

[60]Fullerene diol issued from pentaerythritol derivatives

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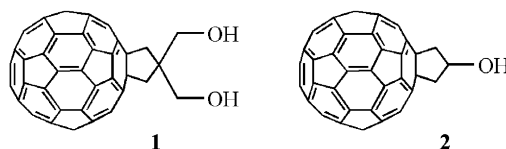
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Abstract—A new [60]fullerene diol is synthesized in good yield, in two steps starting from reaction of C_{60}^{2-} anion with the benzylideneacetal derived from 2,2-bis(iodomethyl)-1,3-propanediol. The corresponding [60]fullerene bis-mesylate is also 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 Diedrich 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.

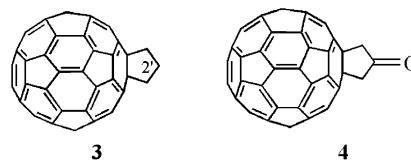
We now wish to report on a simple and efficient synthesis of a new [60]fullerene derivative **1** bearing two primary alcohol groups. In our current work on synthesis of new C_{60} -based triads involving two electron donor units, we were in search of a new fullerene diol the structure of which was as close as possible to the fullerene alcohol **2** we used in synthesis of C_{60} -TTF based dyads⁹ (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}

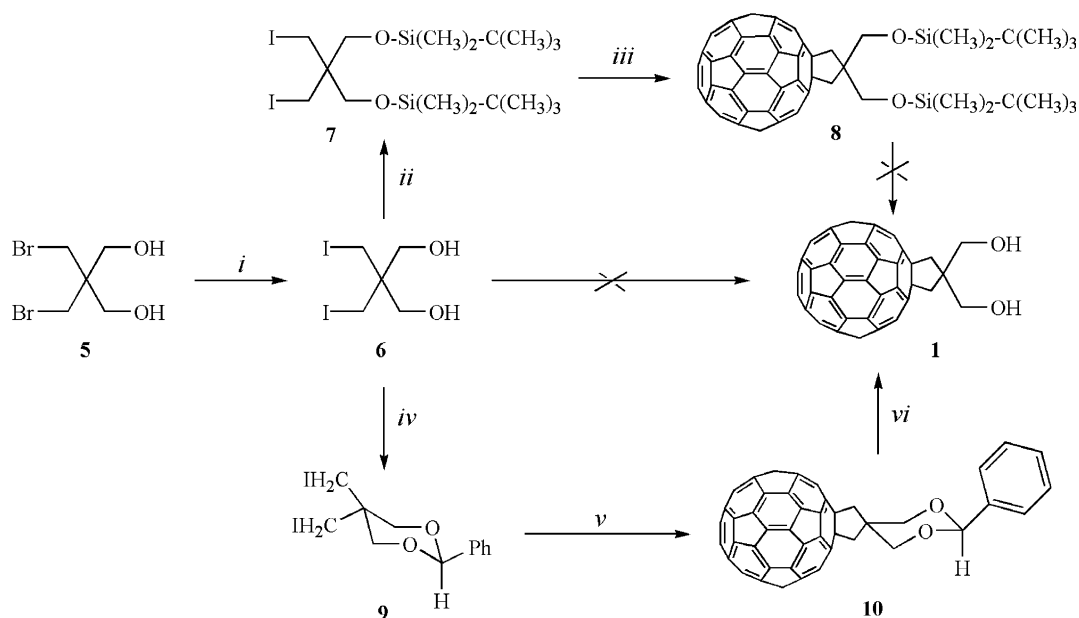
Previously, we have shown that cyclopentano-fused fullerene compounds **3** and **4** are easily formed through reaction of 1,3-diiodo or 1,3-dibromopropane derivatives with C_{60}^{2-} (Scheme 2).^{9,12} The molecular frame thus obtained is particularly attractive thanks to its high overall symmetry, 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 methylene-cyclopropane 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.

Keywords: C_{60}^{2-} ; Pentaerythritol; C_{60} chemistry; Diol.

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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%.

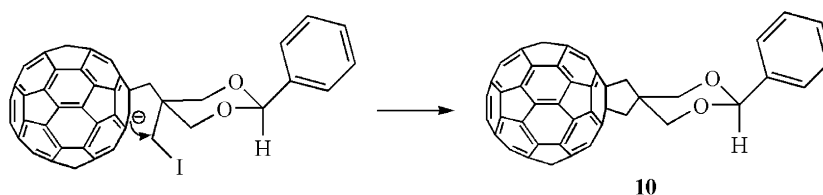
In the fullerene diol **1** the diol unit can be related to the pentaerythritol frame. Following our previous results, a possible straightforward access to this diol **1** might have resulted from the reaction, in acetonitrile, of C_{60}^{2-} with the diiodo diol **6**, easily obtained from the commercially 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 method¹⁹) 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.

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