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Samarium(II) Iodide Promoted Synthesis of 1-ethoxycarbonylmethyl-2-hydrofullerene

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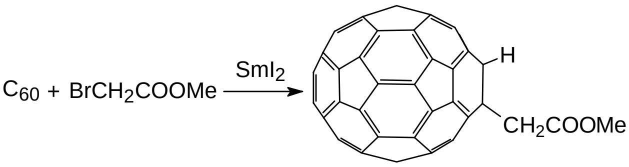
Abstract: the reaction of C_{60} with methyl bromoacetate in the presence of SmI_2 gives the title compound 1-methoxycarbonylmethyl-2-hydrofullerene in good yield.

Keywords: C_{60}, samarium iodide, 1, 2-dihydrofullerene.

The functionalization of fullerenes has attracted great attention and much progress has been made. There are now many methods available for the preparation of fullerene derivatives[1-4]. Theoretical calculations show that C_{60} is fairly electronegative and can be reduced to the hexaanion, which has been proven by cyclic voltammetry[5]. Various carbon anion sources such as the Grignard reagents add to C_{60} to form dihydrofullerene adducts[6]. Samarium(II) iodide(SmI_2) has played an ever increasing role in organic synthesis since it was first introduced by Kagan in the late 1970s[7]. It chemoselectively reduces a large variety of organic groups and promotes many important synthetic reactions with high selectivity[8]. In spite of the numerous reactions reported for C_{60}, SmI_2 was never employed in the synthesis of fullerene derivatives. Here we report the reaction between C_{60} and methyl bromoacetate promoted by SmI_2.

The reaction was carried out as the following: A solution of C_{60} (110 mg, 0.152 mmol) in toluene and a solution of methyl bromoacetate (0.76 mmol) in THF were mixed in a Schlenk flask under nitrogen atmosphere. SmI_2 in THF (3 mmol) was then added to the mixture by syringe. After being stirred at room temperature for 3 h, the reaction mixture was quenched with 4 ml aqueous HCl (0.01 M). The organic layer was separated by centrifugation as a dark-brown solution. The organic solution was washed with water, dried over Na_2SO_4, and purified by flash chromatography on silica gel, eluting with toluene unreacted C_{60} (40 mg) and 1-methoxycarbonylmethyl-2-hydrofullerene can be well separated bands. Removal of the solvent on rotary evaporator gave the product as a dark-brown solid (23 mg, 30% based on converted C_{60}).

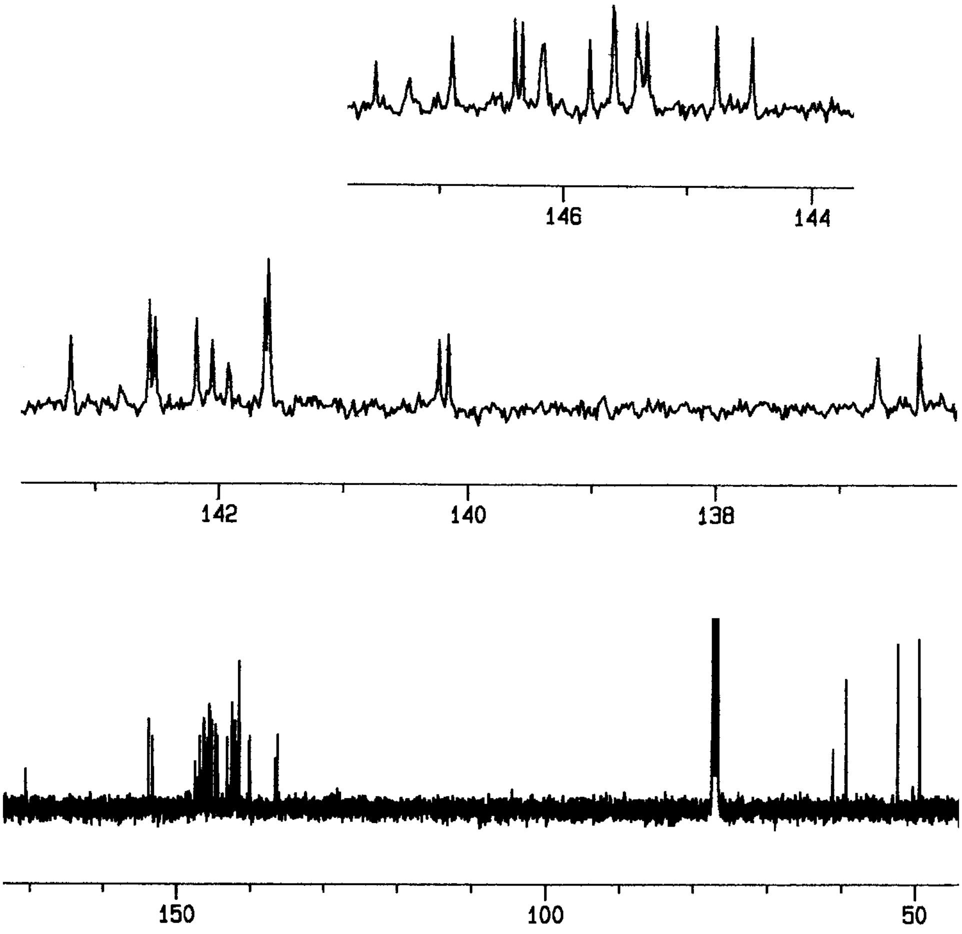


The ethyl analog of the above compound has been reported before by several groups9-11. For example Komatsu and coworkers synthesized C60(H)(CH2COOEt) by a Reformatsky-type of reaction, treating ethyl bromoacetate and zinc with C60 in a vibrating mill without any solvent9. Besides the main product C60(H)(CH2COOEt), three other byproducts were also isolated including a 1,4-dihydrofullerene derivative C60(CH2COOEt)2. The spectroscopic data of the present product confirm its structure as depicted. 1H NMR showed three singlets at 6.77, 4.47 and 4.08 ppm corresponding to the C60H, CH2 and OCH3 protons respectively. 13C NMR indicates the carboxyl carbon at 170.60 ppm (see figure on next page). This is essentially the same as the ethyl anolog reported in the literature (169.68)12. The fullerene sp2 carbons appear as 26 peaks, a few of which are overlapped. The sp3 carbons C and CH of C60 are at 61.06 and 59.25 ppm. These chemical shifts are also essentially the same as those of the ethyl anolog (60.93 and 59.05 ppm)12. The methoxyl and methylene carbons appear at 52.27 and 49.36 ppm. The MALDI-TOF showed the molecular ion peak at 794 m/z.

The mechanism of SmI2 promoted carbon-carbon bond forming reactions has been well studied8. The strong reducing ability of SmI2 is the key feature in almost all reactions involving it. The redox potentials of SmI2 (-1.33 V in THF) and C60 (C60-/C602-= -0.92 V, C602-/C603-= -1.49 V in THF) indicate that C60 can be reduced to the dianion C602-. Huang et al. have reported that C602- potassium reacts with benzyl chloride to form 1-benzyl-2-hydrofullerene13. So one possible route for the formation of 1-methoxycarbonylmethyl-2-hydrofullerene is that C60 first reacts with SmI2 to form C602-, which then reacts with BrCH2COOMe through a mechanism similar to Huang's reaction. Alternatively SmI2 may first react with BrCH2COOMe to form BrSmCH2COOMe, and this Sm salt then reacts with C60 through a mechanism similar to the reaction between Zn, BrCH2COOMe and C60, in which the reduction of BrCH2COOMe by Zn is proposed as the first step9.

Spectral data for 1-methoxycarbonylmethyl-2-hydrofullerene: UV-Vis max (toluene): 433, 328, 281 nm; NMR δ_H(400 MHZ, CDCl3-CS2): 6.77 (s, 1H), 4.47 (s, 2H), 4.08 (s, 3H) ppm. δ_C(100.6 MHZ, CDCl3-CS2): 170.60, 153.86 (2C), 153.32 (2C), 147.51 (1C), 147.24 (1C), 146.90 (2C), 146.39 (2C), 146.33 (2C), 146.16 (4C), 145.78 (2C), 145.59 (4C), 145.40 (2C), 145.32 (2C), 144.76 (2C), 144.48 (2C), 143.20 (2C), 142.56 (2C), 142.51 (2C), 142.18 (2C), 142.05 (2C), 141.92 (2C), 141.63 (2C), 141.60 (6C), 140.23 (2C), 140.15 (2C), 136.69 (2C), 136.35 (2C), 61.06, 59.25, 52.27, 49.36. FT-IR (microscope): 1742, 1633 (broad), 1568, 1512, 1461, 1429, 1405, 1345, 1261, 1199, 1183, 1170, 1144, 1135, 1068, 988, 839, 810, 763, 745, 707, 699, 689, 580, 574, 562, 552, 543, 526, 513, 475 cm-1. MALDI-TOF (m/z): 794 (5%, M+),720 (100%, C60+). Elemental anal. Found: C 91.83%, H 2.06%; Calced for C60(H)(CH2COOMe).2H2O.Toluene: C 91.10%, H 1.97%.

Figure 1 ^{13}C NMR spectrum of 1-methoxycarbonylmethyl-1, 2-dihydrofullerene



Acknowledgment

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