

Mechanism Studies into Additions onto the Fullerene Surface

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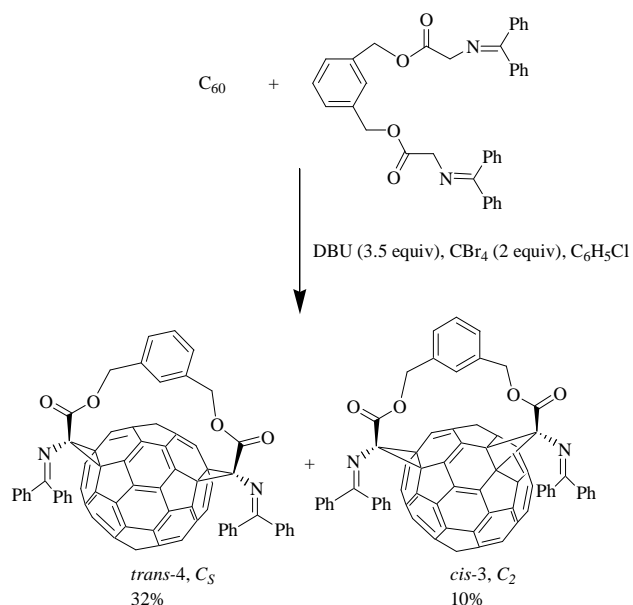
Despite the plethora of synthetic fullerene chemistry in the literature, the corresponding mechanism studies, leading to an understanding of the reaction outcome, has been lacking. We are at the point where there are many circumstances in which the regiochemical outcome of a reaction cannot be reliably predicted.

An example of this lack of understanding arises from comparison of the well established bis-addition to C₆₀ fullerene of benzenedimethanol tethered malonates with the analogous benzenedimethanol tethered iminoglycines which give different regiochemical outcomes (Scheme 1).¹ While it is well established that the Bingel addition of malonate derived materials proceeds via a nucleophilic mechanism, the iminoglycines clearly do not follow the same pathway.

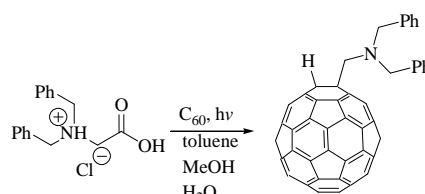
We have attempted to explain the regiochemical outcome of these bisiminoglycine tethered additions using a series of computer-aided molecular modelling studies, with ambiguous results. Currently, we are attempting a series of synthetic-based studies to try and answer these questions.

In an additional mechanistic study, we investigated the amino acid free radical addition to the fullerene sphere. In a published reaction, *N,N*-disubstituted glycine analogues are photolysis with C₆₀, yielding a monosubstituted hydrofullerene adduct (Scheme 2). The suggested (published) mechanism had numerous flaws and we decided to investigate the mechanism with a series of deuterium labeled *N,N*-disubstituted glycine analogues for photolysis with C₆₀. The disubstituted glycine analogues were produced via initial deuterium exchange reactions with glycine, followed by esterification of the acid functionality, double reductive aminations and a final acid hydrolysis to yield the labeled free acid as a hydrochloride salt. The glycine analogues were then photolysed onto the fullerene sphere.

This presentation will give an overview of our attempts to establish fundamental aspects of mechanism as applied to several addition reactions to the C₆₀ fullerene surface.



Scheme 1: Addition of benzenedimethanol tethered iminoglycines to C₆₀ fullerenes and their regiochemical outcomes.



Scheme 2: Photochemical additions to the C₆₀ fullerene.

References

1. The Synthesis and Characterisation of Mono- and Bis-methano[60]fulleryl Amino Acid Derivatives and their Reductive Ring-Opening Retro-Bingel Reactions, Glenn A. Burley, Paul A. Keller, Stephen G. Pyne and Graham E. Ball, *JOC*, **2002**, in press.