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Electrochemical synthesis of a phosphorylated monomethano[60]fullerene

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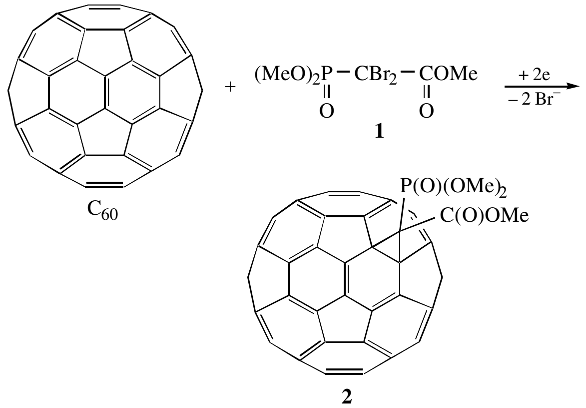
61-(Dimethoxyphosphoryl)-61-(methoxycarbonyl)methano[60]fullerene was produced using the electrochemical reduction of fullerene C_{60} and (dimethoxyphosphoryl)methoxycarbonyldibromomethane at a carbon felt electrode in the *o*-dichlorobenzene–DMF/0.1 M Bu_4NBF_4 system.

The production of water-soluble fullerene substances is of importance for the development of biologically active fullerene-based compounds. This problem can be solved by the encapsulation of hydrophobic fullerene molecules in hydrophilic shells or by the direct introduction of a hydrophilic group into a fullerene molecule. In the latter case, a minimal change in the fullerene structure with a maximal hydrophilicity of the functional group seems optimum. From this point of view, phosphorylated methanofullerenes containing hydrophilic phosphonic acid fragments at the methane carbon are attractive. The well-known syntheses of such derivatives consist in the preparation of dialkoxyphosphorylmethanofullerenes by the Bingel reaction of a fullerene with dialkoxyphosphorylbromomethane in the presence of a base[1–3] or with diazomethyl phosphonate[3] followed by the hydrolysis of ether bonds.

It is well known[4–6] that fullerenes can reversibly accept up to six electrons per molecule in the electrochemical reduction in aprotic media with the formation of a hexa-anion. Anionic intermediates (radical anions, dianions, radical trianions *etc.*) are bases, nucleophiles and electron carriers. It is obvious that these properties increase with the negative charge. Hence, in aprotic media under conditions of electrochemical reduction, a fullerene can act as a nucleophile or a carrier of 1–6 electrons depending on the nature of the substrate. The nucleophilic properties of dianions and the reductive properties of fullerene C_{60} radical anions, dianions and radical trianions were applied in the reactions with organohalogen compounds and metal complexes.[7–17]

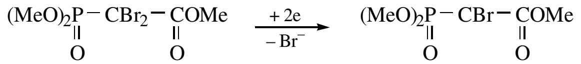
In this work, we studied the applicability of these fullerene properties to the electrosynthesis of phosphorylated methanofullerenes starting from fullerene C_{60} and (dimethoxyphosphoryl)methoxycarbonyldibromomethane **1**.



$$C_{60} + \underset{\textbf{1}}{(MeO)_2P(=O)-CBr_2-C(=O)OMe} \xrightarrow[-2\,Br^-]{+2e} \textbf{2}$$

2

To optimise electrolysis conditions, we initially measured cyclic voltammograms (scan rate of 100 mV s^{-1}) for fullerene and compound **1** in the absence and in the presence of C_{60} in the *o*-dichlorobenzene–DMF (3:1)/0.1 M Bu_4NBF_4 system using a glassy carbon disk electrode. Fullerene C_{60} exhibited four reversible one-electron reduction peaks (E_p/V: −0.91, −1.35, −1.85, −2.37 *vs.* Ag/0.01 M $AgNO_3$). Dibromophosphonate **1** was reduced irreversibly with two-electron transfer in the above range of potentials ($E_p = -0.95$ V). This reduction is typical of the reductive two-electron C–Hal bond cleavage. It is likely that the reduction of the test compound also occurs with the cleavage of the C–Br bond with the formation of carbanion **3**.



$$\underset{\textbf{1}}{(MeO)_2P(=O)-CBr_2-C(=O)OMe} \xrightarrow[-Br^-]{+2e} \underset{\textbf{3}}{(MeO)_2P(=O)-\overset{-}{C}Br-C(=O)OMe}$$

The reduction of a fullerene and dibromophosphonate (1:10) mixture resulted in the superposition of the reduction peak of the phosphonate and the first reduction peak of fullerene C_{60}. Consequently, the electrolysis of the mixture generates the fullerene radical anion and the carbanion of bromophosphonate **3**. Thus, the formation of methanofullerenes can occur *via* two paths: by the interaction of the carbanion with fullerene C_{60} (similarly to the chemical synthesis of methanofullerenes) and by the interaction of the fullerene radical anion with the initial dibromophosphonate. The fullerene radical anion can act as an electron carrier with respect to dibromophosphonate and reduce it to the carbanion. All these mechanisms finally lead to methanofullerenes. The chemical synthesis of methanofullerenes through the monobromophosphonate carbanion gives bismethanofullerenes[1–3] along with monomethanofullerenes. Because the electrochemical reduction also affords carbanions, the voltammetric studies allowed us to assume that a mixture of mono- and bismethanofullerenes is formed in the joint reduction of fullerene and dibromophosphonates. Therefore, to perform the selective synthesis of monomethanofullerenes without the formation of bisadducts, we attempted to generate electrochemically the fullerene dianion and then add the dibromophosphonate to the solution. For this purpose, we performed the preparative reduction of fullerene C_{60} (20 mg) to the dianion in the *o*-dichlorobenzene–DMF (3:1)/0.1 M Bu_4NBF_4 system (20 ml) on a carbon-felt electrode in a diaphragm cell in an argon atmosphere with stirring at room temperature. Initially, the electrolysis was performed in the absence of fullerene C_{60} for the removal of proton donors; next, fullerene C_{60} was reduced. The electrolysis was performed at a constant current of 2 mA for 50 min; the theoretical quantity of electricity (2 F) was passed. The colour of the solution changed in the course of electrolysis. After the completion of electrolysis, a double excess of dibromophosphonate **1** was added to the solution. According to reversed-phase HPLC data ($\lambda = 328$ nm), the parent fullerene was absent from the solution. Seven unidentified fullerene products were detected: however, monomethano[60]fullerene was not formed. It is likely that the products were formed already at the stage of fullerene reduction because of the interaction of anionic fullerene intermediates with solution components without the participation of dibromophosphonate. We did not detect the interaction of the anionic intermediates with solution components during the voltammetric measurements (in a matter of seconds). However, this interaction occurred under conditions of long preparative electrolysis. This result suggests that the joint reduction of the fullerene and the dibromophosphonate should be performed to minimise side reactions with the medium.

We performed the preparative reduction of a mixture of fullerene C_{60} (20 mg, 0.028 mmol) and compound **1** (16.9 mg, 0.038 mmol) under the above-specified electrolysis conditions.

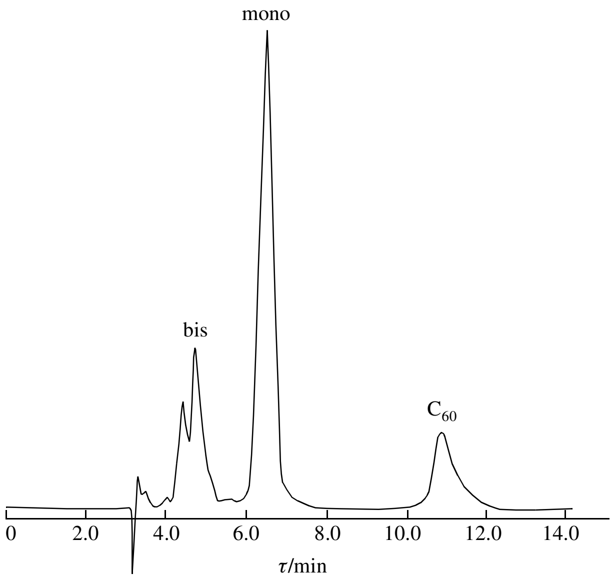


Figure 1 Chromatogram of the reaction mixture. HPLC conditions: Partisil-5 ODS-3 (C_{18}) column (250×4.6 mm); mobile phase, toluene–acetonitrile (1:1, v/v); UV-VIS detection at 328 nm.

After the electrolysis, the solution was stirred for 1 h in an argon atmosphere and then analysed by HPLC. According to the chromatogram (Figure 1), 61-(dimetoxyphosphoryl)-61-(methoxycarbonyl)methano[60]fullerene **2** is the main product, in which the addend is attached to the fullerene sphere at the 6,6-bond. In addition, bismethanofullerenes were formed, and a small amount of fullerene C_{60} remained unreacted. A 100 mg amount of fullerene C_{60} was subjected to electrolysis under the specified conditions. The combined solution (100 ml) was washed with water and concentrated. The residue was chromatographed on a column with SiO_2 [mobile phase: hexane, hexane/toluene (1:10)]. After evaporating the solvent, 10 mg of product **2** (9.6% yield on a reacted C_{60} basis) were obtained; the main spectral characteristics of the product† are consistent with published data.[1]

Thus, we performed the electrochemical synthesis of a phosphorylated monomethano[60]fullerene. This result suggests that electrosynthesis can be applied to prepare other monomethanofullerenes by the joint reduction of fullerenes and dibromophosphonates.

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† Compound **2**: ^{1}H NMR ($CDCl_3$) δ: 4.09 (s, 3H), 4.16 (d, 6H, *J* 9.38 Hz). ^{31}P NMR ($CDCl_3$) δ: 13.21. UV ($CHCl_3$, λ_{max}/nm): 308.7, 426.9, 489.8, 696.5. IR (KBr, ν/cm^{-1}): 526.5, 573, 1031, 1183, 1234, 1271, 1429, 1738, 2814, 2953. Found (%): P, 3.28. Calc. for $C_{65}H_9O_5P$ (%): P, 3.44.