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# [60]Fullerene diol issued from pentaerythritol derivatives

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**Abstract**—A new [60]fullerene diol is synthesized in good yield, in two steps starting from reaction of $C_{60}^{2-}$ anion with the benzyl-ideneacetal derived from 2,2-bis(iodomethyl)-1,3-propanediol. The corresponding [60]fullerene bis-mesylate is also formed in a similar way starting from bis-iodo bis-mesylate compound in the same series. The scope of this fullerene diol in synthesis is exemplified by its easy esterification with 4-formyl benzoyl chloride.
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In the past decade, the functionalization of [60]fullerene has brought about numerous works, because of the specific and very attractive physical properties exhibited by $C_{60}$ derivatives.[1–3] In order to still extend the possibilities of functionalizing [60]fullerene, in particular when the $C_{60}$ core has to be linked to two other units in the final desired $C_{60}$ derivative, several bis-functionalized $C_{60}$-based synthons have been introduced in the recent years. A double Bingel reaction was first involved in a tether-directed functionalization, as proposed by Diederich and co-workers.[4] Thus were obtained bis(methano)[60]fullerene dicarboxylic acids.[5,6] A similar strategy allowed Nierengarten's group to obtain another fullerene dicarboxylic acid,[7] while this same group could also synthesize a fullerene diol starting from a mono Bingel reaction.[8] The final isolation of all of these synthons was achieved after a multi-step process.

We now wish to report on a simple and efficient synthesis of a new [60]fullerene derivative **1** bearing two primary alcohol groups. In our current work on synthesis of new $C_{60}$-based triads involving two electron donor units, we were in search of a new fullerene diol the structure of which was as close as possible to the fullerene alcohol **2** we used in synthesis of $C_{60}$-TTF based dyads[9] (Scheme 1). On the other hand, only some works are published on the synthesis of fullerene derivatives bearing an alcohol substituted unit and acting as a building block in fullerene chemistry, despite the importance of
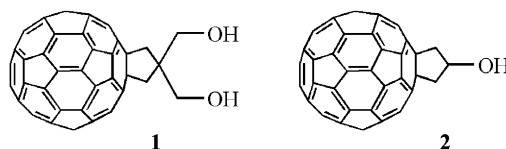


**Scheme 1.**

this group for further syntheses.[10] Besides, to our knowledge, only two fullerene compounds bearing two alcohol function groups is reported so far.[8,11]

Previously, we have shown that cyclopentano-fused fullerene compounds **3** and **4** are easily formed through reaction of 1,3-diiodo or 1,3-dibromopropane derivatives with $C_{60}^{2-}$ (Scheme 2).[9,12] The molecular frame thus obtained is particularly attractive thanks to its high overall symmetry, which gives a key role to any functional unit attached to the 2′-position in the fused C5 ring. This molecular frame was already obtained, but its synthesis based on the cycloaddition of a methylenecyclopropane moiety to the $C_{60}$ core appeared to be rather difficult.[13]
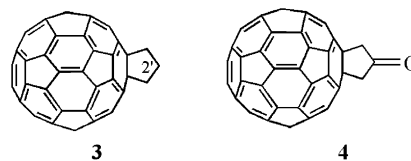


**Scheme 2.** Examples of $C_{60}$ derivatives issued from functionalization of $C_{60}^{2-}$ anion.
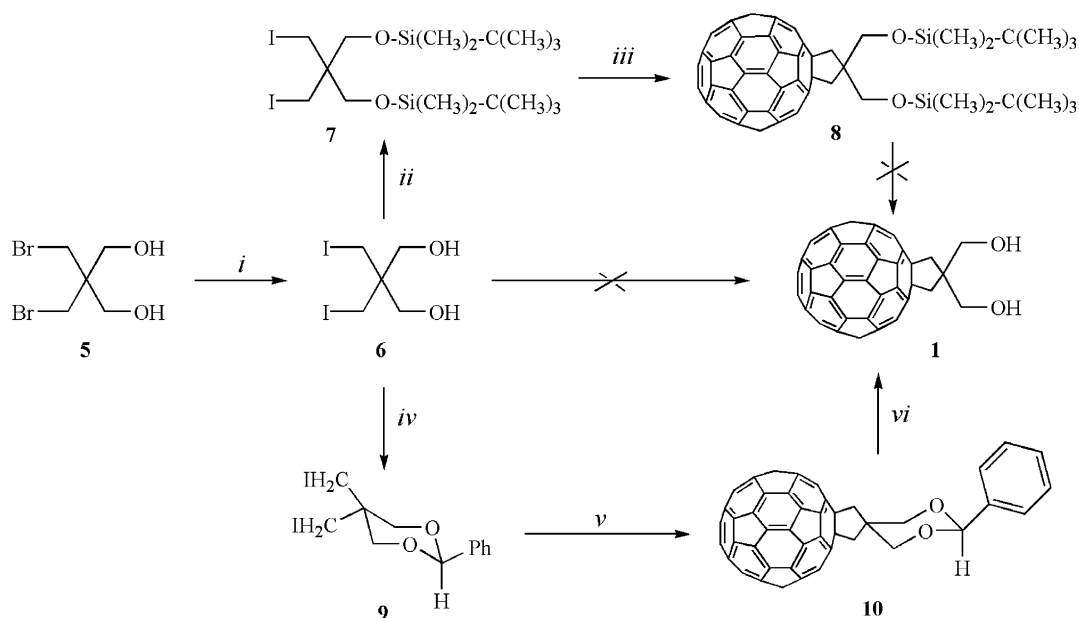
**Scheme 3.** Synthesis of diol **1**. Reagents and conditions: (i) NaI excess, refluxing acetone, 3 days, 96%; (ii) TBDMSCl (2.5 equiv), imidazole (2.5 equiv), DMF, 24 h, 69%; (iii) $C_{60}^{2-}$, 1 week, 13%; (iv) benzaldehyde (0.833 equiv), TsOH cat, toluene, reflux (Dean–Stark app.), 2 days, 83%; (v) $C_{60}^{2-}$, 40 °C, 7 days, 50%; (vi) $CF_3CO_2H$, $H_2O$, silica, 65 °C, 3 days, 45%.

In the fullerene diol **1** the diol unit can be related to the pentaerythritol frame. Following our previous results, a possible straightforward access to this diol **1** might have resulted from the reaction, in acetonitrile, of $C_{60}^{2-}$ with the diiodo diol **6**, easily obtained from the commercially available dibromo diol **5** through usual methods (Scheme 3). However the fullerene diol **1** could not be formed in these conditions, although the red colour due to the $C_{60}^{2-}$ anion has progressively disappeared in the reaction mixture. This result remains unexplained so far,[14] and prompted us to protect the alcohol groups of compound **6** before the reaction with $C_{60}^{2-}$ anion.

The diiodo diol **6** was first transformed into the corresponding bis-(*tert*-butyldimethylsilyl) derivative **7** according to usual procedures, then the latter derivative was reacted at room temperature in acetonitrile with $C_{60}^{2-}$.[15] The expected silylated fullerene derivative **8** was obtained (13% yield), but removing the protecting groups using $Bu_4N^+F^-$ salt gave no defined compound (Scheme 3). From these disappointing results, we turned towards protecting methods more specifically used with 1,3-diols. The acetal **9** was prepared from the diiodo diol **6** and benzaldehyde in the presence of *p*-toluenesulfonic acid.[16] Thus the compound **10** was obtained after reaction of the acetal **9** with $C_{60}^{2-}$ in acetonitrile. The reaction was very slow at room temperature (7% yield after

two days), and required an optimization of the experimental conditions. This weak reactivity is likely due to the following reasons. It is now clearly established that the reaction of $C_{60}^{2-}$ anion with halo-derivatives RX is a three step process, in which the last step, namely a nucleophilic substitution, is the slower because of the delocalized negative charge borne by the $C_{60}$ core in the intermediate $[C_{60}R]^-$ anion.[17] Moreover, the reactivity of the second iodo-carbon from the compound **9** may be still slowed down due to the rigid and crowded structure of this moiety (Scheme 4).

Finally, depending on the temperature and the reaction time, the best results were obtained with 30 equiv diiodo compound **9**, and one week reaction at 50 °C. In this case, the compound **10** was obtained in 50% yield, and this result could be reproduced on a $C_{60}$ gram scale, the most part of unreacted compound **9** being recovered.

The final deprotection of the acetal **10** required testing several methods, some of them ($CF_3CO_2H/CH_2Cl_2/$ $H_2O$, reflux $H_2SO_4$ 0.01 M,[18] Conia's method[19]) being unsuccessful. Aqueous trifluoroacetic acid was found as the best reagent, provided suitable proportions of acid and water are used, along with added silica, which was necessary for an efficient deprotection. Thus, after three days at 65 °C, the fullerene diol **1** was formed in
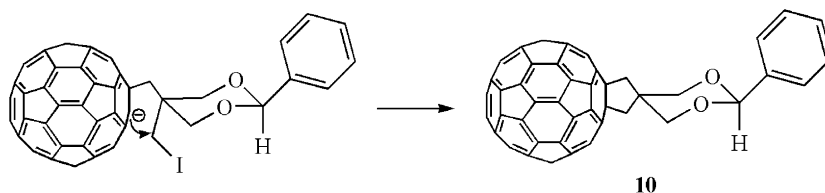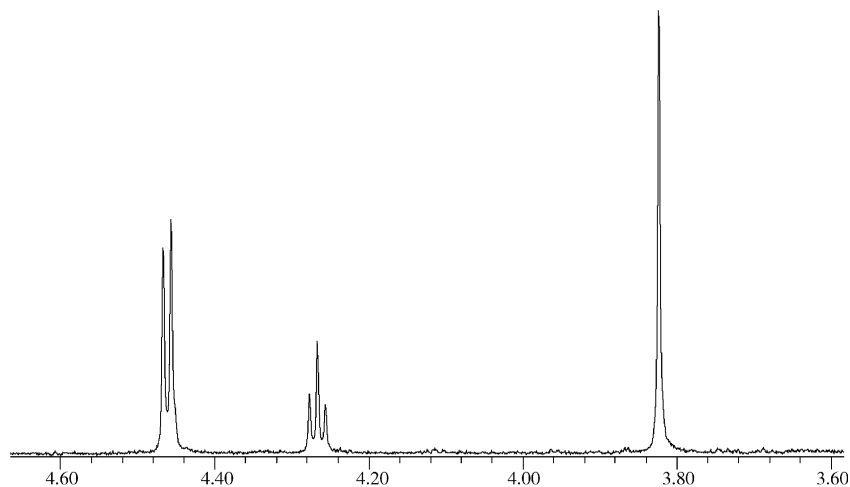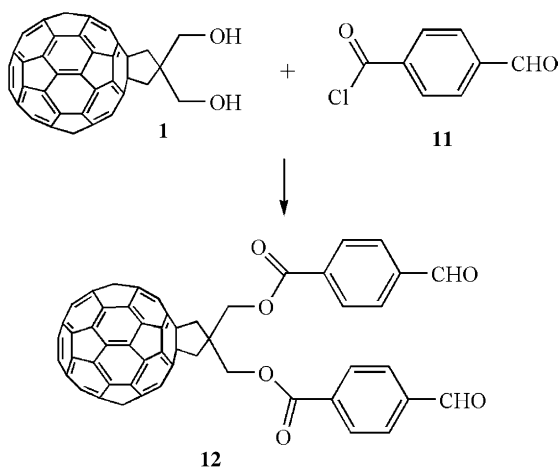


**Scheme 4.**

**Figure 1.** $^1$H NMR spectrum of fullerene diol **1**.

50–60% conversion yield, 10–20% starting acetal **10** being recovered (Scheme 3).

The fullerene diol **1**, although not very soluble in most organic solvents, was isolated as a pure compound through silica gel column chromatography (eluent: $CS_2$/acetone 98:2), and fully and unambiguously identified by means of usual analytical methods (see $^1$H NMR spectrum, Fig. 1).[22] This diol is very stable and can be stored without degradation for several months.

The reactivity of the diol **1** has been tested towards several acid chlorides. As an example, the reaction of 4-formylbenzoyl chloride **11**, freshly prepared from 4-formylbenzoic acid,[20] could easily give rise to the corresponding dialdehyde **12** in 30% yield, this reaction being performed in chlorobenzene in the presence of DMAP (Scheme 5).

In complement, we were also interested in studying the reactivity of the bis-iodo bis-mesylate compound **13** versus $C_{60}^{2-}$ anion in order to compare with previous results reported by Meier et al. These authors mention that, unlike saturated halo-derivatives, sulfonate esters



**Scheme 5.** Synthesis of derivative **12**.
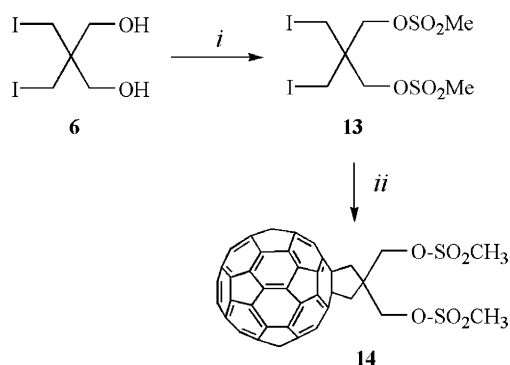


**Scheme 6.** Synthesis of bis-mesylate **14**. Reagents and conditions: (i) triethylamine (2.5 equiv), $CH_2Cl_2$, 0 °C, then methanesulfonyl chloride (2.5 equiv), 3 h, 80%; (ii) $C_{60}^{2-}$, 40 °C, 1 week, 8%.

$R–SO_3R'$ do not react with $C_{60}^{2-}$.[21] As expected, the reaction of compound **13** with $C_{60}^{2-}$ (40 °C, one week) has given rise to the bis-mesylate fullerene derivative **14** in 8% isolated yield after column chromatography (Scheme 6). This low yield is, in part, related to the difficult separation, in column chromatography, of the compound **14** from unreacted $C_{60}$. In agreement with the results reported by Meier et al., the corresponding bis-iodo fullerene derivative was not observed.

In conclusion, we have developed and optimized an efficient procedure for the preparation of a new fullerene diol in good yield, starting from $C_{60}^{2-}$ anion. This fullerene diol can be considered as a promising building block in fullerene chemistry. In particular various highly functionalized $C_{60}$-based covalent assemblies can be built starting from this diol, as we shortly will show.

### Acknowledgements

## References and notes

1. Hirsch, A. *Top. Curr. Chem.* **1999**, *199*, 1–65.
2. Wudl, F. *J. Mater. Chem.* **2002**, *12*, 1959–1963.
3. Nierengarten, J.-F. *New J. Chem.* **2004**, *28*, 1177–1191.
4. Isaacs, L.; Haldimann, R. F.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2339–2342.
5. Rapenne, G.; Diederich, F. *New J. Chem.* **1999**, *23*, 1125–1127.
6. Hino, T.; Hamada, M.; Kinbara, K.; Saigo, K. *Chem. Lett.* **2002**, 728–729.
7. Felder, D.; Guttiérez Nava, M.; Carréon, M. del Pilar; Eckert, J.-F.; Luccisano, M.; Schall, C.; Masson, P.; Gallani, J.-L.; Heinrich, B.; Guillon, D.; Nierengarten, J.-F. *Helv. Chim. Acta* **2002**, *85*, 288–319.
8. Felder, D.; Nierengarten, H.; Gisselbrecht, J.-P.; Boudon, C.; Leize, E.; Nicoud, J.-F.; Gross, M.; Van Dorssaeler, A.; Nierengarten, J.-F. *New J. Chem.* **2000**, *24*, 687–695; Nierengarten, J.-F.; Felder, D.; Nicoud, J.-F. *Tetrahedron Lett.* **2000**, *41*, 41–44.
9. Allard, E.; Delaunay, J.; Cheng, F.; Cousseau, J.; Ordúna, J.; Garín, J. *Org. Lett.* **2001**, *3*, 3503–3506.
10. (a) Meier, M. S.; Poplawska, M. *Tetrahedron* **1996**, *52*, 5043–5052; (b) An, Y.-Z.; Anderson, J. L.; Rubin, Y. *J. Org. Chem.* **1993**, *58*, 4799–4801; (c) Ikeda, A.; Nobukuni, S.; Udzu, H.; Zhong, Z.; Shinkai, S. *Eur. J. Org. Chem.* **2000**, 3287–3293.
11. Allard, E.; Delaunay, J.; Cousseau, J. *Org. Lett.* **2003**, *5*, 2239–2242.
12. Allard, E.; Rivière, L.; Delaunay, J.; Dubois, D.; Cousseau, J. *Tetrahedron Lett.* **1999**, *40*, 7223–7226.
13. (a) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wuld, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594–1595; (b) Yamago, S.; Tokuyama, H.; Nakamura, E. *J. Org. Chem.* **1993**, *58*, 4796–4798; (c) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807–815.
14. We have also observed that the reaction between 1,3-diiodo-2-propanol $ICH_2–CHOH–CH_2I$ and $C_{60}^{2-}$ in acetonitrile gives rise to the alcohol $C_{60}(CH_2)_2CHOH$ **2** only as traces. Besides, a test experiment has shown that $C_{60}^{2-}$ anion remains stable in the presence of propan-2-ol.
15. *Typical procedure*: In a glove box, sodium methanethiolate $CH_3S^-Na^+$ in excess is added to a suspension of 100 mg $C_{60}$ in 80 mL acetonitrile, and this mixture is stirred for 24 h at room temperature. Then the unreacted sodium methanethiolate is filtered off, and the halo derivative (20–30 equiv) is added to the resulting $C_{60}^{2-}$, $2Na^+$ red solution. After, this resulting reaction mixture is taken out off the glove box and is stirred at room temperature or warmed to 40–50 °C. When the reaction time is over, the solid reaction products are filtered off, and isolated through column chromatography.
16. (a) Hannig, E.; Wilhelm, H. *Die Pharmazie* **1969**, *24*, 32–34; (b) Meskens, F. A. *Synthesis* **1981**, 501–522.
17. (a) Fukuzumi, S.; Suenobu, T.; Hirasaka, T.; Arakawa, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 9220–9227; (b) Allard, E.; Cheng, F.; Chopin, S.; Delaunay, J.; Rondeau, D.; Cousseau, J. *New J. Chem.* **2003**, *27*, 188–192.
18. Hann, R. M.; Richtmyer, N. K.; Diehl, H. W.; Hudson, C. S. *J. Am. Chem. Soc.* **1950**, *72*, 561–566.
19. Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63–65.
20. (a) Maggini, M.; De Faveri, C.; Scorrano, G.; Prato, M.; Brusatin, G.; Guglielmi, M.; Meneghetti, M.; Signorini, R.; Bozio, R. *Chem. Eur. J.* **1999**, *5*, 2501–2510; (b) Bolognesi, M. L.; Marucci, G.; Angeli, P.; Buccioni, M.; Minarini, A.; Rosini, M.; Tumiatti, V.; Melchiorre, C. *J. Med. Chem.* **2001**, *44*, 362–371.
21. Meier, M. S.; Bergosh, R. G.; Gallagher, M. E.; Spielmann, H. P.; Wang, Z. *J. Org. Chem.* **2002**, *67*, 5946–5952.
22. Selected analytical data. *Compound* **1**. NMR: $^1H$ ($CS_2$/acetone-$d_6$): 3.82 (s, 4H, $CH_2$–$C_{60}$), 4.27 (t, 2H, O$H$, $^3J$ = 5.1 Hz), 4.46 (d, 4H, $CH_2$–OH, $^3J$ = 5.1 Hz); $^{13}C$ (DMSO-$d_6$/chlorobenzene) only some carbon atoms have been assigned: 70.76 ($CH_2$–OH), 63.78 ($CH_2$–OH), 50.89 ($CH_2$–$C_{60}$), 46.70 ($CH_2$–$C_{60}$). IR (KBr) (cm$^{-1}$): 525 ($C_{60}$), 3402 (OH). UV ($CH_2Cl_2$), $\lambda$ (nm): 431, 326, 304, 255. MS (ESI): $M_{theo}$ = 822.07, $M^{.-}_{obs}$ = 822.07. Cyclic voltammetry (o-DCB/acetonitrile (95:5), $n$-$Bu_4NPF_6$, 100 mV s$^{-1}$): $E_{1/2}$ (vs Fc/Fc$^+$) = −1.150, −1.525, −2.070 V. *Compound* **10**. $^1H$ NMR ($CS_2$/$CDCl_3$): 3.54 (s, 2H, $CH_2$–$C_{60}$), 4.17 (s, 2H, $CH_2$–$C_{60}$), 4.48 (d, 2H, $CH_2$–O, $^2J$ = 11.3 Hz), 5.17 (d, 2H, $CH_2$–O, $^2J$ = 11.3 Hz), 5.81 (s, 1H, $CH$–O), 7.39–7.45 (m, 3H, $H_{ar}$), 7.63–7.65 (m, 2H, $H_{ar}$). IR (KBr) (cm$^{-1}$): 526 ($C_{60}$), 1119 (CO ketal), 1638 (C=C). UV ($CH_2Cl_2$), $\lambda$ (nm) ($\varepsilon$, L mol$^{-1}$ cm$^{-1}$): 431 (3470), 325 (32,400), 308 (33,400), 256 (113,000), 246 (104,000). MS (MALDI-TOF): $M_{theo}$ = 910, $M^{.+}_{obs}$ = 910. Cyclic voltammetry (o-DCB/acetonitrile (95:5), $n$-$Bu_4NPF_6$, 100 mV s$^{-1}$): $E_{1/2}$ (vs Fc/Fc$^+$) = −1.145, −1.520, −2.045 V. Compound **12**. $^1H$ NMR ($CDCl_3$): 4.00 (s, 4H, $CH_2$–$C_{60}$), 5.37 (s, 4H, $CH_2$–O), 8.01 (d, 4H, $H_{ar}$, $J$ = 8.2 Hz), 8.33 (d, 4H, $H_{ar}$, $J$ = 8.2 Hz), 10.14 (s, 2H, $CH$O). MS (MALDI-TOF): $M_{théo}$ = 1086, $M^+_{obs}$ = 1086. Cyclic voltammetry (o-DCB, $n$-$Bu_4NPF_6$, 100 mV s$^{-1}$): $E_{1/2}$ = −1.17, −1.55 V. Compound **14**. $^1H$ NMR ($CS_2$/acetone-$d_6$): 3.25 (s, 6H, $SO_2$–$CH_3$), 3.96 (s, 4H, $CH_2$–$C_{60}$), 5.10 (s, 4H, $CH_2$–$OSO_2$). IR (KBr) (cm$^{-1}$): 526 ($C_{60}$), 1176, 1358 ($SO_2$).