Intermediates Observed During Retro-Cyclopropanation Reactions

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The discovery of electrochemically-induced reactions of malonate derivatives of C60 opened up a new line of research a few years ago. We discovered that bis-malonate adducts (Bingel adducts) can be electrochemically isomerized via what we believe is a "walk-on-the-sphere" mechanism to yield a unique isomer distribution, with a predominance of the trans-2 (and trans-1) isomers. If the electrolyses are conducted further, the malonate adducts are eventually removed from the C60 sphere, in a process we have described as the retro-Bingel reaction. Several uses for this reaction have already been published, most notably for the separation and purification of constitutional isomers and enantiomeric forms of the higher fullerenes, C76 and C84. Mechanistic information about these reactions has been largely lacking until recently. New electrochemical experiments have uncovered the presence of stable intermediates during the electrolytic processes involving phosphonate derivatives of methanofullerenes as well as for C70 malonate derivatives. These experiments will be presented, along with characterization of the intermediates involved.