Chemical and Electrochemical retro-cyclopropanation reactions of C_{60} -derivatives

M^a Angeles Herranz,¹ Luis Echegoyen,¹ Marcel Beulen,¹ José Rivera,¹ Nazario Martín,² Beatriz Illescas² and Marta C. Díaz²

¹ University of Miami, Department of Chemistry, 1301 Memorial Drive, Coral Gables, FL 33124, U.S.A.

² Universidad Complutense de Madrid, Departamento de Química Orgánica I, Madrid E-28040, Spain

The electrochemical retro-Bingel reaction was recently reported by Diederich and Echegoyen [1]. The reaction, an electrolytic reduction, removes di[alkoxycarbonyl]-methano adducts to yield the parent fullerenes. The potential for using these addends as protecting groups in fullerene chemistry prompted the use of chemical reaction conditions to effect these transformations [2]. However, the results obtained using (Mg/HgBr₂/THF/80° C) were not reproducible in some cases.

We have recently reported how the range of fullerene adducts that can be removed via electrolytic reduction also includes spyromethano-type adducts [3]. In order to investigate the mechanisms and possible applications of these new electrochemical reactions, we have synthesized compounds **1-3** in Figure 1. These compounds have as a common characteristic the nitrophenyl group, which when reduced exhibits a strong and easily recognizable EPR signal.

We have also attempted chemical retro-Bingel reactions with these spyromethanofullerrenes following the synthetic procedures previously described [3]. We have also changed the protocol and introduced 18C6 and the yields are considerably improved and more reproducible. Even in the absence of the highly toxic $HgBr_2$ the reaction works very well. These results will be presented and discussed in detail.

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[2] N. N. P. Moonen, C. Thilgen, L. Echegoyen, F. Diederich, *Chem. Commun.*, **2000**, 335-336.

[3] (a) M. W. J. Beulen, L. Echegoyen, J. Rivera, M. A. Herranz, A. Martín-Domenech, N. Martín, *Chem. Commun.*, 2000, 917-918; (b) M. W. J. Beulen, J. Rivera, M. A. Herranz, A. Martín-Domenech, N. Martín, L. Echegoyen, *Chem. Commun.*, 2001, 407-408; (c) M. W. J. Beulen, J. Rivera, M. A. Herranz, B. Illescas, N. Martín, L. Echegoyen, *J. Org. Chem.*, 2001, 66, 4393-4398.

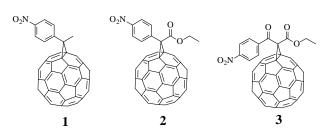


Figure 1. New nitro-compound derivatives 1-3 studied in retro-Bingel processes.