Synthesis and NMR Characterisation of Mono- and Bis-methano[60]fullerlylglycine Derivatives and their Reductive Ring-Opening Retro-Bingel Reactions

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The pioneering investigations into the chemical reactivity of [60]fullerene have provided a precedent towards the design and synthesis of novel and sophisticated architectures that may have applications in medicinal chemistry and the material sciences.1,2 Further, with the increasing degree of complexity of fullerlylglycine derivatives comes the necessity for a larger range of reliable techniques for the unequivocal characterization of such molecules. Such techniques should rely heavily on direct methods of characterization (e.g. NMR spectroscopy) rather than the current, well used comparative techniques.

With these principles in mind we embarked on a program to investigate the regioselective synthesis and characterization of fullerlylglycine derivatives with multiple amino acid functionalities with a view to utilize such molecules as templates for molecules to be used in nanotechnology.

Therefore, the addition of N-(diphenylmethylene)glycinate (Ph2C=NCH2CO2R) to [60]fullerene under Bingel conditions gives methano[60]fullerlylglycinates (I, Figure 1) which upon treatment of with sodium cyanoborohydride, in the presence of a protic or a Lewis acid results in a novel reductive ring opening reaction giving the corresponding 1,2-dihydro[60]fullerlylglycinates. These compounds resulted from the reductive ring-opening of one methanoimino ester moiety and a retro-Bingel reaction of the other.5 Under analogous reductive ring-opening-retro-Bingel conditions, the non-tethered bis-methano[60]fullerlylglycinates afforded the 1,2-dihydro[60]fullerlylglycinates. Thus it was concluded that the tether is not the driving force for the regenerative elimination of one of the methano groups.

This study clearly demonstrates that much has yet to be understood about tethered fullerene reactions before generalizations on regiochemical outcomes can be made. These differences in regiochemistry may indicate that these reactions proceed via different mechanisms and experiments are in progress to understand these differences. Furthermore, we have demonstrated the importance of 2D INADEQUATE NMR experiments for the unequivocal assignment of the regiochemistry of [60]fullerlylglycinates which are more superior than the more widely used comparative techniques (UV-visible).

Using the corresponding tethered bis-N-(diphenylmethylene)glycine esters derived from meta- and para-benzenedimethanol scaffolds, the corresponding diethyl esters derivatives prepared by trans-esterification. Reductive ring-opening reactions on the naphthy-tethered bis-methano[60]fullerenes gave none of the expected bis-fullerlylglycinates rather the reductive ring-opening-retro-Bingel products, the 1,2-dihydro[60]fullerlylglycinates. These compounds resulted from the reductive ring-opening of one methanoimino ester moiety and a retro-Bingel reaction of the other.6 Under analogous reductive ring-opening-retro-Bingel conditions, the non-tethered bis-methano[60]fullerlylglycinates afforded the 1,2-dihydro[60]fullerlylglycinates. Thus it was concluded that the tether was not the driving force for the regenerative elimination of one of the methano groups.

REFERENCES

Figure 1: Fullerlylglycine derivatives.

Figure 2: Bisaddition yielding bis-methano[60]fullerlylglycinates.