Reductive electrolysis of [60]fullerene mono-methanoadducts in THF leads to the formation of bis-adducts in high yields

Marcel W. J. Beulen,[a] José A. Rivera,[b] M. Ángeles Herranz,[c] Ángel Martín-Domenech[c] Nazario Martín*[c] and Luis Echegoyen*[a]

[a] *Department of Chemistry and Center for Supramolecular Science, University of Miami, Coral Gables, Florida 33124, USA. E-mail: echegoyen@miami.edu*
[b] *Department of Chemistry, Pontifical Catholic University of Puerto Rico, Ponce, Puerto Rico 00731, USA*
[c] *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, E-28040-Madrid, Spain*

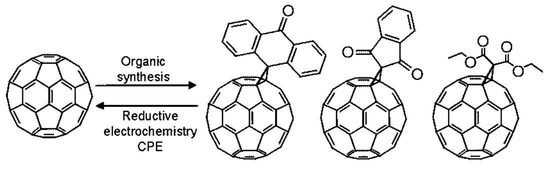
Received (in Columbia, MO, USA) 30th October 2000, Accepted 19th January 2001
First published as an Advance Article on the web 9th February 2001

A new reaction, electrolytically induced adduct transfer between [60]fullerene mono-adducts, leads to bis-adducts with a unique regioisomer distribution.

Cyclopropanation of fullerenes by the addition of malonate derivatives (the Bingel reaction) has been widely used for the preparation of fullerene adducts.[1] The groups of Diederich and Echegoyen reported the reverse of this reaction, the retro-Bingel reaction, an electrolytic reduction reaction performed in dichloromethane, which efficiently removes di[alkoxycarbonyl]methano (Bingel) adducts to yield the parent fullerene (see Scheme 1).[2] The 'Bingel–retro-Bingel' strategy as a protection–deprotection scheme has already found several uses in fullerene chemistry, such as the isolation of enantiomerically pure C_{76}[2a] and of a new C_{2v}-C_{78} bis-adduct,[2b] and in the separation of constitutional isomers of C_{84}.[2c] The groups of Diederich and Echegoyen also described a chemical retro-Bingel reaction (using Mg/Hg, THF, heat) which also efficiently removes the Bingel addends.[3]

Very recently we reported that the range of fullerene adducts that can be removed *via* electrolytic reduction is not limited to di[alkoxycarbonyl]methano adducts (see fullerene **3**), but includes those present in structures **1** and **2** (Scheme 1). Controlled potential electrolysis (CPE) in dichloromethane after the first (**2**) and third (**1**) electrochemical reduction wave induces the efficient removal of the adducts, to form the parent C_{60}.[4]

While electrolytic reduction can lead to the efficient removal of the adducts mentioned, it has been shown that methanoadduct formation can also result from the reaction between electrolytically prepared fullerene anions and dihalo-compounds, even with dichloromethane.[5] Dichloromethane reacts efficiently with the [60]fullerene trianion to form methanofullerenes of the type $C_{60}>(CH_2)_n$,[5b] and forms similar adducts with C_{84} [$C_{84}>(CH_2)_n$] during the reductive retro-Bingel reaction of di[alkoxycarbonyl]methano-adducts of C_{84}.[2c] In order to avoid these reactions and to further explore the potential and mechanism of the electrolytic methods of fullerene adduct removal, we decided to investigate the electrolysis of compounds **1–3** in THF. In the process we found an electrochemically induced intermolecular reaction that leads to the formation of multiple fullerene adducts.[6]



4 1 2 3

Scheme 1 Protective group system for fullerenes: synthesis of methanofullerenes **1–3** and subsequent adduct removal by reductive electrochemistry.

The cyclic voltammograms of the methanofullerenes **1** and **2** in THF are shown in Fig. 1.[7] These compounds exhibit irreversible electrochemistry in THF, similar to that observed in dichloromethane. Compound **1** exhibits, in addition to several reversible electrochemical processes, an irreversible reduction process between the first and third reduction potentials whilst **2** undergoes an initial two-electron reduction, followed by a one-electron reduction. The irreversible behavior presumably results from the cleavage of one of the cyclopropane bonds connecting the addend to C_{60} after reduction.[8]

Compounds **1** and **2** were subjected to CPE in 0.1 M NBu_4PF_6–THF and the products were separated and analyzed. CPE of **1** was performed at *ca.* 100–150 mV more cathodic than the third, reversible, reduction wave (Fig. 1, arrow a); 2.7 electrons per molecule were discharged and clear changes in the CV and OSWV were observed, indicating that a chemical reaction had taken place. Subsequent re-oxidation at 0 V and purification of the product mixture by column chromatography (eluent: toluene) yielded fullerene products in *ca.* 91% yield. Analysis of this mixture by HPLC, UV–VIS spectroscopy, and MALDI-TOF spectrometry clearly showed the formation of C_{60} as the main product (41%). Thus reductive electrochemistry removes the addend in THF (as also observed in CH_2Cl_2), leading to the formation of C_{60}. A second fraction (39%) containing the starting material **1** was also recovered. Interestingly and unexpectedly, a third fraction (11%) with a higher polarity was also isolated. Analysis showed this fraction to be composed of the bis-adducts: fullerenes with two spiro-anthraquinone groups attached (MALDI-TOF: *m/z* 1104).

CPE of **2** in THF was performed after the first two-electron reduction wave (Fig. 1, arrow b), and 1.8 electrons per molecule were discharged. Re-oxidation and purification yielded 81% of fullerene products, consisting of 40% C_{60}, 27% recovered **2**, and 14% of bis-adducts. Adduct removal is also the main

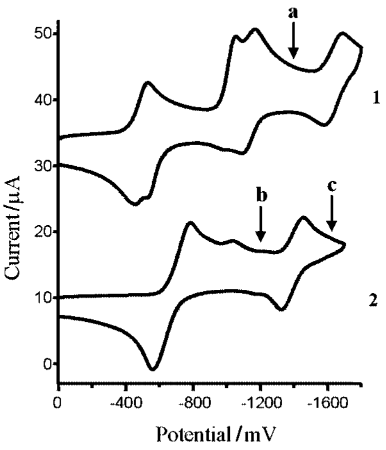


Fig. 1 Cyclic voltammograms of **1** and **2** in THF.

DOI: 10.1039/b008769f

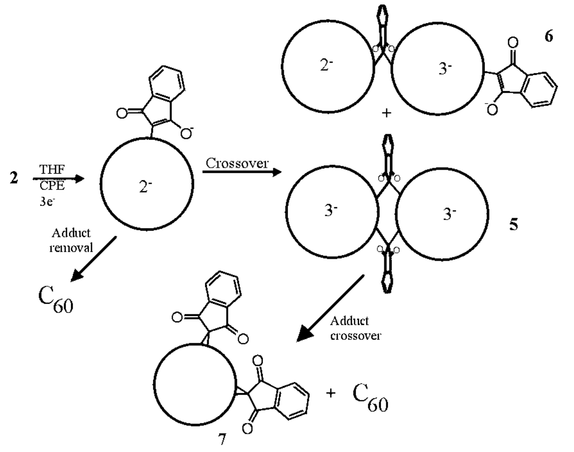
reaction pathway but again a significant amount of regioisomeric bis-adducts was isolated (MALDI-TOF: m/z 1010). A separate CPE experiment conducted after the second reduction wave (Fig. 1, arrow c) discharged 3.0 electrons and led to similar results (C_{60} : **2** : bis-adducts **7** = 35 : 30 : 19%).

As stated in the introduction, Bingel-adduct removal from fullerenes like **3** by electrochemical (CH_2Cl_2) or chemical reduction (THF) yields C_{60} and starting material (Scheme 1).[2] However, no bis-adduct formation was observed using either of these reductive methods. In view of the results already described for **1** and **2** in THF, we decided to electrolyze **3** in the same solvent. CPE after the second reduction wave of **3** discharged 2.6 electrons, considerably less than the typical value obtained in CH_2Cl_2 (4.0 electrons). Re-oxidation and purification gave fullerene products in a quantitative yield, with 62% C_{60} and 38% **3**. Interestingly, no bis-adducts were detected. Thus profound mechanistic differences exist between the behavior of **1** and **2** and that of **3** under electrolytic conditions.

Our electrochemical experiments show that in THF (but not in CH_2Cl_2) there is a second reaction pathway, besides simple addend removal, that leads to bis-adduct formation. The regioisomer distribution of these bis-adducts is of great interest, as this could provide information on the mechanism of this intermolecular adduct crossover reaction. The unambiguous assignment of regioisomers of several fullerene bis-adducts has been described in detail by Hirsch *et al.*[9] The quantities of bis-adducts that are isolated from the electrolysis experiments in THF are small (typically *ca.* 0.5 mg), thus for characterization purposes we prepared a large amount of the bis-adduct regioisomer mixture (defined as **7**) using the same synthetic procedures used to prepare the original compound, **2**.[10] We separated the regioisomeric bis-adducts **7** on a preparative HPLC column (eluent: toluene). The structures of the different fractions were assigned by ^{1}H NMR spectroscopy and UV–VIS spectroscopy: *trans*-2 14%, *trans*-3 16%, *e* 41%, *cis*-3 5%, *cis*-2 19%. The regioisomers of the bis-adducts obtained by electrolysis were then assigned using HPLC. The two CPE-experiments performed with **2** at different reductive potentials yield similar regioisomer distributions, which are clearly different from that obtained by the regular synthetic route (CPE-b: *trans*-2 3%, *trans*-3 7%, *e* 37%, *cis*-3 49%; CPE-c: *trans*-2 6%, *trans*-3 11%, *e* 43%, *cis*-3 37%).[11] The electrochemical formation of the *cis*-3 bis-adduct as one of the predominant regioisomers is particularly remarkable. Such a relatively large percentage of the *cis*-3 bis-adduct regioisomer had never been seen before during the preparation of bis-Bingel-adducts[9] or bis-methanofullerenes **7**, nor during bis-adduct formation obtained *via* ‘shuffle-isomerization’ of bis-Bingel adducts[12] or by retro-Bingel of tris-adducts.[13] This offers a possible clue about the mechanism of the reaction in THF.

A possible mechanism to explain these observations is shown in Scheme 2 for **2**. Reductive electrochemistry heterolytically opens the cyclopropane ring, leading to charge formation in the addend as well as in the fullerene core.[8] Two pathways are then possible: (1) the addend can be removed from the fullerene, leading to C_{60} formation, or (2) the anionic addend can add to another fullerene *via* the depicted intermediate **6**, leading to the corresponding bis-adducts.[14] One possible explanation for the favored formation of the *cis*-3 and *e* isomers is the existence of an intermediate like **5**, where both addends interact with the two fullerene cores. Molecular mechanics modeling[15] shows that **5** is highly unfavored for the *trans* isomers while the resulting *cis*-1 and *cis*-2 bis-adducts products have higher energy than the *cis*-3 and *e*.

In conclusion, we have shown an electrolytically induced adduct transfer between fullerenes. The unique bis-adduct regioisomer distribution found deviates significantly from that obtained by the direct synthetic route. These observations are potentially useful for the preparation of specific regioisomer bis-adducts. Mechanistic studies are underway to understand these reaction pathways.



Scheme 2 Possible mechanism for the formation of bis-adducts from electroreduced **2**.

Financial support for this work from the National Science Foundation through grant CHE-9816503, the Netherlands Organization for Scientific Research (NWO, talent stipendium, M. W. J. B.) and the DGICYT of Spain (PB98-0818) is greatly apreciated. We also thank to the Fulbright Foundation (Project 99125) for financial support.

Notes and references

1 C. Bingel, *Chem. Ber.*, 1993, **126**, 1957.
2 (*a*) R. Kessinger, J. Crassous, A. Herrmann, M. Rüttimann, L. Echegoyen and F. Diederich, *Angew. Chem., Int. Ed.*, 1998, **37**, 1919; (*b*) C. Boudon, J.-P. Gisselbrecht, M. Gross, A. Herrmann, M. Rüttimann, J. Crassous, F. Cardullo, L. Echegoyen and F. Diederich, *J. Am. Chem. Soc.*, 1998, **120**, 7860; (*c*) J. Crassous, J. Rivera, N. S. Fender, L. Shu, L. Echegoyen, C. Thilgen, A. Herrmann and F. Diederich, *Angew. Chem., Int. Ed.*, 1999, **38**, 1613.
3 N. N. P. Moonen, C. Thilgen, L. Echegoyen and F. Diederich, *Chem. Commun.*, 2000, 335.
4 M. W. J. Beulen, L. Echegoyen, J. A. Rivera, M. Ángeles Herranz, Á. Martín-Domenech and N. Martín, *Chem. Commun.*, 2000, 917.
5 (*a*) P. L. Boulas, Y. Zuo and L. Echegoyen, *Chem. Commun.*, 1996, 1547; (*b*) M. W. J. Beulen and L. Echegoyen, *Chem. Commun.*, 2000, 1065.
6 A precedent for a similar reaction involving a C_{70} mono-adduct was described previously, but only traces of bis-adducts were detected by HPLC: R. Kessinger, N. S. Fender, L. E. Echegoyen, C. Thilgen, L. Echegoyen and F. Diederich, *Chem. Eur. J.*, 2000, **6**, 2184.
7 For full details of our electrochemical setup and general characterization methods see ref. 5(*b*).
8 B. Knight, N. Martín, T. Ohno, E. Ortí, C. Rovira, J. Veciana, J. Vidal-Gancedo, P. Viruela, R. Viruela and F. Wudl, *J. Am. Chem. Soc.*, 1997, **109**, 9871; N. Martín, L. Sánchez, B. Illescas and I. Pérez, *Chem. Rev.*, 1998, **98**, 2527.
9 A. Hirsch, I. Lamparth and H. R. Karfunkel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 437; A. Hirsch, I. Lamparth and H. R. Karfunkel, in *Fullerenes: Recent advances in the chemistry and physics of fullerenes and related materials; The regiochemistry of nucleophilic addition reactions to C_{60}*, ed. K. M. Kadish and R. S. Ruoff, The Electrochemical Society, Inc., Pennington, NJ, 1994, p. 734.
10 Full details of the organic synthesis and characterization of the bis-adducts **7** will be published elsewhere.
11 The regioisomers of the bis-adduct of **1** could not be assigned due to the small quantity. However, HPLC measurements indicated a similar regioisomer pattern with three predominant isomers.
12 R. Kessinger, M. Gómez-López, C. Boudon, J.-P. Gisselbrech, M. Gross, L. Echegoyen and F. Diederich, *J. Am. Chem. Soc.*, 1998, **120**, 8545.
13 L. E. Echegoyen, F. D. Djojo, A. Hirsch and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 4994.
14 The formation of bis-adducts *via* reaction of addends in solution (completely removed from the fullerene instead of attached to a fullerene) is unlikely, as the removed addend is not stable in the electrolyte solution. For example, we were not able to isolate any trace of addend after an electrolysis experiment, performed either in THF or dichloromethane.
15 Software used for molecular mechanics: PC Spartan Pro.