a C_{60} molecule contains 30 active (6,6)-bonds (along the facets between two six-membered cycles) with a pronounced olefinic character, that are similar to the electron-acceptor polyene in their chemical properties.[1] Fullerene C_{60} adds nucleophiles, radicals, and carbenes, enters into cycloaddition reactions,[2–5] and both mono- and polyaddition products can be formed due to the polyenic structure of the C_{60} molecule.[6,7]

Hydrosilylation is one of the simplest and most popular methods for synthesis of various organosilicon compounds.[8] The possibilities of this reaction for fullerene C_{60} are almost unstudied. There is only one publication on the synthesis of C_{60}-containing polysiloxanes by the hydrosilylation reaction.[9] Studies in this area may reveal a perspective route for the synthesis of novel silicon-containing fullerene derivatives.

This work studied the hydrosilylation of C_{60} by excess Ph_2SiH_2 in *o*-xylene resulting in the formation of fullerene C_{60} derivatives with an even number of silicon-containing substituents.

$$C_{60} + n\ H_2SiPh_2 \xrightarrow[170\ ^\circ C]{H_2PtCl_6} C_{60}H_n(HSiPh_2)_n$$

n = 2, 4, 6

The formation of $C_{60}H_2(HSiPh_2)_2$, $C_{60}H_4(HSiPh_2)_4$, and $C_{60}H_6(HSiPh_2)_6$ compounds was confirmed by mass spectrometry, ^1H, ^{13}C NMR, and IR spectroscopy, and HPLC.

The HPLC analysis of a toluene solution of the reaction products showed traces (<1%) of the unreacted fullerene and of a mixture of its derivatives.

The high mass range of the mass spectrum of the mixture contains groups of peaks that can be interpreted as follows: m/z 720—725 corresponds to the $[C_{60}]^+$ ion; m/z 776—780 probably corresponds to superposition of the $[C_{60}Si_2]^+$—$[C_{60}Si_2H_4]^+$ ions; peaks with m/z 835—839 can be assigned to the $[C_{60}Si_4H_3]^+$ and $[C_{60}Si_4H_4]^+$ ions; finally, weak peaks with m/z 896, 897 correspond to ions containing C_{60}, 6 Si atoms, and hydrogen. It is impossible to unambiguously state the number of H atoms in these ions, because some of the peaks characteristic of this type of ions could not be seen in the spectrum because of their low intensity. All of these ions can be considered to be fragments formed of molecular ions from fullerene derivatives of the general formula $C_{60}H_n(HSiPh_2)_n$ (n = 2, 4, 6) or from products of their decomposition.

The IR spectrum of products of the reaction of Ph_2SiH_2 with C_{60} contains bands caused by vibrations in the $-SiHPh_2$ group. This group can be distinctly identified by an intense Si—H band at 820 cm^{-1}, the absence of $\delta(SiH_2)$ absorption at 930 cm^{-1} and $\rho(SiH_2)$ absorption at 590 cm^{-1}, and the existence of bands at 2135 (ν(SiH)), 1590, 1485, 1430, 1120, 730, 695, and 490 cm^{-1} (SiPh). In addition, the spectrum contains weak bands in the region of ν(Si—C) (880 and 670 cm^{-1}) and several weak bands (1330, 1300, 1260, 1240, 1220, and 1190 cm^{-1}) characteristic of δ(CH) vibrations at the tertiary C atom and skeletal vibrations of C—C in saturated hydrocarbons. These absorption bands can be presumably assigned to vibrations in the fullerene skeleton, which is partially saturated due to the addition of diphenylsilane.

The ^1H NMR spectrum of the reaction products contains multiplets of protons of the phenyl cycle at 7.45—7.65 ppm and broad signals in the regions of 5.40—5.50 and 4.50—4.65 ppm, which can be assigned to protons directly bound to the C_{60} ring and the Si atom, respectively. The low-field shift of the signals of protons bound to the fullerene ring (δ 5.40—5.50), compared to the signals of protons at the sp^3-hybridized C atoms of other organic compounds, is characteristic of C_{60} derivatives (δ 6.04 for $HC_{60}Me$,[2] 5.93 for $C_{60}H_2$,[11] and 5.20 for C_{60}-polysiloxanes[9]) and can be explained by the strong electron-acceptor effect of the fullerene ring.[10,11]

The ^{13}C NMR spectrum of the mixture of products exhibits signals of C atoms of fullerene and phenyl groups in the region of 130—150 ppm and signals in the region of 59—64 ppm, which can be assigned to the C atoms of the fullerene ring bound to Si and H atoms.

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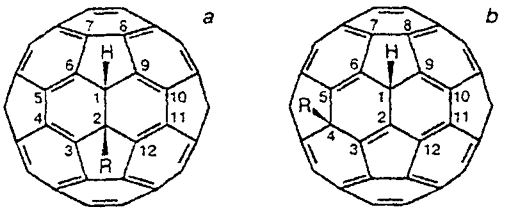

Fig. 1. Scheme of 1,2- (*a*) and 1,4-addition (*b*) of diphenylsilane on (6,6)-bonds of fullerene C_{60}.

Silicon-containing fullerene derivatives most probably are the products of 1,2-addition of diphenylsilane at active (6,6)-double bonds of C_{60}, since the formation of 1,4-isomers requires higher energy because the localization of double bonds in the fullerene C_{60} ring changes in such a way that the (6,5) edge becomes doubly bound (Fig. 1).[7,10,11]

The even number of silicon-containing substituents in the compounds obtained may be the result of the fact that polyaddition to C_{60} is controlled by the electronic structure of the functionalized molecule itself. This results, as a rule, in the formation of the most thermodynamically stable compounds.[12,13]

The silicon-containing fullerene derivatives obtained are stable only in an inert atmosphere. In the presence of the oxygen and moisture of air, they completely transform into the insoluble state.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer. Mass spectra (EI) were obtained on a Kratos MS 890 instrument (70 eV, ionization chamber temperature 280 °C). Several drops of a solution were deposited onto a quartz needle and dried, and the needle was placed directly in the ionization chamber. IR spectra were recorded on a Specord M-80 spectrophotometer. HPLC analysis of products was carried out on a Waters instrument (refractometric detector R-401, Stirogel column "Microgel-5," 25 °C, toluene as eluent, flow rate of the eluent 1 mL min^{-1}).

Diphenylsilane (110 mg, 0.6 mmol) and H_2PtCl_6 catalyst (4 mL, 0.1 *M* solution in Pr^{i}OH) were added to a solution of C_{60} (22 mg, 0.03 mmol) in *o*-xylene (5 mL) in a glass ampule in an argon flow. The ampule was blown with argon, sealed off, and heated at 170 °C for 15 h. The solution changed its color from violet to brown. Then the ampule was opened, the solvent and excess Ph_2SiH_2 were removed *in vacuo*, and the residue was washed with anhydrous hexane and dried *in vacuo*. ^{1}H NMR (300 MHz, C_6D_6), δ: 4.50—4.65 (m, *n* H, SiH); 5.40—5.50 (m, *n* H, CH); 7.45—7.65 (m, 5*n* H, *n* C_6H_5). ^{13}C NMR (75.47 MHz, C_6D_6, 0.03 mol mL^{-1} Cr(acac)$_3$), δ: 148.5, 147.5, 146.3, 145.7, 145.5, 145.3, 144.5, 144.3, 142.3, 141.7, 141.2, 140.4, 139.6, 138.0, 137.5, 136.0. 134.0, 132.5, 64.0, 63.5, 62.9, 62.0, 60.6, 59.2. MS, *m/z* (I_{rel} (%)): 720 (100), 722 (70), 723 (4), 724 (4), 725 (1), 758 (5), 759 (8), 775(8), 776 (4), 777 (11), 778 (8), 779 (2), 780 (2), 835 (6), 836 (8), 837 (6), 838 (2), 896 (0.8), 897 (0.9). IR (KBr), ν/cm^{-1}: 190, 670, 695, 730, 820, 880, 1120, 1190, 1220, 1240, 1260, 1300, 1330, 1430, 1485, 1590, 2135.

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