

Reaction of [60]Fullerene with 1-(4-Methoxyphenyl)-1-(trimethylsilyloxy)ethylene

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[60]Fullerene reacts with 1-(4-methoxyphenyl)-1-(trimethylsilyloxy)ethylene in the presence of the complex of KF and 18-crown-6 to form a monoadduct **2**; the structure of this compound was characterized by FAB-MS, UV-VIS, FTIR, ¹H NMR, ¹³C NMR, HMQC and HMBC spectroscopic analysis.

The fascinating structure and properties of fullerene have led to rapid development of its chemistry. In recent papers in this area, both experimental and theoretical results have disclosed the electron-deficient character of this carbon cluster.¹ For example, addition of several nucleophilic reagents to fullerene, such as the reactions of [60]fullerene with *tert*-butyllithium or Grignard reagents, have been reported.² Here we report the reaction of [60]fullerene and the silyl enol ether of 4-methoxyacetophenone in the presence of the complex of KF and 18-crown-6. The silyl enol ether is a versatile reagent in organic synthesis, under the influence of KF/18-crown-6 or tetrabutylammonium fluoride it can generate *in situ* nucleophilic species and reacts with electrophilic compounds such as aldehydes and ketones to introduce a carbonyl group.³

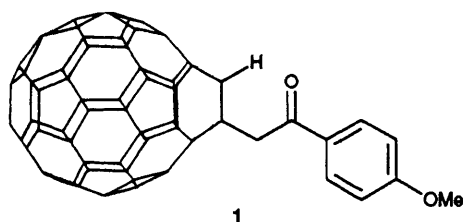
The reaction was carried out as follows. In the presence of the complex of KF/18-crown-6, [60]fullerene and

1-(4-methoxyphenyl)-1-(trimethylsilyloxy)ethylene were dissolved in toluene and heated to 60 °C with stirring for 1 h then acid was added to remove excess of silyl enol ether. The product was obtained by flash column chromatography on silica gel using a mixture of *n*-hexane and methylene chloride as eluent. The yield of **2** was 13% (based on the consumed [60]fullerene).

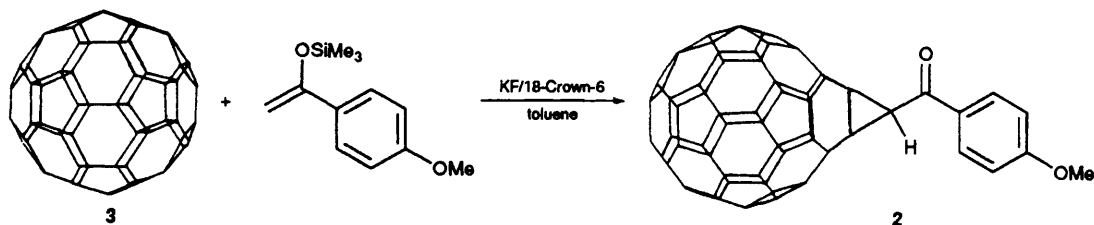
Our original purpose was to obtain compound **1** from the above reaction, but we were surprised to find that the product we obtained was **2**† (Scheme 1). The structure of this pure adduct was determined based on the following spectral data.

The FAB-MS spectrum displays a peak at 869 (relative intensity, 25%, M⁺ + 1 for C₆₉H₈O₂) as well as the base peak for [60]fullerene at 720 which arises from loss of C₉H₈O₂. In the FTIR spectrum (KBr pellet) there are four strong bands at 1425.0, 1165.6, 575.0 and 525.0 cm⁻¹ corresponding to vibrations of [60]fullerene skeleton, and a band at 1675.0 cm⁻¹, which suggests the presence of a conjugate carbonyl group in this molecule. The electronic absorption spectrum between 190 and 400 nm in *n*-hexane is virtually identical with that of [60]fullerene, but subtle differences are observed in the visible region. The absorption band at 406 nm in [60]fullerene shifts to 428 nm, and the weak bands of [60]fullerene at 532 and 592 nm are not found in this molecule.

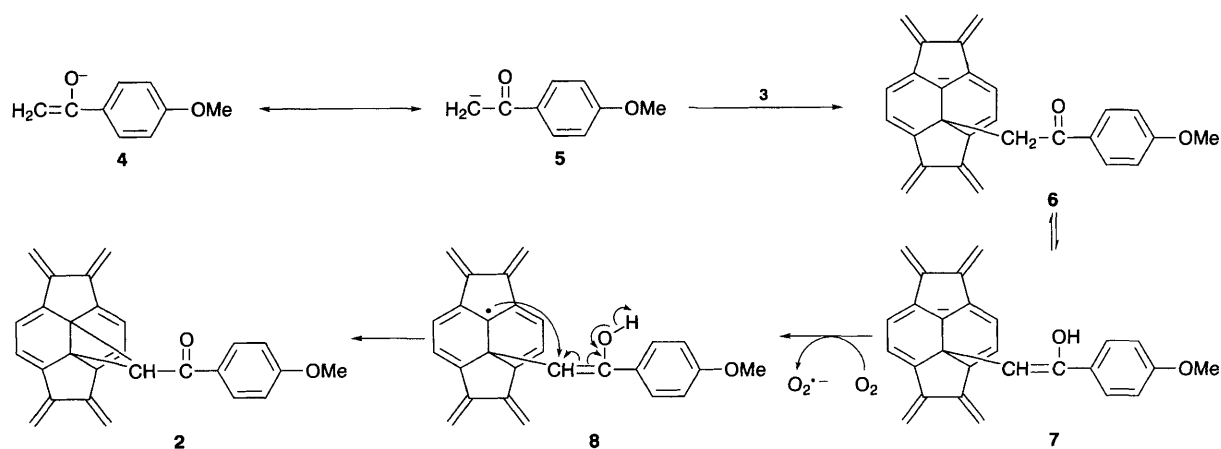
The NMR spectra give the most important information for the structure of **2**. ¹H NMR (600 MHz, CDCl₃) shows a singlet at δ 3.97 for the methoxyl group, aromatic protons at δ 7.15 and 8.46 (AA'XX' multiplet), and a singlet for one proton at δ 5.61.



1



Scheme 1



Scheme 2

The ^{13}C NMR (150.9 MHz, CDCl_3) spectrum exhibits 33 signals, of which 27 correspond to the [60]fullerene framework. 20 peaks are found to have an intensity of 2 C and 2 peaks of 1 C. Overlapping signals are observed at δ 142.27, 142.98, 144.62, 144.67 and 145.18, with these peaks having a relative intensity of 4, 3, 4, 3 and 4 C respectively. The remaining signals at δ 188.01, 128.86, 131.35, 114.59, 164.69 and 55.73 are assignable to a *para*-anisoyl moiety. In the HMQC and HMBC spectra, the ^1H resonance at δ 5.61 shows a one-bond correlation with the carbon signal at δ 44.36 and two- and three-bond correlations with the ^{13}C resonances at δ 72.49, 146.93 and 148.18 respectively, these data suggest a methanofullerene structure as shown in Fig. 1 for this monoadduct. This structure is strongly supported by the results reported by Bingel,⁴ Prato *et al.*⁵ and Tokuyama *et al.*⁶

As to the mechanism of this reaction, we can not provide enough evidence to explain how the cyclopropane derivative formed, but we think that a process involving a free radical intermediate might take place. As described in Scheme 2 with catalysis by the complex of KF/18-crown-6, the silyl enol ether loses its trimethylsilyl group to give the nucleophilic species 4 and 5, 5 then reacts readily with 3 to form the substituted fulleride anion 6. According to previous work,^{1,2} the nucleophilic additions to [60]fullerene occur preferentially at the 6-6 junction, and we believe that the negative charge is located at the *ortho*-position of the substituent group both in 6 and its isomer 7. Since the reaction was carried out in air, it is not surprising that the anions 6 and 7 will be oxidized by oxygen to a free radical intermediate 8 and give the final product 2 by rearrangement. As evidence for this explanation, we found that when the reaction was carried out in anhydrous toluene and under a strict nitrogen atmosphere, the reaction took place very slowly (based on the conversion rate of [60]fullerene) even at higher temperatures (110 °C). When the reaction was complete, the resulting products were found to be sparsely soluble in organic solvents such as toluene, chloroform and carbon disulfide and compound 2 was not found among the products according to the HPLC analysis.‡ The low solubility of the products made their separation almost impossible.

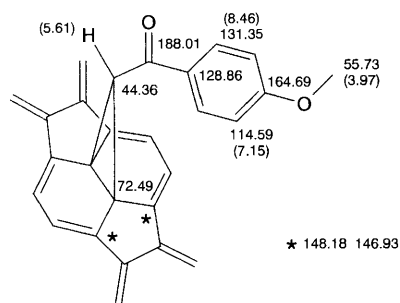


Fig. 1 ^{13}C and ^1H NMR (in parentheses) data of 2

We have established the result of the reaction of [60]fullerene and 1-(4-methoxyphenyl)-1-(trimethylsilyloxy)ethylene; we have also studied the reaction of [60]fullerene with 1-phenyl-1-(trimethylsilyloxy)ethylene, and similar results were obtained.§

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Footnotes

† Spectroscopic data for 2: TLC Rf = 0.73 [silica gel, *n*-hexane–methylene chloride (1/1)]. UV–VIS λ_{max} (*n*-hexane) 214s, 257s, 328s, 428w nm. FTIR (KBr pellet) ν/cm^{-1} 2924.2, 2839.8, 1675.0, 1596.9, 1509.4, 1425.0, 1262.5, 1243.7, 1225.0, 1165.6, 1025.0, 840.6, 609.3, 575.0, 525.0. ^1H NMR (600 MHz, CDCl_3) δ 3.97 (s, 3H, OCH_3), 5.65 (s, 1H, cyclopropyl H), 7.15, 8.46 (AA'XX' multiplet, 4H, aromatic). ^{13}C NMR (150.9 MHz, CDCl_3) δ 44.36 (cyclopropyl C), 55.73 (OCH_3), 72.49 (2C), 114.59 (aryl C), 128.86 (aryl C), 131.35 (aryl C), 136.61 (2C), 139.49 (2C), 140.96 (2C), 141.20 (2C), 142.11 (2C), 142.27 (4C), 142.51 (2C), 142.78 (2C), 142.98 (3C), 143.04 (2C), 143.17 (1C), 143.34 (2C), 143.71 (2C), 143.95 (2C), 144.33 (2C), 144.62 (4C), 144.67 (3C), 144.74 (2C), 144.89 (1C), 145.08 (2C), 145.18 (4C), 145.29 (2C), 145.46 (2C), 145.62 (2C), 146.93 (2C), 148.18 (2C), 164.69 (aryl C), 188.01 (CO). FAB-MS m/z 869 ($\text{M}^+ + 1$ of $\text{C}_{69}\text{H}_8\text{O}_2$, 25), 720 (C_{60} , 100%).

‡ Experimental conditions: stationary phase, silica gel Si60 (5 μm); column dimension, 240 \times 5 mm; mobile phase, *n*-hexane–methylene chloride (1 : 1 v/v); flow rate, 1.0 ml min^{-1} ; detection, UV at 330 nm.

§ The reaction of [60]fullerene and 1-phenyl-1-(trimethylsilyloxy)ethylene was carried out under the same conditions. ^1H NMR (300 MHz, CDCl_3) of the monoadduct: δ 5.67 (s, 1H, cyclopropyl H), 7.69 (m, 1H, aromatic), 7.78 (m, 2H, aromatic), 8.49 (m, 2H, aromatic).

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