A new route for the selective synthesis of [6,6]-methanofullerenes. Electrosynthesis of $C_{61}HCMe_3$ and $C_{61}HCN$

Pierre L. Boulas, Yuhong Zuo and Luis Echegoyen*†

Department of Chemistry, University of Miami, Coral Gables, Florida 33124, USA

A new fast and simple route for the selective synthesis of methanofullerenes that uses the reaction between the C_{60} dianion and diodo- or dibromo-reagents is described.

Several synthetic pathways have been proposed for the production of methanofullerenes and homofullerenes.[1–6] Among them, the addition of diazo compounds to [60]fullerene and [70]fullerene is, to date, the most versatile route[2a,3] and it remains one of the most popular ways to synthesize methanofullerenes and homofullerenes.

For the first time we have explored the electrosynthetic route to generate methanofullerenes and these results are reported here. Electrosynthesis was shown to be quite useful for the synthesis of dimethylated C_{60}[7a] and 1,2-*o*-xylyl[60]fullerene.[7b] Evans *et al.* have studied the role of the C_{60} anions as electrogenerated bases.[7c,7d] However, the full synthetic possibilities of the technique have not been exploited, and to our knowledge only two compounds have been reported and fully characterized resulting from electrosynthesis.[7a,7b]

As we report now, electrosynthesis is a fast and simple procedure for the generation of methanofullerenes. C_{60}^{2-} reacts readily with a variety of ipso-brominated and iodated reagents to form [6,6]-methanofullerenes. Thus, $C_{61}H_2$ **1**, $C_{61}(CO_2Et)_2$ **2**, $C_{61}HCMe_3$ **3** and $C_{61}HCN$ **4** were obtained from the reactions of C_{60}^{2-} with diiodomethane, diethyldibromomalonate, 1,1-diiodo-2,2-dimethylpropane and dibromoacetonitrile, respectively. Compounds **1**[2d] and **2**[4a] were previously prepared and characterized while **3** and **4** were hitherto unreported.‡ Of particular interest in the present work was the isomeric nature of the species formed (methanofullerenes *vs.* homofullerenes).

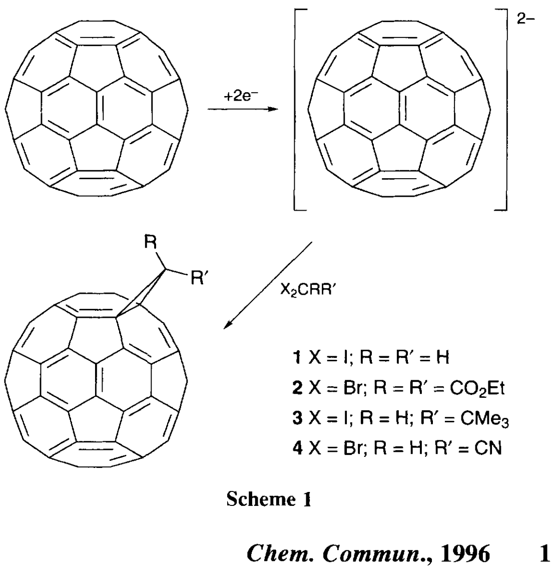
The same procedure was used to electrosynthesize compounds **1**–**4** which were then characterized by mass, UV–VIS, IR and ^1H NMR spectroscopy.§,¶ In a typical experiment, *ca.* 11 mg of C_{60} were suspended in *ca.* 10 ml of oxygen free MeCN–toluene (1/3, *v*/*v*) mixture containing 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate ($TBAPF_6$). A potential of −0.7 V was then applied for *ca.* 1 h to generate a deep red solution of C_{60}^{2-}. An excess of dibromo- or diiodo-reagent was then added and the mixture was allowed to react with no potential applied. When no change in the rest potential was detected for over 1 h, the reaction was considered complete.‖ The overall process is summarized in Scheme 1.

Once the reaction was over, the solvent mixture was evaporated and the resulting solid washed with acetonitrile to remove the supporting electrolyte ($TBAPF_6$) and unreacted reagent. When possible, $C_{61}RR'$ was separated from C_{60} by column chromatography using hexane–toluene mixtures with increasing ratios of toluene.

The ^1H NMR spectra of **1** and **2** are similar to the spectra reported for the [6,6]-closed $C_{61}H_2$ and $C_{61}(CO_2Et)_2$ respectively.[2d,4] In the case of **3**, the ^1H NMR spectrum shows two singlets at δ 1.74 (*tert*-butyl protons) and 3.96 (methine bridge proton). The chemical shift of the methine proton for **3** is very close to the one measured for the methine proton in [6,6]-closed $C_{61}H_2$ (δ 3.96 *vs.* 3.93). This strongly suggests that **3** also adopts the [6,6]-closed structure. In the spectrum of **4**, the H of the methine bridge appears at δ 4.59 which indicates that this proton sits above a 6-membered ring. If this proton was located over a 5-membered ring, it would have probably appeared at a chemical shift larger than δ 6.35 because of the double effect of the ring current from the five membered ring and the deshielding effect of the cyano group. Therefore, the ^1H NMR spectroscopic results strongly suggest that all of the electrosynthesized derivatives have the methanofullerene [6,6]-closed structure.

The UV–VIS spectra of the compounds **1**–**4** in toluene all possess absorption maxima at *ca.* 430 and 680–700 nm and this indicates, in agreement with the NMR results, that they all are methanofullerenes rather than homofullerenes.[2d]

It appears that by fine tuning the applied potential during the electrosynthetic experiment, one can not only improve the yield for the formation of compounds **1**–**4** but also generate the corresponding bis-adducts. This is shown in Fig. 1 for the electrosynthesis of $C_{61}HCMe_3$ and $C_{62}H_2(CMe_3)_2$. A MeCN–toluene (1 : 2) solution of C_{60} monoanion was generated by bulk electroreduction at −0.22 V and I_2CHCMe_3 added to the solution. The OSWV of the solution at this point showed only the reduction peaks associated with C_{60} ($E_{1/2}$ = 0.00 and −0.44 V). This proves that the monoanion is not reactive with this diiodo compound. Note that the first half-wave reduction potential of C_{60} was arbitrarily set at 0 V and used as an internal reference. A potential of −0.42 V was then applied for *ca.* 3 min and this led to a partial reduction of C_{60}^{-} to C_{60}^{2-}. As expected, the OSWV of the solution after a few minutes showed the appearance of new peaks at −0.09 and −0.53 V associated with the reductions of $C_{61}HCMe_3$. After *ca.* 5 min, a potential of −0.42 V was again applied for *ca.* 3 min and the system allowed to react for 5 min. As expected, the OSWV of the solution shows an enhancement of the reduction peaks of $C_{61}HCMe_3$ associated with a decrease in the reduction peak of C_{60}. This process was repeated over a period of 2.5 h and the resulting voltammograms are displayed in Figs. 1(*a*) and 1(*b*). Fig. 1(*a*) shows clearly that, during the initial stages of the experiment, the cathodic current associated with the reduction of $C_{61}HCMe_3$ increases while that for the C_{60} reduction decreases. Iso-



Scheme 1

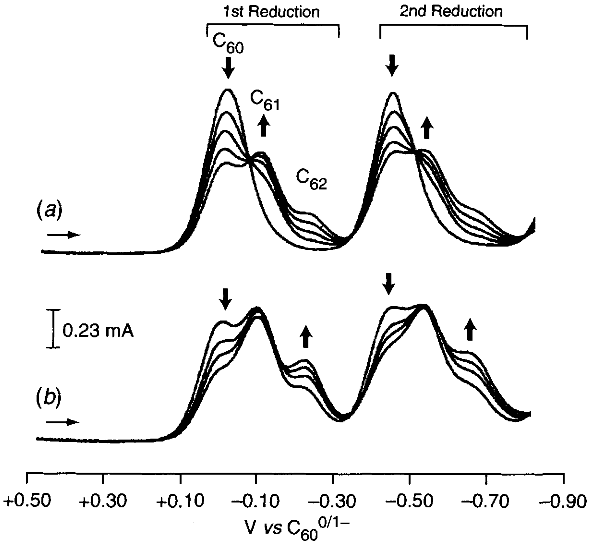


Fig. 1 OSWV's at a platinum mesh electrode, of a solution of C_{60} in MeCN–toluene (1 : 2) containing 0.1 mol dm^{-3} $TBAPF_6$, in presence of I_2CHCMe_3. C_{61} and C_{62} represent $C_{61}HCMe_3$ and $C_{62}H_2(CMe_3)_2$, respectively. The successive voltammograms were recorded after a potential of −0.42 V has been applied for 3 min and the mixture left to react for *ca.* 5 min and this had been repeated twice. (*a*) Voltammograms recorded during the first 80 min and (*b*) during the last 60 min. The voltammograms were recorded using a sweep width of 25 mV, frequency of 15 Hz and a potential step of 4 mV.

potential points are observed suggesting the presence of only two species in equilibrium, namely C_{60} and $C_{61}HCMe_3$. After *ca.* 60 min, new peaks clearly emerge at −0.22 and −0.65 V and these are associated with the first two reductions of $C_{62}[HCMe_3]_2$.** The bis-adduct is generated by the reaction of I_2CHCMe_3 and $[C_{61}HCMe_3]^{2-}$ electrogenerated during the iterative bulk electroreductions at −0.42 V. As shown in Fig. 1(*b*), the appearance of these new species, $C_{62}H_2(CMe_3)_2$, destroys the iso-potential points previously observed. This is easily understood since the situation observed involves three species; C_{60}, the mono- and bis-adducts.

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Footnotes

† E-mail: lechegoyen@umiami.ir.miami.edu

‡ As mentioned by one of the reviewers, a paper reporting the synthesis of $C_{60}(CHCN)$ by treating a mixture of [60]fullerene and CH_2BrCN with LDA appeared in the literature while this paper was submitted: A. N. Benito, A. D. Darwish, H. W. Kroto, M. F. Meidine, R. Taylor and D. R. M. Walton, *Tetrahedron Lett.*, 1996, **7**, 1085. The C_s symmetry of $C_{60}(CHCN)$ that we proposed in the present paper is actually confirmed by the work described in this recent publication.

§ Bulk electrolyses and Osteryoung Square Wave Voltammetric (OSWV) measurements were performed using a BAS100W Electrochemical Analyser (Bioanalytical Systems). The working and counter electrodes were both made of Pt mesh and separated by a fritted glass. The reference electrode was a $Ag/AgNO_3$ electrode. A new reference electrode was made for each experiment. In order to minimize experimental errors due to the reference electrode, we chose to refer all the potentials measured relative to the first reduction potential of C_{60}. Thus, all the reduction potentials reported in this article are in V *vs.* C_{60}/C_{60}^-. All electrosyntheses were carried out at the vapour pressure of the solvent system. Details for the electrochemical experiments can be found in ref. 2*c*. UV–VIS spectra were recorded at room temperature using a UV-2101 PC Shimadzu UV–VIS scanning spectrophotometer. IR spectra were recorded using a 2000 FTIR Perkin Elmer spectrometer. NMR spectra were acquired on a Varian VXR-400.

¶ *Selected spectroscopic data* for **1** [isolated as a *ca.* 1/1 (C_{60}/**1**) mixture]: yield = *ca.* 20%; FAB-MS: major peaks at 734 and 720 amu; R_f (toluene) = 1; UV–VIS (toluene): λ_{max}/nm 332, 406*, 432, 520^{bb} and 694^{wb} [bb = broad band; wb = weak band; the data associated with C_{60} are indicated by a star (*)]; ^1H NMR [CS_2–$CDCl_3$ (7 : 3)] δ 3.93 (s). For **2**: yield = 20%; FAB-MS: major peaks at 878 and 720 amu; R_f (toluene) = 0.8; UV–VIS (toluene): λ_{max}/nm 336, 428, 490^{bb} and 686.5^{wb}; ^1H NMR [CS_2–$CDCl_3$ (7 : 3)] δ 1.50 (t, *J* 7.2 Hz) and 4.52 (q, *J* 7.2 Hz). For **3** [isolated as a *ca.* 1 : 1 (C_{60} : **3**) mixture]: yield = *ca.* 20%; FAB-MS: major peaks at 790 and 720 amu; R_f (toluene) = 1; UV–VIS (toluene): λ_{max}/nm 335.5, 406*, 433, 501^{bb} and 703^{wb}; IR (drop coating on NaCl window): ν_{max}/cm^{-1} 524, 580, 669, 710, 861, 1020, 1062, 1095, 1178, 1207, 1234, 1267, 1294, 1364, 1428, 1460, 1727 and 1746; ^1H NMR [CS_2–$CDCl_3$ (7 : 3)] δ 1.74 (s) and 3.95 (s); ^{13}C NMR [CS_2–$CDCl_3$ (7 : 3), 10 mmol dm^{-3} Cr(acac)] δ 29.40 (bridgehead C), 29.51 [$C(CH_3)_3$], 29.70 [$C(CH_3)_3$], 29 resonances [2 × 1C, 25 × 2C, 2 × 4C (not fully resolved)] in the region δ 129.85–151.61; we were unable to observe the resonance of the bridging carbon in this solvent mixture (CS_2–$CDCl_3$) which suggests that it is located at δ *ca.* 77. For **4**: yield = 30%; FAB-MS: major peaks at *m/z* 759 and 720; R_f (toluene) = 1; UV–VIS (toluene): λ_{max}/nm 330, 428.5, 488^{bb} and 687^{wb}; IR (KBr pellet) ν_{max}/cm^{-1} 1401, 1182, 724, 656, 564 and 527; ^1H NMR [CS_2–$CDCl_3$ (7 : 3)] δ 4.59 (s).

|| For the syntheses of $C_{61}H_2$ and $C_{61}HCMe_3$, the final rest potential was measured at −0.1 V which is more negative than the first reduction potential of C_{60}, $C_{61}H_2$ and $C_{61}HCMe_3$. Thus, a bulk reoxidation at 0.3 V was necessary because exposing the mixture to ambient atmosphere before reoxidation would have possibly led to decomposition of $[C_{61}H_2]^-$ or $[C_{61}HCMe_3]^-$ present in solution. However, this was not the case for the syntheses of $C_{61}(CO_2Et)_2$ and $C_{61}HCN$ for which the final rest potential measured was 0.3 V thus eliminating the need for a bulk reoxidation of the mixture.

** During the electrosynthesis of compounds **1**–**4**, minor amounts of the bis-adducts are formed. For example, the FAB mass spectrum of the electrogenerated bis-adduct $C_{62}(CO_2Et)_2$ displayed the expected peak at *m/z* 1036.

References

1 (*a*) A. Hirsch, in *The Chemistry of Fullerenes*, Thieme, Stuttgart, 1994; (*b*) R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685; (*c*) P. Fagan, *Acc. Chem. Res.*, 1992, **25**, 134; (*d*) J. Hawkins, *Acc. Chem. Res.*, 1992, **25**, 150.

2 (*a*) T. Suzuki, Q. Li, K. C. Khemani, F. Wudl and O. Almarsson, *Science*, 1991, **254**, 1186; (*b*) F. Paolucci, M. Marcaccio, S. Roffia, G. Orlandi, F. Zerbetto, M. Prato, M. Maggini and G. Scorrano, *J. Am. Chem. Soc.*, 1995, **117**, 6572; (*c*) F. Arias, L. Echegoyen, R. S. Wilson and Q. Lu, *J. Am. Chem. Soc.*, 1995, **117**, 1422; (*d*) A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt and R. C. King, *J. Am. Chem. Soc.*, 1995, **117**, 5492; (*e*) L. Isaacs and F. Diederich, *Helv. Chim. Acta*, 1993, **76**, 2454; (*f*) R. Gonzales, J. C. Hummelen and F. Wudl, *J. Org. Chem.*, 1995, **60**, 2618; see also references cited therein.

3 (*a*) F. Diederich, L. Isaacs and D. Philp, *Chem. Soc. Rev.*, 1994, 243; (*b*) F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157.

4 (*a*) C. Bingel, *Chem. Ber.*, 1993, **126**, 1957; (*b*) A. Hirsch, L. Lamparth and H. R. Karfunkel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 437.

5 (*a*) A. Vasella, P. Uhlmann, C. A. A. Waldraff, F. Diederich and C. Thilgen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1388; (*b*) H. Tokuyama, M. Nakamura and E. Nakamura, *Tetrahedron Lett.*, 1993, **34**, 7429; (*c*) Y. Z. An, Y. Rubin, C. Schaller and S. W. McElvany, *J. Org. Chem.*, 1994, **59**, 2927.

6 Y. Wang, J. Cao, D. I. Schuster and S. R. Wilson, *Tetrahedron Lett.*, 1995, **36**, 6843.

7 (*a*) C. Caron, R. Subramanian, F. D'Souza, J. Kim, W. Kutner, M. T. Jones and K. M. Kadish, *J. Am. Chem. Soc.*, 1993, **115**, 8505; (*b*) K. M. Kadish, P. L. Boulas, M. N. Vijayashree, R. Subramanian, X. Gao, S. Mead, Z. Tan and M. T. Jones in *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, ed. R. S. Ruoff and K. M. Kadish, The Electrochemical Society Proceeding Series, Pennington, NJ, 1995, p. 213; (*c*) M. E. Niyazymbetov and D. H. Evans, *J. Electrochem. Soc.*, 1995, **142**, 2655; (*d*) M. E. Niyazymbetov, D. H. Evans, S. A. Lerke, P. A. Cahill and C. C. Henderson, *J. Phys. Chem.*, 1994, **98**, 13 093.

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