Efficient Method for the Cleavage of Fullerene Oxides with Several Aromatic Amines under Ultrasonic Irradiation

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(Received November 17, 2006, Revised & Accepted January 31, 2007)

Abstract: The cleavage of fullerene oxides with several aromatic amines such as 4-nitroaniline, 3-nitroaniline, 4-isopropylaniline in the present of FeCl₃ occurred under ultrasonic irradiation in air at 25–43 °C. The aminated fullerenes were confirmed by MALDI-TOF-MS and UV-vis spectra.

Keywords: fullerene oxides, aromatic amines, FeCl₃, ultrasonic irradiation, aminated fullerenes

I. Introduction

Since the discovery of fullerene by Kroto et al.
in 1985, the research in this area has become one of the most popular topics in physics, chemistry, and material science, and fullerene oxides have attracted much attention. A variety of synthetic methods are at hand to introduce the epoxide functionality to fullerenes. Also, fullerene oxides show an interesting reaction behavior both with themselves and with fullerenes in reactions. β-Amino alcohols have been synthesized by opening of the epoxide ring with an excess of several aromatic amines at elevated temperatures. One of the most fascinating developments in chemical synthesis during recent years is application of ultrasound over the conventional thermal heating for chemical reactions. In recent years a large number of chemical transformations has been reported using ultrasonics. It is well documented in the literature that the ultrasonic irradiation not only accelerates chemical reactions but also reduces the number of steps, which are required for normal reactions. The application of ultrasound has gained popularity among synthetic chemists not only to improve classic chemical reactions by shortening reaction
times and improving yields, but as well to promote new reaction.\footnote{14} We have employed ultrasonic irradiation for the opening of fullerene oxide rings by reacting with an excess of aromatic amines, such as 4-nitroaniline, 3-nitroaniline, and 4-isopropylaniline in the presence of FeCl$_3$.\footnote{3}

\section*{2. Experimental}

Fullerene[C$_{60}$] used in this work was 99.0\% purity of Tokyo Chemical Inc (TCI). The oxidant used was 3-chloroperoxo benzoic acid (Fluka, 99.0\%). Aromatic amines used were 4-nitroaniline (Aldrich, 99\%), 3-nitroaniline (Aldrich, 99\%), 4-isopropylaniline (Aldrich, 99\%). The ultrasonic irradiation of all samples was conducted in continuous mode with an Ultrasonic Generator UG 1200 made by Hanil Ultrasonic Co, LTD. Ultrasonic equipment employed in this research having frequency 20 kHz, power 750 W, the configuration of the equipment is a horn type system, and the size of the horn tip is 13 mm in diameter. All the samples were analyzed by MALDI-TOF-MS (Voyager DE STR) and the matrix was cyano-4-hydroxy cinnamic acid. The electronic absorption spectra were obtained by a UV-visible spectrophotometer (Shimadzu UV-1601 PC).

1. Reaction of fullerene[C$_{60}$] with 3-chloroperoxo benzoic acid

A solution of C$_{60}$ (20 mg, 0.028 mmol) which was dissolved in 60 mL of benzene was reacted by refluxing with 3-chloroperoxo benzoic acid (96 mg, 2.56 mmol) for 5 h. The resulting solution was evaporated and then the remaining solid material was washed with methanol to remove excess 3-chloroperoxo benzoic acid, and dried in a vacuum oven to prepare fullerene oxides[C$_{60}$(O)$_n$](n\geq 1).

2. Reaction of fullerene oxides with 4-nitroaniline under ultrasonic irradiation

A solution of [C$_{60}$(O)$_n$](n\geq 1) (10 mg, 0.013 mmol) and 4-nitroaniline (18 mg, 0.13 mmol) in 30 mL of tetrahydrofuran dissolved in the presence of FeCl$_3$ (2 mg, 0.012 mmol) under ultrasonic irradiation for 24 h. Each resulting solution was evaporated, so that the remaining material was obtained as a solid.

3. Reaction of fullerene oxides with 3-nitroaniline under ultrasonic irradiation

A solution of [C$_{60}$(O)$_n$](n\geq 1) (10 mg, 0.013 mmol) and 3-nitroaniline (18 mg, 0.13 mmol) in 30 mL of tetrahydrofuran dissolved in the presence of FeCl$_3$ (2 mg, 0.012 mmol) under ultrasonic irradiation for 24 h. Each resulting solution was evaporated, so that the remaining material was obtained as a solid.

4. Reaction of fullerene oxides with 4-isopropylaniline under ultrasonic irradiation

A solution of [C$_{60}$(O)$_n$](n\geq 1) (10 mg, 0.013 mmol) and 4-isopropylaniline (18 mg, 0.13 mmol) in 30 mL of tetrahydrofuran dissolved in the presence of FeCl$_3$ (2 mg, 0.012 mmol) under ultrasonic irradiation for 24 h. Each resulting solution was evaporated, so that the remaining material was obtained as a solid.

\section*{3. Results and Discussion}

In our early studies, we have reported several oxidation methods of fullerenes with various oxidants under ultrasonic irradiation.\footnote{15} The oxidation of fullerene[C$_{60}$] may proceed through a nucleophilic attack of oxidant to a $\sigma$-$\sigma$ bond (\(\sigma\)-\(\sigma\) ring junction) of fullerene, followed by heterolytic breakage of the O-O bond in oxidant. The common mechanism for fullerene oxidation involves oxygen atom transfer to fullerene [C$_{60}$]. It is suggested that fullerene oxides [C$_{60}$(O)$_n$](n\geq 1) may be used as oxygen transferring materials. Furthermore, fullerene oxides[C$_{60}$(O)$_n$](n\geq 1) are interesting starting materials for the formation of other fullerene based...