4966 *J. Org. Chem.* **1995**, *60*, 4966–4967

Chlorosilanes and Silyl Triflates Containing C_{60} as a Partial Structure. A Versatile Synthetic Entry Linking the C_{60} Moieties with Alcohols, Phenols, and Silica

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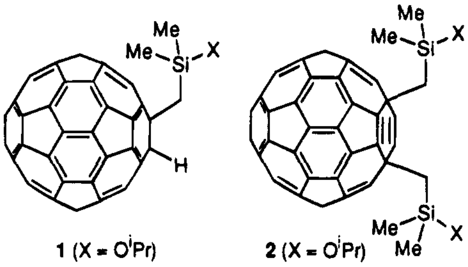
Received March 29, 1995 (Revised Manuscript Received May 31, 1995)

Interest in the chemical reactivity of C_{60} has led to the development of numerous functionalization methods for it.[1] Besides the fascinating soccer ball-shaped structure and electric nature of C_{60}, the introduction of functional groups to C_{60} has revealed novel properties not native toC_{60} alone. For example, amphiphilic fullerene derivatives that are soluble in water have been subjected to biological testing[2] and to study of their LB properties;[3] the introduction of electron-donating side chains has resulted in new donor–acceptor systems,[4] and attachment of functional groups active in polymerization has provided a synthetic route to polymers that retain the redox behavior of C_{60} itself.[5] A current challenge is the development of an efficient and versatile method for the synthesis of *fullerene derivatives with defined structures*. Although the electric properties of C_{60} impose serious limitations on the direct use of transformation reagents, this has been partially circumvented by working with fullerene derivatives of known structure.[6–9] For instance, derivatives having CO_2H,[6] OH,[6,7] and NH[8] groups are useful for further transformation; various organic substrates have been linked to the fullerene unit through ester or amide groups. Nucleophilic aromatic substitution of some C_{60}-cycloadducts has offered alternative access to derivatives having ionophoric, electrophilic, and chromophilic units.[9] In this paper, we wish to report a unique solution to this problem using novel chlorosilanes and silyl triflates having partial C_{60} structures. The organosilicon reagents Me_3SiCl and Me_3SiOTf are frequently used to protect OH groups.[10] Our new achievement is the conversion of the isopropoxy groups of the silylmethylated C_{60}, $C_{60}(H)[CH_2Si(O^iPr)Me_2]$ (**1**) and $C_{60}[CH_2Si(O^iPr)Me_2]_2$ (**2**),[11] to the corresponding chlorides, **3** and **4**, and triflates, **5** and **6** (Figure 1). The high oxophilicity of the silicon atoms of the chlorides and triflates in turn resulted in an expeditious way to link various alcohols, phenols, and even silicas to C_{60} moieties.



1 (X = O^{i}Pr)
3 (X = Cl)
5 (X = OTf)

2 (X = O^{i}Pr)
4 (X = Cl)
6 (X = OTf)

Figure 1.

Two types of isopropoxy silyl compounds, $C_{60}(H)[CH_2Si(O^iPr)Me_2]$ (**1**) and $C_{60}[CH_2Si(O^iPr)Me_2]_2$ (**2**), are easily obtained from C_{60} and $ClMgCH_2SiMe_2(O^iPr)$ as reported earlier.[11] Treatment of **1** with 3 equiv of $AlCl_3$ in C_6D_6 resulted in changes in the ^1H NMR spectrum indicative of the formation of $C_{60}(H)(CH_2SiClMe_2)$ (**3**).[12] Treatment of **3**, prepared in toluene, with a large excess of MeOH in the presence of pyridine at room temperature for 1 h afforded the corresponding silyl ether $C_{60}(H)(CH_2Si(OMe)Me_2)$ (**7b**) in 90% yield. Following the same sequence, NMR evidence suggested the formation of $C_{60}(CH_2SiClMe_2)_2$ (**4**),[12] and its methanolysis afforded the corresponding methoxy ether $C_{60}[CH_2Si(OMe)Me_2]_2$ (**8b**) in 75% yield. Other chlorinating reagents, such as BCl_3, $SOCl_2$, and PCl_5, were also effective for the conversion of **1** or **2** to **3** or **4**, respectively.

These chlorosilanes are useful for the preparation of alkoxysilanes by reaction with alcohols; however, a large excess of alcohol is required to attain a high yield of a product, and this is a drawback. We discovered that the addition of AgOTf and 2,6-lutidine to the reaction mixture, which would be likely to result in formation of the corresponding silyl triflate (**5**), was effective in raising the yield. As shown in Table 1, the corresponding silyl ethers were obtained in good yields using only a small excess of alcohol or phenol.[13] Similarly, the isopropoxy groups of **2** were converted to other alkoxy groups via the corresponding silyl triflate **6** (Scheme 1).

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[11] Nagashima, H.; Terasaki, H.; Kimura, E.; Nakajima, K.; Itoh, K. *J. Org. Chem.* **1994**, *59*, 1246. In this paper, two candidates for the structure of **2** were proposed from spectroscopy. Our further study using semiempirical MO calculations suggested that the structure depicted in Figure 1 is thermodynamically more favorable.

[12] Proton resonances for Si*Me*, SiC*H*$_2$, and C_{60}*H* in C_6D_6: **1** δ 0.46 (s), 2.55 (s), 6.54 (s); **3** δ 0.62 (s), 2.65 (s), 6.15 (s). Those for Si*Me* and SiC*H*$_2$ in C_6D_6: **2** δ 0.41 and 0.42 (two s), 2.43 and 2.58 (AB pattern, J = 14.65 Hz); **4** δ 0.55 and 0.58 (two s), 2.50 and 2.67 (AB pattern, J = 14.65 Hz). All of these compounds easily reacted with moisture to form the corresponding silanol, $C_{60}(H)[CH_2Si(OH)Me_2]$ (**7a**) or $C_{60}[CH_2Si(OH)Me_2]_2$ (**8a**).

[13] In a typical example, a mixture of **1** (0.012 mmol, 10 mg) and freshly sublimed $AlCl_3$ (0.036 mmol, 4.8 mg) was stirred in CH_2Cl_2 at room temperature for 1 h. To the resulting solution was added AgOTf (0.012 mmol, 3.1 mg), and the mixture was further stirred at room temperature for 5 min. Then, 2,6-lutidine (0.036 mmol, 4.2 μL) and *p*-methoxyphenol (0.018 mmol, 2.2 mg) were added, and the mixture was stirred for 0.5 h. After the workup, purification with a silica gel column by eluting with toluene–hexane gave **7c** (10 mg, 84%).

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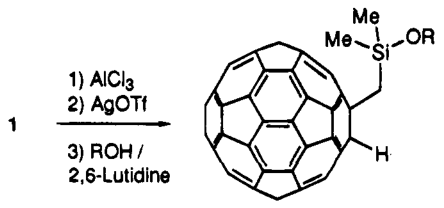
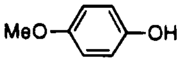
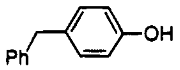
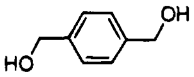
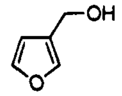
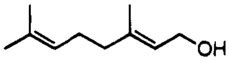
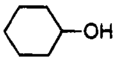
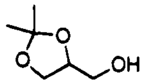
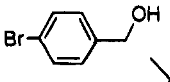
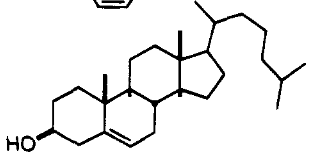
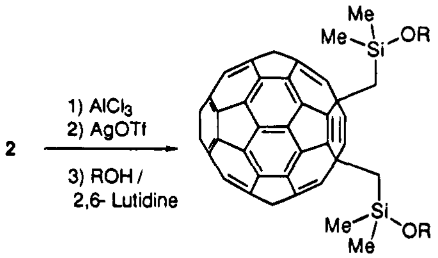
Table 1[a]



ROH	Product	Yield(%)
	7c	84
	7d	75
	7e[b)]	71
	7f	92
	7g	95
	7h	73
	7i	88
	7j	89
	7k	70

[a] All reactions were carried out according to the procedure described in the text. [b] Only one OH group was silylated.

Scheme 1



ROH = MeOH 8b (R = Me; 76%)
ROH= cyclohexanol 8h (R = C_6H_{11}; 75%)

Silicas modified by various organochlorosilanes are commonly used as stationary phases for high-performance liquid chromatography (HPLC).[14,15] The chlorosilanes **3** and **4** are potential reagents for making unique surface modifications of silicas and in fact, treatment of silica with **3** and pyridine in refluxing toluene gave modified silica. Its carbon content was 7.18%, suggesting that 0.21 molecule of C_{60} is present per 100Å^2 of silica surface. Clear evidence that the $HC_{60}CH_2SiMe_2-$ group exists on the surface was obtained from experiments using the modified silica as a stationary phase for micro-HPLC.[16] A mixture of C_{60} and C_{70} was well separated using a mixture of toluene and hexane (1:1) as the mobile phase as shown in Figure 2.[17] No separation occurred using unmodified silica as a stationary phase.

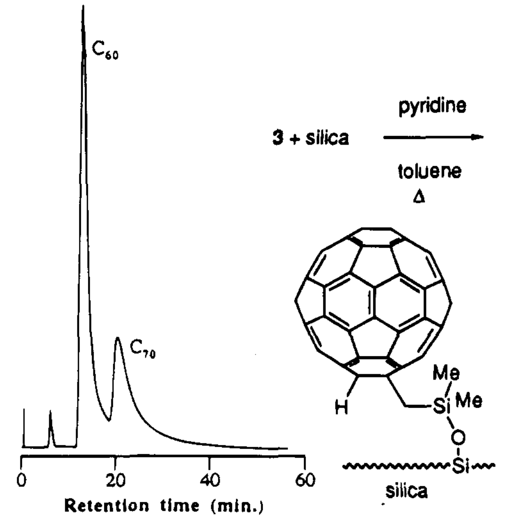


Figure 2.

These results clearly demonstrate that the silyl triflates **5** and **6** are versatile reagents for linking C_{60} moieties to a variety of alcohols and phenols through Si–O bonds. Chlorosilane **3** was also useful as a silylating reagent for silica. The silylation of OH groups with these reagents offers new access to C_{60} derivatives that may have novel properties. Organosilicon chlorides or triflates have been widely accepted in organic synthesis not only as silylating reagents for OH groups but also for a variety of nucleophiles.[10] Additional applications of these organosilicon reagents containing C_{60} units to the synthesis of a wide variety of fullerene derivatives are under investigation.

Acknowledgment. Financial support by the Ministry of Education, Science, and Culture of the Japanese government (Grant-in-Aid for Special Research Project, 05233105) and measurement of mass spectra by Professor Shoji Eguchi, Dr. Masatomi Ohno, and Mr. Kazumoto Kondo (Nagoya University) are acknowledged.

Supporting Information Available: Experimental details and characterization data of all the new compounds and ^1H and ^{13}C spectra of **7b** – **7k**, **8b** and **8h** (16 pages).

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(16) Micro-HPLC (or microscale HPLC, microbore HPLC) is expected to have several advantages, e.g., low consumption of both mobile phases and stationary phases, which facilitates the use of exotic and expensive phases, and facile coupling with mass spectrometry, being a major focus of recent research and development effort in column technology. Ishii, D., Ed. *Introduction to Microscale High-Performance Liquid Chromatography*; VCH: Wenheim, 1987. Yang, F. J., Ed.: *Microbore Column Chromatography*; Marcel Dekker, Inc.: New York, 1989.

(17) In a typical example, **3** synthesized from **1** (0.12 mmol, 100 mg) and $AlCl_3$ (0.36 mmol, 48 mg) in toluene at room temperature was treated with silica (100 mg, supplied by Shiseido, Yokohama, Japan; particle diameter was ca. 5 μm, average pore size 120 Å, surface area ca. 270 m^2/g) in the presence of pyridine (0.35 mmol, 28 μL) at 100 °C for 12 h. After filtration, the brown solid materials were washed with toluene, chloroform, and methanol to give the modified silica (122 mg). Although separation of C_{60} and C_{70} with micro-HPLC has been extensively studied with octadecylsilica bonded phases,[18] good separation has not been achieved using a mixture of toluene and hexane as a mobile phase, which are advantageous to charge the fullerenes to micro-HPLC with a minimum amount of the solvents.

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