Silylmethylations of C_{60} with Grignard Reagents: Selective Synthesis of $HC_{60}CH_2SiMe_2Y$ and $C_{60}(CH_2SiMe_2Y)_2$ with Selection of Solvents

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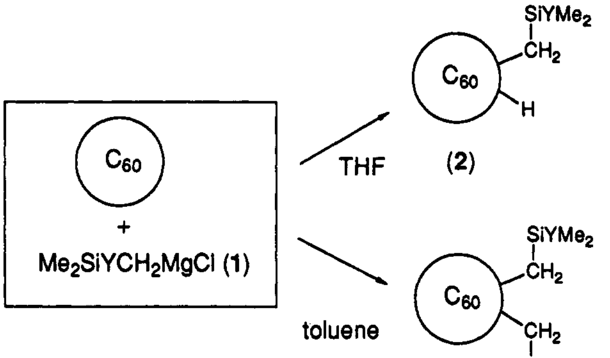
Summary: Addition reactions of Me_2SiYCH_2MgCl (**1**) to C_{60} provided two products, $HC_{60}CH_2SiYMe_2$ (**2**) and $[Me_2YSiCH_2]_2C_{60}$ (**3**) (Y = Me, H, CH=CH$_2$, Ph, O^{i}Pr). Selective preparation of either **2** or **3** was accomplished by selection of the solvent; **2** was formed in THF, whereas **3** was produced in toluene.

The potential utility of fullerene derivatives as biologically active compounds or sources for materials science has recently resulted in intensive efforts to achieve efficient functionalization of fullerenes.[1-3] Although addition of Grignard or lithium reagents across the carbon–carbon double bonds in C_{60}, which was reported by Wudl in an early stage of fullerene research,[4a] is an attractive synthetic method for alkyl derivatives of fullerenes, well-characterized adducts were limited to only $^tBuC_{60}H$ or $EtC_{60}H$ reported by Fagan[4b] and Hirsch,[4c] which were obtainable by the reaction of C_{60} with ^tBuLi or EtMgBr followed by protonation. Detailed studies on the addition of several organolithium or Grignard reagents to C_{60} or C_{70} were reported recently by Hirsch and co-workers which provided a general synthetic route to alkylhydrofullerenes $RC_{60}H$ or $RC_{70}H$ by this method.[4d] In this paper, we wish to report that addition of Grignard reagents, Me_2YSiCH_2MgCl (**1**), to C_{60} unexpectedly provides two types of silicon-containing fullerene derivatives, $Me_2YSiCH_2C_{60}H$ (**2**) and $(Me_2YSiCH_2)_2C_{60}$ (**3**). In contrast to the fact that the product **2** is a homologue of $RC_{60}H$,[4b-d] **3** is an unprecedented type of compound and has never been isolated as the product of the addition of Grignard reagents.[5] Of particular importance is that selective preparation of **2** and **3** can be achieved with selection of the appropriate solvent; **2** was formed in THF, whereas **3** was done in toluene (Scheme 1).

Preparation of **2** was done by the reaction of C_{60} with **1** in THF. In a typical example, a suspension of C_{60} (450 mg, 0.625 mmol) in THF (72 mL) was treated with three portions of a THF solution of Me_3SiCH_2MgCl (**1a**) (0.8 N, total 1.5 mmol) over 5 h, then the mixture was quenched with 2 N H_2SO_4. A high-performance liquid chromatogram of the crude product (559 mg) showed formation of a single product (73%) and recovery of C_{60} (18%). Purification of the crude materials with preparative HPLC gave brown solids (>99% purity, 197 mg, 39% yield[6]). The FAB mass spectrum of this compound (M = 808) and the following NMR data, which are similar to those of $RC_{60}H$ (R = Et, ^{t}Bu),[4b,4c] are compatible with $Me_3SiCH_2C_{60}H$ (**2a**).[7] Three sharp singlets assignable as methyl and methylene protons on the (trimethylsilyl)methyl group and a proton directly attached to the C_{60} core appeared at 0.62, 2.96, and 6.45 ppm, respectively, in ^1H NMR spectrum. ^{13}C NMR resonances derived from the C_{60} moiety consist of 30 carbons in the aromatic region (135–160 ppm, quarternary carbons) and two carbons around 61 ppm (one CH and one quarternary carbon). Those from the trimethylsilyl group appeared at 0.46 (CH_3) and 38.6 (CH_2) ppm. Using a procedure similar to that used for the synthesis of **2a** in THF, **2b–d** with over 99% purity were isolated in 26, 23, 15, and 14% after purification with preparative HPLC.[6] These data suggest that the addition of **1** in THF provides a general access to **2**.

Scheme 1



Y = Me (**1a**, **2a**, **3a**), H (**1b**, **2b**, **3b**), Ph (**1c**, **2c**, **3c**)
CH=CH$_2$ (**1d**, **2d**, **3d**), O^{i}Pr (**1e**, **2e**, **3e**)

Formation of a product different from **2** in the reaction of C_{60} with **1** was first discovered in the reaction of C_{60} with **1e** by changing the solvent from THF to toluene. A

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[5] The reaction can be regarded as dialkylation of fullerenes. Very recently, successful dimethylation of C_{60} using an electrochemical method was reported. See: Caron, C.; Subramanian, R.; D'Souza, F.; Kim, J.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 8505.

[6] The recovery of C_{60} (10–20%) was not considered to calculate the yields of **2** and **3**. Although **2** or **3** was formed as the major product on HPLC, its isolated yield was low (5–40%). This is mainly attributed to a significant loss of the product during the purification with HPLC.

[7] **2a**: mp 215–216 °C dec; ^1H NMR (270 MHz, $CDCl_3$) δ 0.62 (s, 9H, $SiMe_3$), 2.96 (s, 2H, $SiCH_2$), 6.45 (s, 1H, $C_{60}H$); NOE was observed between the HC_{60} and the CH_2Si, suggesting that these groups are located close to each other; ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 0.46 ($SiMe_3$), 38.56 ($SiCH_2$), 61.29 (CH, J_{CH} = 139.6 Hz), 61.79 ($SiCH_2C$), 134.31–157.52 (30 peaks derived from the C_{60} core); FAB mass calcd for $C_{64}H_{12}Si$ 808, found 808. Detailed data for **2a–e** are given in the supplementary material.

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solution of C_{60} (500 mg, 0.7 mmol) in toluene (830 mL) was treated with 50 portions of a THF solution of **1e** (0.4 M, total 3.5 mmol, 15 mL) at room temperature for 5 h. A high-performance liquid chromatogram of the crude product (600 mg) suggests the formation of a compound with a retention time different from **2e** as a major product (purity on analytical HPLC, 55%). Purification of the crude product with a silica gel column (benzene–hexane) afforded the product with >90% purity (300 mg) with a recovery of C_{60} (100 mg). Further purification with preparative HPLC gave 250 mg of the product with >99% purity (36% yield[6]). NMR spectra of this compound showed three characteristic points that differ from the spectra of **2**. First, there was no ^1H resonance assignable to the proton directly attached to the C_{60} core. Second, two protons of the $C_{60}CH_2Si$ moiety were magnetically inequivalent and split into an AB pattern with a typical geminal coupling constant (J_{HH} = 14.65 Hz). Methyl groups either on the silicon atom or in the isopropoxy group were also magnetically inequivalent, providing ^1H and ^{13}C resonances as independent peaks with close chemical shifts. Third, ^{13}C NMR resonances derived from the C_{60} moiety appeared at 130–160 ppm (31 peaks) and at 54.90 ppm (1 peak), and all of them were assigned as quaternary carbons. These NMR data as well as a FAB mass spectrum (M = 982) suggest that the product is consistent with $C_{60}[SiCH_2(OiPr)Me_2]_2$ (**3e**).[8] The reactions of C_{60} with **1a–d** in toluene were rather more sluggish than those in THF; however, in the reactions with **1a**, **1c**, or **1d**, the corresponding disilylmethylated compound, which was never seen in THF, was formed as the major product on HPLC. In the experiments carried out to date, **3a**, **3c**, and **3d** with >99% purity were isolated in 5, 6, and 5% yields, respectively.[6] Although further elaboration is required to raise the isolated yield of **3**, the results suggest that preparation of **3** can, in principle, be made by changing the solvent from THF to toluene.

The structures of **2** and **3** are proposed from their ^1H and ^{13}C NMR data. The number of carbons derived from C_{60} observed in ^{13}C NMR was 32 in both **2** and **3**, suggesting the existence of C_s or C_2 symmetry in the molecule. NMR data of **2** are consistent with the molecule containing a symmetry plane including the proton and the organosilyl group on the C_{60} core depicted as **A** in Figure 1. A similar structure was proposed for $RC_{60}H$ (R = Et, ${}^tBu$).[4b,c] In contrast, **3** contains two equivalent CH_2SiYMe_2 groups, of which two methylene protons are magnetically inequivalent. A reasonable explanation for these results is that the molecule contains a symmetry plane bisecting the line connecting the two silylmethyl groups in **3**, which are adjacent to the asymmetric carbons of the C_{60} core. Two possible structures consistent with the NMR data can be proposed for **3** as shown in **B** and **C** in Figure 1.[9]

In summary, addition of Me_2YSiCH_2MgCl to C_{60} with proper selection of the solvent provides a selective synthetic method of two different types of the silylmethylated fullerenes, **2** and **3**. It is important from synthetic viewpoints that various substituents (Y) including Me, H, phenyl, vinyl, and ${}^iPrO$ are able to be introduced on the silicon atom, any of which is potentially useful for further transformation of the product. Furthermore, synthetic utility of the Me_2SiY groups themselves for successful transformation to the other functional groups is well known in organic synthesis.[11] Thus, **2** and **3** could be an attractive starting point for various fullerene derivatives by way of chemical modification of the organosilyl groups in **2** and **3**.[12] As the simplest example, we have already achieved successful preparation of a cyclic siloxane **4** by hydrolysis of **3e** in 76% yield,[13] which is the first well-characterized siloxane containing C_{60}. Further synthetic studies are now in progress.

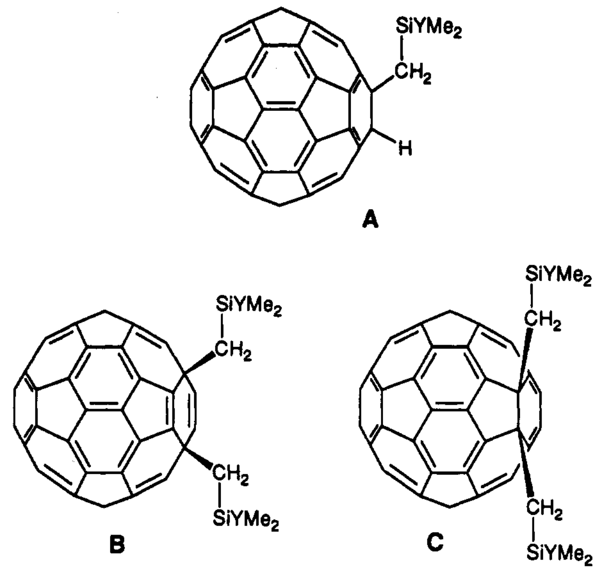
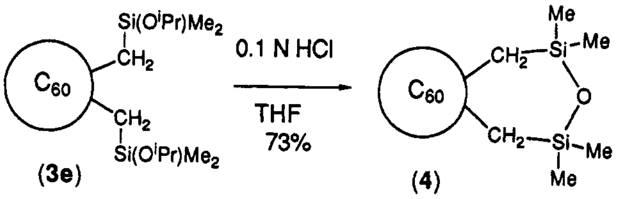


Figure 1.

Scheme 2



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[8] **3e**: mp 175–180 °C dec; ^1H NMR δ 0.47 (s, 6H, SiMe), 0.48 (s, 6H, SiMe), 1.18 (d, 6H, J = 5.86 Hz, Me of iPr), 1.19 (d, 6H, J = 5.87 Hz, Me of iPr), 2.48 (d, 2H, J = 14.65 Hz, SiCH), 2.64 (d, 2H, J = 14.65 Hz, SiCH), 4.20 (sep, 2H, J = 5.86 Hz); ^{13}C NMR ($CDCl_3/CS_2$) δ 0.90 (SiMe), 0.94 (SiMe), 25.57 (Me of ${}^iPr$), 25.60 (Me of iPr), 33.10 (CH_2Si), 54.90 ($SiCH_2C$), 65.10 (CH of ${}^iPr$), 131.8–157.7 (31 peaks derived from the C_{60} core); FAB mass calcd for $C_{72}H_{30}Si_2O_2$ 982, found 982. Detailed data for **3a** and **3c–e** are given in the supplementary material.

[9] The formation of **3** poses a question on the mechanism of the addition of Grignard reagents to fullerenes. The compound **2** having the structure **A** was formed by the addition of **1** to the carbon–carbon double bond at the junction of two six-membered rings followed by protonation.[4b] In contrast, the structure **B** or **C** resulted from the introduction of two organosilyl groups at the junction of the five- and six-membered rings or at the 1,4-positions of the six-membered ring, respectively. Since the addition modes to give **B** or **C** were reported in the reactions of C_{60} with radical species,[4b,10] the addition of **1** in toluene may involve radical processes.

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[12] Chemical modification of organic substituents on fullerenes under weakly basic to strongly acidic conditions; Yamago, S.; Tokuyama, H.; Nakamura, E.; Prato, M.; Wudl, F. *J. Org. Chem.* **1993**, *58*, 4796. An, Y.-Z.; Anderson, J. L.; Rubin, Y. *Ibid.* **1993**, *58*, 4799.

[13] **4**: mp > 300 °C; ^1H NMR ($CDCl_3$) δ 0.41 (s, 6H, SiMe), 0.52 (s, 6H, SiMe), 2.43 (d, 2H, J = 15.14 Hz, SiCH), 2.64 (d, 2H, J = 15.14 Hz, SiCH); ^{13}C NMR ($CDCl_3/CS_2$) δ 1.76 (SiMe), 1.85 (SiMe), 29.82 (CH_2Si), 54.46 ($SiCH_2C$), 134.32–162.30 (31 peaks for the C_{60} core); FAB mass calcd for $C_{66}H_{16}Si_2O$ 880, found 880. Detailed spectral data are given in the supplementary material.

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Supplementary Material Available: General experimental details and characterization data for **2a–e**, **3a–d**, and **4** and ^{1}H and ^{13}C NMR and UV spectra of **2a**, **3e**, and **4** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.