Elastomer
Vol. 42, No. 1, pp 1~8 (2007)

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)

초음파 조건에서 방향족 아민 화합물을 사용한 풀러렌 산화물 쪼개짐 반응

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(2006년 11월 17일 접수, 2007년 1월 31일 수정 및 채택)

ABSTRACT : The cleavage of fullerene oxides with several aromatic amines such as 4-nitroaniline, 3-nitroaniline, 4-isopropylaniline in the present of $FeCl_3$ occurred under ultrasonic irradiation in air at 25~43 ℃. The aminated fullerenes were confirmed by MALDI-TOF-MS and UV-vis spectra.

요 약 : 풀러렌 산화물 쪼개짐 반응은 $FeCl_3$를 첨가한 초음파 조건에서 4-nitroaniline, 3-nitroaniline, 4-isopropylaniline 등의 방향족 아민 화합물과 풀러렌 산화물을 반응시켜 일어났다. MALDI-TOF-MS와 UV-vis 스펙트라를 사용하여 풀러렌 산화물 쪼개짐 반응으로 생성된 화합물이 아민화 풀러렌 유도체임을 확인하였다.

Keywords : fullerene oxides, aromatic amines, $FeCl_3$, ultrasonic irradiation, aminated fullerenes

Ⅰ. Introduction

Since the discovery of fullerene by Kroto *et al.* in 1985,[1] the research in this area has become one of the most popular topics in physics, chemistry, and material science,[2,3] and fullerene oxides have attracted much attention.[4] A variety of synthetic methods[5-10] 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.[11] One of the most fascinating developments in chemical synthesis during recent years is application of ultrasound[12] over the conventional thermal heating for chemical reactions. In recent years a large number of chemical transformations has been reported using ultrasonics.[13] 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

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times and improving yields, but as well to promote new reaction.[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]

Ⅱ. Experimental

Fullerene[C_{60}] used in this work was 99.0% purity of Tokyo Chemical Inc (TCI). The oxidant used was 3-chloroperoxy 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-chloroperoxy benzoic acid

A solution of C_{60} (20 mg, 0.028 mmol) which was dissolved in 60 ㎖ of benzene was reacted by refluxing with 3-chloroperoxy 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-chloroperoxy 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 ㎖ 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 ㎖ 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 ㎖ 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.

Ⅲ. Results and Discussion

In our early studies, we have reported several oxidation methods of fullerenes with various oxidants under ultrasonic irradiation.[15] The oxidation of fullerene[C_{60}] may proceed through a nucleophilic attack of oxidant to a σ-σ bond (σ-σ 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 entities.[15]

Using the MALDI-TOF-MS spectra, we identified the $[C_{60}(O)_n](n \geq 1)$ formed in the reaction of C_{60} with 3-chloroperoxy benzoic acid. MALDI-TOF-MS data reported in Figure 1 show the formation of $[C_{60}(O)_n](n \geq 1)$ observed at m/z 720(C_{60}), 736($C_{60}O_1$), 752($C_{60}O_2$), 768($C_{60}O_3$), 784($C_{60}O_4$), 800($C_{60}O_5$), 816($C_{60}O_6$) in the MALDI-TOF-MS spectrum. The most intense peak was at m/z 720 in the MALDI-TOF-MS spectrum in Figure 1 which is due to the unreacted fullerene[C_{60}] and the fragmentation of fullerene oxides[$C_{60}(O)_n$] $(n \geq 1)$. It has been observed from the literature that is a limited success for the cleavage of epoxides by aromatic amines,[11] whereas the present synthetic method has been found successful in the ring cleavage of epoxides by 4-nitroaniline.[16] In continuation of these efforts, it was considered of interest to investigate the ring opening of fullerene oxides with amino nucleophiles under ultrasonic irradiation. We wish to report an efficient cleavage of fullerene oxide rings with aromatic amines to

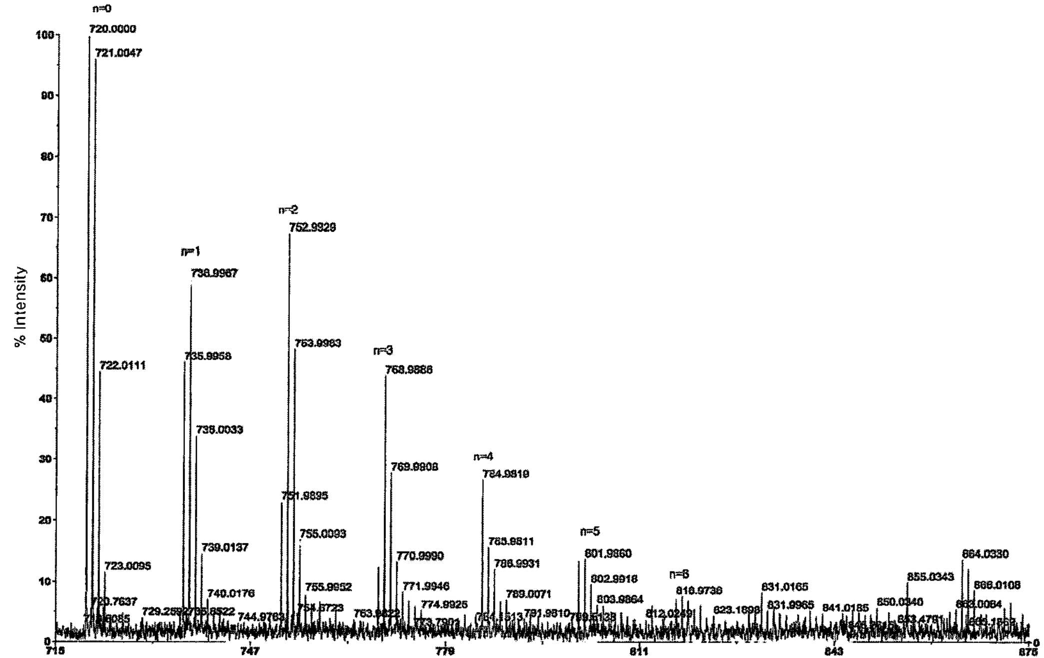
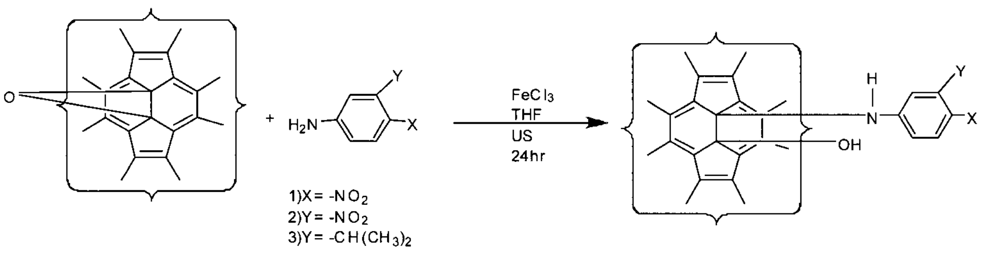


Figure 1. MALDI-TOF-MS spectrum of $[C_{60}(O)_n]$ $(n \geq 1)$.

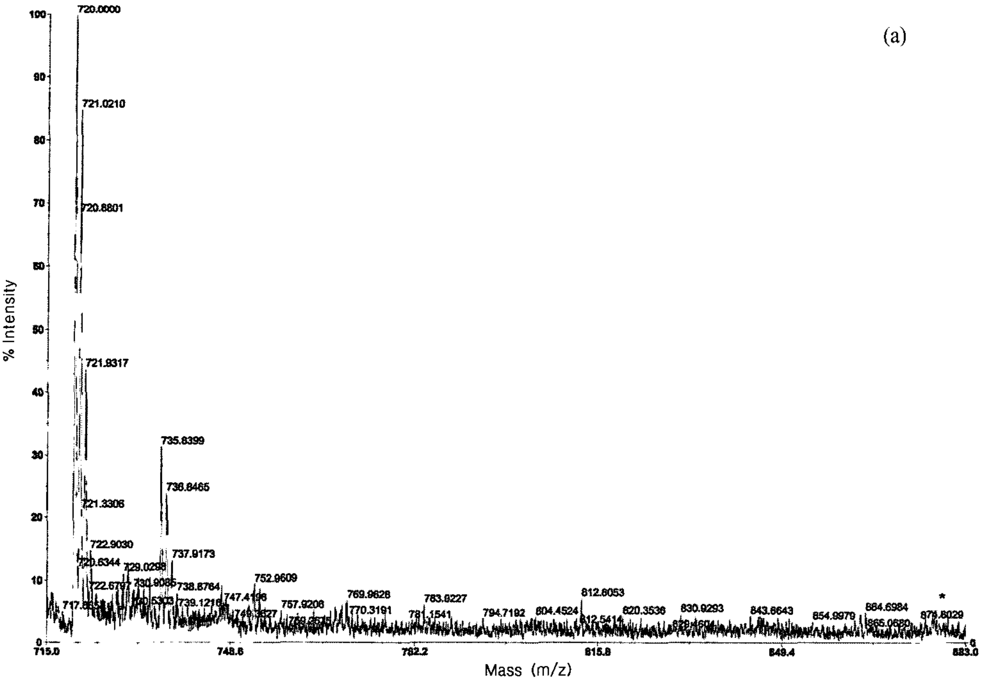


Scheme 1

produce aminofullerenols in the presence of $FeCl_3$ under ultrasonic conditions for the first time (Scheme 1).

However, there are reports on the use of $FeCl_3$ as a catalyst for the alcoholysis of epoxides.[17-18] We examined the reaction of fullerene oxides with various aromatic amines in the presence of $FeCl_3$ by ultrasound in THF. As seen from the results, a number of aromatic amines has been employed for the cleavage of different epoxides particularly ring deactivated amines such as 4-nitroaniline, 3-nitro aniline, 4-isopropylaniline. This reaction has also been carried out in the absence of ultrasound in this process. It is presumed that the opening of the epoxide group with the amino functionality in the presence of ultrasonic irradiation is facilitated by acoustic cavitation in the reaction medium. The MALDI-TOF-MS analysis reported in Figure 2 (a) - (c) shows the formation of various aminofullerenol, because the peak of various aminofullerenols observed at m/z720(C_{60}), 736($C_{60}O_1$), 874($C_{60}OH(NHC_6H_4p\text{-}NO_2)$) in 4-nitroaminofullerenol at m/z 720(C_{60}), 736($C_{60}O_1$), 874($C_{60}OH(NHC_6H_4m\text{-}NO_2)$) in 3-nitroaminofullerenol at m/z720(C_{60}), 736 ($C_{60}O_1$),871($C_{60}OH(NHC_6H_4p\text{-}C(CH_3)_2)$) in 4-isopropylaminofullerenol in the MALDI-TOF-MS spectrum.

The electronic absorption bands (λ_{max}) of $[C_{60}(O)_n](n \geq 1)$ and pure C_{60} in tetrahydrofuran were shown in Figure 3. Due to the breaking of the conjugated 6-6 ring junction by addition of oxygen in the fullerene $[C_{60}]$, the bands of electronic absorption were blue-shifted (330 nm→324 nm) in the UV-visible spectra. Also, electeronic absorption bands(λ_{max}) of several different kind of amino fullerenol in tetrahydrofuran were observed at 364 nm in 4-nitroaminofullerenol, at 339 nm in 3-nitroaminofullerenol, at 360 nm in 4-isopropylaminofullerenol in Figure 4 (a)-(c). When ultrasound was not used, the rate of reaction of fullerene oxides with various aromatic amines was slower than the reaction carried out with ultrasound. There



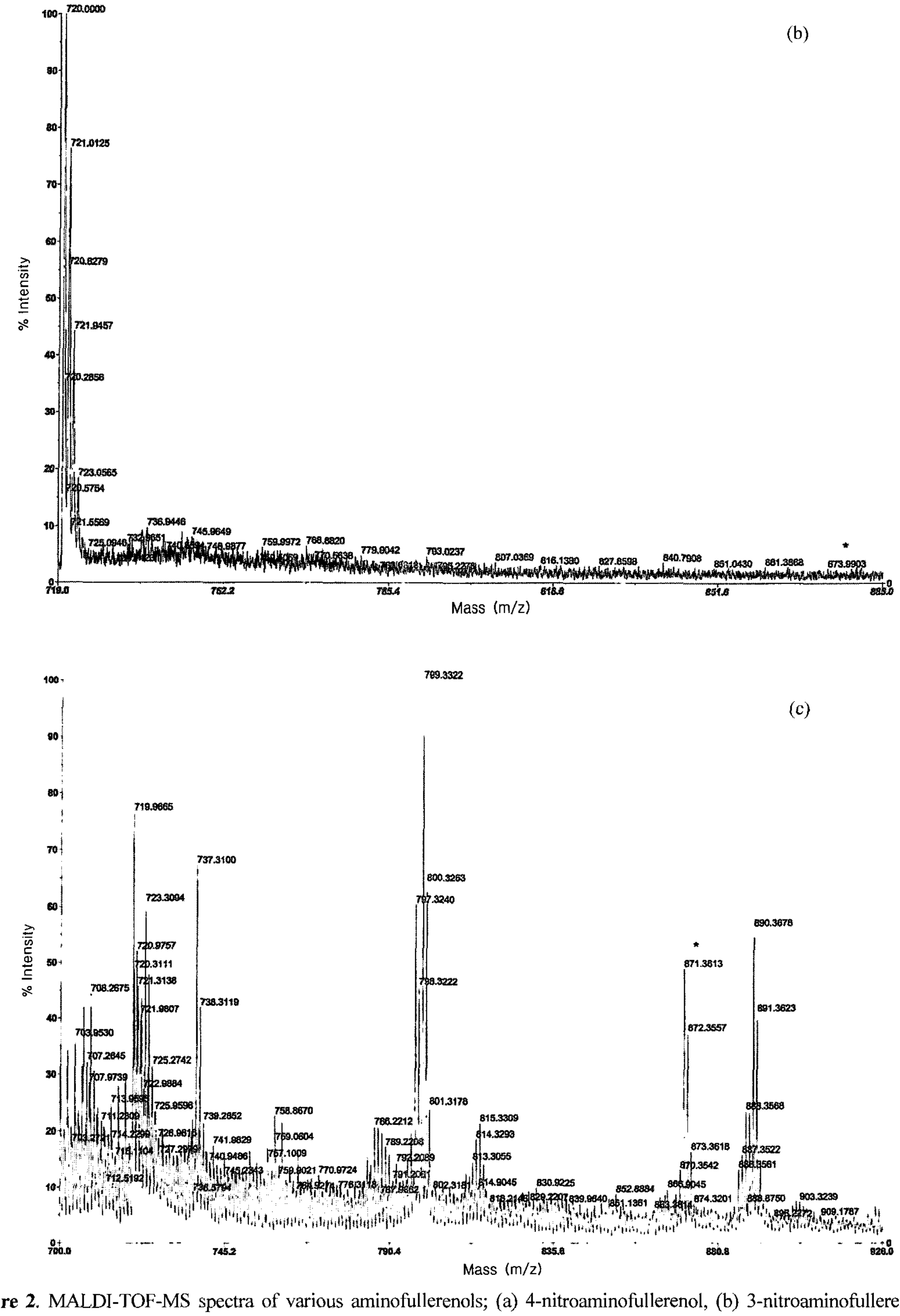


Figure 2. MALDI-TOF-MS spectra of various aminofullerenols; (a) 4-nitroaminofullerenol, (b) 3-nitroaminofullerenol, (c) 4-isopropylaminofullerenol.

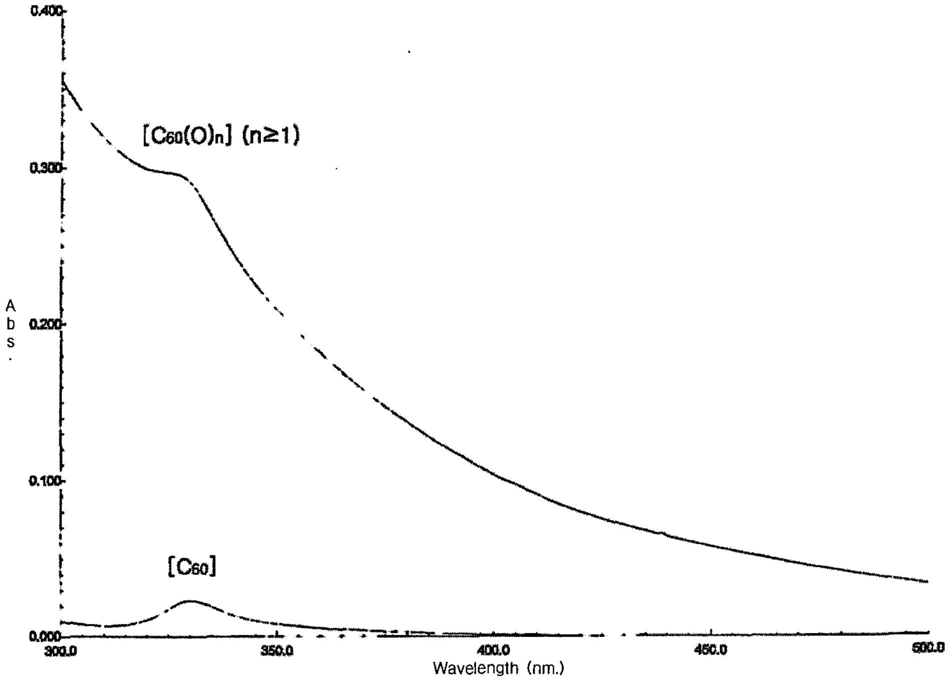


Figure 3. UV-visible spectra of fullerene[C_{60}] and fullerene oxide [$C_{60}(O)_n$]($n \geq 1$) in tetrahydrofuran.

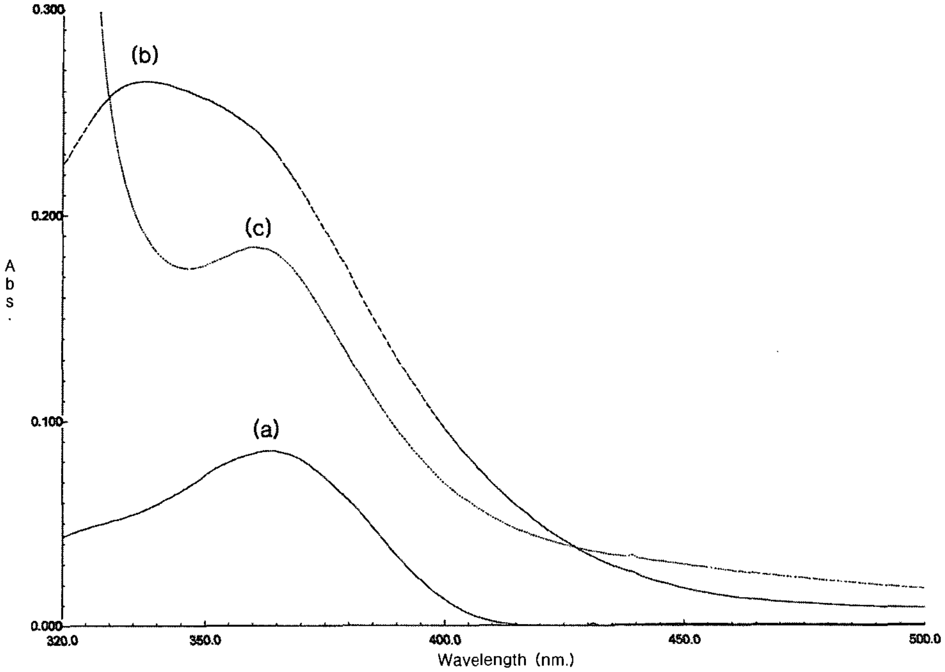


Figure 4. UV-visible spectra of various aminofullerenols; (a) 4-nitroaminofullerenol, (b) 3-nitroaminofullerenol, and (c) 4-isopropylaminofullerenol in tetrahydrofuran.

fore, ultrasound promoted the reaction efficiency in the mild condition.

Ⅳ. Conclusion

We have investigated an efficient method for the cleavage of fullerene oxide rings with several aromatic amines such as 4-nitroaniline, 3-nitroaniline, and 4-isopropylaniline in the presence of $FeCl_3$ under ultrasonic irradiation. This method is applicable to a variety of aromatic amines especially ring deactivated aromatic amines to afford the corresponding cleavage products under mild conditions. We are presently attempting to broaden the scope of this process to other nucleophilies and epoxides and study the influence of ultrasonic irradiation

Acknowledgements

We thank to researcher J. B. Seo at the Korea Basic Science Institute Seoul for obtaining the MALDI-TOF-MS spectra. This work was supported by Sahmyook University funding in Korea and also, grants from Ministry of Commerce, Industry, and Energy.

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