Pergamon

Tetrahedron Letters, Vol. 38, No. 44, pp. 7737-7740, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10066-1

Cyclopropanation of C_{60} with Malonic Acid Mono-esters

Jean-François Nierengarten* and Jean-François Nicoud

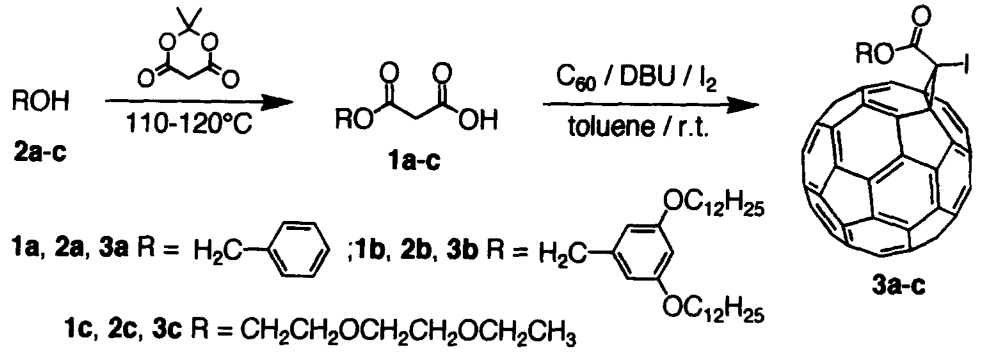
Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg,
Université Louis Pasteur et CNRS, 23 rue du Loess, 67037 Strasbourg, France

Abstract: Reaction of C_{60} with malonic acid mono-esters in the presence of iodine and diazabicyclo[5.4.0]undec-7-ene (DBU) provides the corresponding 61-iodo-1,2-methano[60]fullerene-61-carboxylates. This cyclopropanation of C_{60} seems to occur *via* a carbenoid intermediate. © 1997 Elsevier Science Ltd.

Among the large number of functionalized C_{60} derivatives,[1] the methanofullerenes[2] have been one of the most studied class. Since the first reported synthesis of a methanofullerene by Wudl and co-workers in 1991,[3] research in this field has expanded rapidly in many different directions, including material science and biological applications. The synthetic methods utilized to produce methanofullerenes may be divided into three categories: (i) thermal addition of diazo compounds, followed by thermolysis or photolysis,[3,4] (ii) addition of free carbenes to C_{60},[5] and (iii) reactions which proceed by an addition-elimination mechanism.[6] Although the first method always produces a mixture of [5,6]-open fulleroids and [6,6]-closed methanofullerenes, the second and third methods give pure methanofullerenes. The cyclopropanation of C_{60} with stabilized α-halocarbanions,[6a] the so-called Bingel reaction, appears to be one of the most efficient tools for the synthesis of methanofullerenes. This reaction is formulated as an addition of the stabilized α-halocarbanions to C_{60}, followed by an intramolecular displacement of halide by the anionic center generated on the fullerene core. The reaction is fast, clean and proceeds in fair to good yields. Additionally, it has been shown that nucleophilic cyclopropanation of C_{60} is possible starting directly from malonates. In this case, the α-halomalonate is generated *in situ*, and direct treatment of C_{60} with malonates in the presence of iodine[7] or CBr_4[8] and base affords the corresponding methanofullerenes in good yields.

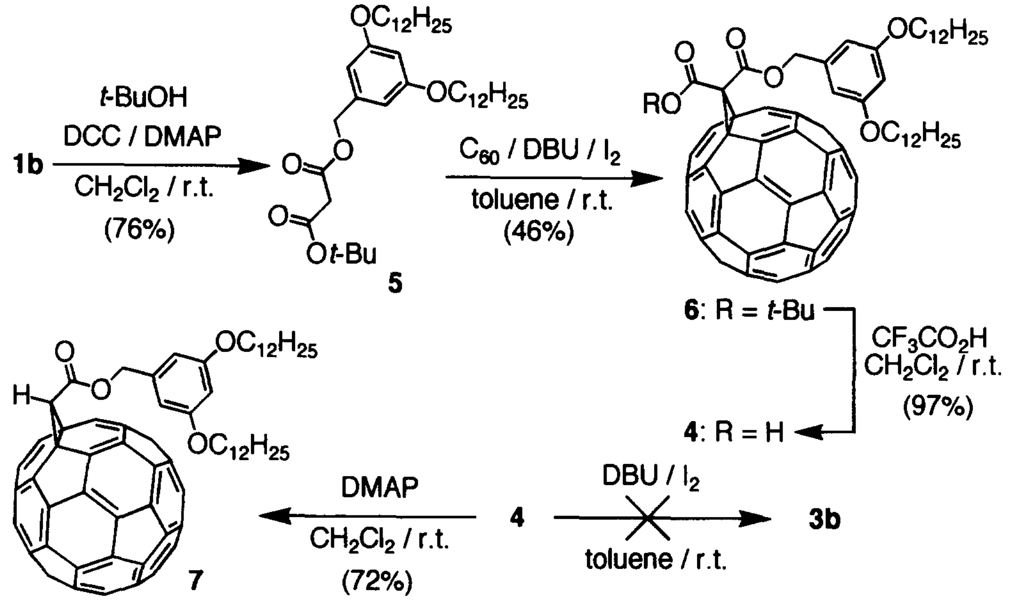
We report herein the reaction of C_{60} with malonic acid mono-esters in the presence of iodine and diazabicyclo[5.4.0]undec-7-ene (DBU). The malonic acid mono-esters **1a-c** were prepared in quantitative yields by reaction of the corresponding alcohols **2a-c** with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) at 110-120°C for 3 hrs[9] (*Scheme 1*). Alcohol **2b** was obtained in 76% yield by alkylation of 3,5-

dihydroxybenzyl alcohol with 1-bromododecane in DMF at 60°C with K_2CO_3 as base. Treatment of C_{60} with **1a-c** in the presence of iodine and DBU in toluene at room temperature for 24 hrs afforded surprisingly the corresponding 61-iodo-1,2-methano[60]fullerene-61-carboxylates **3a-c** in 25 to 28% yield. In a typical procedure, DBU (5 eq.) was added to a stirred solution of C_{60} (300 mg), **1b** (1.1 eq.) and I_2 (3 eq.) in toluene (300 ml) at room temperature. After 12 hrs, an additional portion of **1b** (0.5 eq.) and I_2 (1 eq.) was added and the mixture stirred for another 12 hrs. The reaction mixture was filtered through a pad of SiO_2 (toluene) and evaporated. Column chromatography on SiO_2 yielded the unreacted C_{60} (83 mg, eluent: hexane/toluene 4:1) and **3b** (hexane/toluene 4:3). Crystallization from CH_2Cl_2/hexane afforded pure **3b** (141 mg, 25% yield, or 34% based on the non-recovered C_{60}). The structure of **3b** is confirmed by FAB-MS, which depicts the molecular ion peak at *m/z* 1363.2 (MH^+, $C_{93}H_{56}O_4I$ requires 1363.3). The ^{13}C-NMR spectrum is also in full accordance with the structure of **3b**.[10] The 32 expected fullerene resonances (31 between δ = 136 and 148 ppm, four of which show half intensity, and one at δ = 75.47 ppm) as well as the 19 expected non-fullerenic signals are observed for C_s symmetrical **3b**. Whereas the resonances of the methanobridge C atoms appear at δ = 14.81 (**3a**), 14.37 (**3b**), and 14.47 ppm (**3c**), the methanobridge C atoms of the corresponding C–H analogues resonate typically around 39 ppm.[4b-c,7c] This shielding effect is characteristic of the presence of iodine.[11]



Scheme 1. Cyclopropanation of C_{60} with malonic acid mono-esters.

Since the malonic acid derivatives of C_{60} are known to give facile decarboxylation under basic conditions,[6f,7c] the formation of methanofullerenes **3a-c** could be the result of a decarboxylation of the Bingel addition product derived from **1a-c**, followed by quenching of the resulting carbanion with I_2. In order to prove the formation of the Bingel addition product as an intermediate, the stepwise preparation of **3b** was attempted *via* methanofullerene-dicarboxylic acid mono-ester **4**. The preparation of compound **4** is depicted in *Scheme 2*. *N,N'*-Dicyclohexylcarbodiimide (DCC)-mediated esterification of **1b** with *t*-BuOH in CH_2Cl_2 at room temperature yielded the mixed malonate ester **5** in 76% yield. The methanofullerene **6** was obtained in 46% yield by treatment of C_{60} with **5** in the presence of DBU and I_2 in toluene at room temperature. Selective cleavage of the *tert*-butyl ester moiety[7c] of **6** with CF_3CO_2H in CH_2Cl_2 at room temperature afforded the desired carboxylic acid **4** in 97% yield. When compound **4** was subjected to the reaction conditions used for the preparation of **3b** from **1b** (DBU / I_2 / toluene / room temperature), only traces of **3b** could be detected (< 1%) and compound **7** was the only isolable product (30 to 40% yield). In order to prevent the reaction of the carbanion resulting from the decarboxylation with DBU-H^+ and the formation of **7**, NaH was used as base; however only decomposition products were obtained and no traces of **3b** could be detected. It has to be noted that the reaction of compound **4** with a catalytic amount of 4-dimethylaminopyridine[7c] (DMAP) in CH_2Cl_2 at room temperature for 5 hrs afforded **7** in a good yield (72%). In this case, the unstable carbanion resulting from the decarboxylation reaction is immediately quenched by the more acidic DMAP-H^+ resulting from the reaction of DMAP with the carboxylic acid function of **4**; therefore, the conversion of **4** into **7** is clean under this conditions.



Scheme 2. Preparation of methanofullerene-dicarboxylic acid mono-ester **4** and its decarboxylation.

Since all the attempted transformations of **4** into **3b** failed under the experimental conditions used for the preparation of **3b** from **1b**, the cyclopropanation of C_{60} with malonic acid mono-esters in the presence of I_2 and DBU seems not to occur *via* the formation of the corresponding Bingel addition product. As an alternative, we suppose that the α-iodocarbanion formed *in situ* might be not nucleophilic enough to react with C_{60} and the formation of the corresponding diiodomalonate derivative occurs. Subsequent decarboxylation and iodine displacement could yield a carbenoid intermediate able to react with C_{60} to form the corresponding methanofullerene. This cyclopropanation appears to be similar to the addition of dichlorocarbene to C_{60} described by Nogami and co-workers.[5c] The pyrolysis of sodium trichloroacetate in a mixture of benzene and diglyme generates dichlorocarbene, which then adds to C_{60} to give the corresponding methanofullerene in 26% yield.

Acknowledgements: We thank A. Van Dorsselaer and R. Hueber for recording the mass spectra, R. Graff and J.-D. Sauer for high-field NMR measurements, and C. Schall for the preparation of compound **1b**.

References and Notes

1. a) Hirsch, A. *The Chemistry of the Fullerenes*, Thieme, Stuttgart, **1994**; b) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.
2. For a review on methanofullerenes, see Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243.
3. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarson, Ö. *Science* **1991**, *254*, 1186.
4. See for examples: a) Smith, A. B. III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829; b) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231; c) Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 2454; d) Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364.
5. See for examples: a) Vasella, A.; Uhlmann, P.; Waldraff, C. A. A.; Diederich, F.; Thilgen, C. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1388; b) Tokuyama, H.; Nakamura, M.; Nakamura, E. *Tetrahedron Lett.* **1993**, *34*, 7429; c) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *Tetrahedron Lett.* **1993**, *34*, 6911; d) An, Y.-Z.; Rubin, Y.; Schaller, C.; McElvany, S. W. *J. Org. Chem.* **1994**, *59*, 2927; e) Timmerman, P.; Anderson, H. L.; Faust, R.; Nierengarten, J.-F.; Habicher, T.; Seiler, P.; Diederich, F. *Tetrahedron* **1996**, *52*, 4925.
6. See for examples: a) Bingel, C. *Chem. Ber.* **1993**, *126*, 1957; b) Hirsch, A.; Lamparth, I. S.; Karfunkel, H. R. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 437; c) Anderson, H. L.; Faust, R.; Rubin, Y.; Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1366; d) Bestmann, H. J.; Hadawi, D.; Röder, T.; Moll, C. *Tetrahedron Lett.* **1994**, *35*, 9017; e) Wang, Y.; Cao, J.; Schuster, D. I.; Wilson, S. R. *Tetrahedron Lett.* **1995**, *36*, 6843; f) Lamparth, I.; Schick, G.; Hirsch, A. *Liebigs Ann.* **1997**, 253.
7. a) Bingel C. presentation at the meeting *New Perspectives in Fullerene Chemistry and Physics*, Rome (Italy), **1994**; b) Nierengarten, J.-F.; Gramlich, V.; Cardullo, F.; Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2101; c) Nierengarten, J.-F.; Herrmann, A.; Tykwinski, R. R.; Rüttimann, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 293.
8. Camps, X.; Hirsch, A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1595.
9. Chen, B.-C. *Heterocycles* **1991**, *32*, 529.
10. Spectroscopic data for **3b**: UV/VIS (CH_2Cl_2): 256 (120700), 321 (43760), 426 (2960), 479 (1780), 682 (180); IR ($CHCl_3$): 1737 (C=O); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (t, 6H, J = 6 Hz), 1.26 (m, 36H), 1.74 (m, 4H), 3.90 (t, 4H, J = 6 Hz), 5.45 (s, 2H), 6.41 (t, 1H, J = 2 Hz), 6.62 (d, 2H, J = 2 Hz); ^{13}C-NMR ($CDCl_3$, 125 MHz): 14.20, 14.37, 22.72, 26.17, 29.29, 29.39, 29.47, 29.65, 29.66, 29.67, 29.72, 31.94, 68.11, 69.26, 75.47, 101.97, 107.18, 136.60, 137.31, 139.12, 140.82, 140.96, 142.02, 142.13, 142.18, 142.36, 142.81, 142.88, 142.96, 142.98, 143.06, 143.24, 143.57, 143.77, 144.19, 144.29, 144.48, 144.67, 144.69, 144.70, 144.71, 144.74, 145.09, 145.15, 145.18, 145.25, 145.33, 145.47, 147.77, 160.43, 165.99; FAB-MS: 1363.2 (MH^+, 10%), 719.9 (C_{60}^+, 100%); Elemental analysis calc. for $C_{93}H_{55}O_4I$: C 81.93%, H 4.07%; found: C 81.76%, H 4.12%.
11. Günther, H. *NMR-Spektroskopie*, Thieme, 2. Ed., Stuttgart, **1983**.

(*Received in France* 17 *July* 1997; *accepted* 6 *September* 1997)