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Synthesis of C_{60} Nitroxide Derivatives

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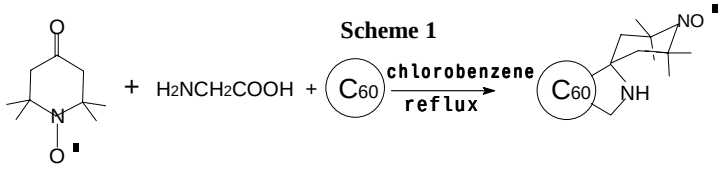
Abstract: C_{60} derivatives covalently linked with the nitroxide radical of 2, 2, 6, 6-tetramethylpiperidine-1-oxyl have been synthesized by the following new method: C_{60} reacts with 4-oxo-2, 2, 6, 6-tetramethyl-piperidinyloxyl (4-oxo-TEMPO) and an amino acid .

Keywords: Fulleropyrrolidine; nitroxide; 1, 3-dipolar cycloaddition.

Maggini [1] first reported the synthesis of fulleropyrrolidine derivatives by 1, 3 dipolar cycloaddition, which proved to be one of the most effective method to obtain fullerene monoadduct derivatives. In 1995, Corvaja[2] reported the synthesis of C_{60} derivative covalently linked with a nitroxide radical 2, 2, 6, 6-tetramethylpiperidine-1-oxyl by 1, 3 dipolar cycloaddition using C_{60}, TOAC and paraformaldehyde as the reactants. This compound is unique in the study of the intramolecular interaction of a radical species with the C_{60} core. Here we report another method to synthesize the same derivative: C_{60} reacts with 4-oxo-TEMPO and glycine (**Scheme 1**).

Scheme 1



Experimental

C_{60} was purchased from Wuhan University with the purity of 99.9%. 4-oxo-TEMPO was synthesized according to the literature [3].

A solution of C_{60}, glycine, 4-oxo-TEMPO in chlorobenzene was refluxed under nitrogen for 16h, and the product was isolated by column chromatography (silica gel, toluene as eluent).

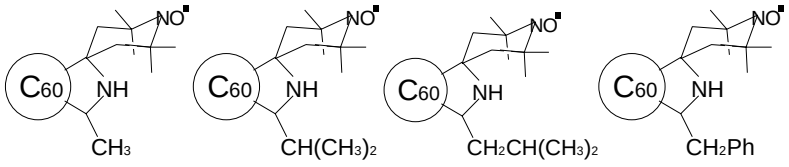
Results and Discussion

The structure of the product was characterized by a series of methods. The results demonstrate that the product obtained is: 3, 4 -Fulleropyrrolidine-2-spiro-4'- (2', 2', 6',

6'-tetramethylpiperidine-1'-oxy). The UV-Vis spectra are different from that of C_{60}. The derivative has a peak at 224 nm and a shoulder at 271 nm whereas C_{60} has two peaks at 213 nm and 255 nm. The derivative has a new peak at 309 nm, which forms a platform with the peak of 328 nm while C_{60} has only a sharp peak at 328 nm. Pure C_{60} has a highly transparent region in 420-440 nm but the derivative shows a sharp peak at 432 nm. It is a typical peak of C_{60} [6, 6] adduct [4]. Another difference between the derivative and C_{60} is in the 460-620 nm region. In this region, C_{60} has distinct fine structures but these bands are obscured in the derivative. The derivative product shows its molecular ion peaks $(M+H)^+$ at m/z 905 (Mw=903.7) and characteristic fragment peak at 720 corresponding to C_{60}^+. The ESR spectra of the derivative exhibit a triplet centered at g=2.005 with a_N=1.49 mT in toluene. The value is characteristic of TEMPO-based radical. All the characterization proves that the goal compound was indeed obtained.

Using this method, we can design and synthesize a series of compounds: C_{60} reacting with 4-oxo-TEMPO and amino acid (alanine, valine, leucine, phenylalanine…) will result in the following compounds (**1, 2, 3, 4**…) (**Scheme 2**)

Scheme 2



1 **2** **3** **4**

TOAC is usually obtained by a series of reactions from 4-oxo-TEMPO whereas 4-oxo-TEMPO is easily acquired. Due to this reason the new method of synthesizing the fullerene nitroxide derivatives is much more attractive.

Acknowledgments

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