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단 신

[C_{60}]풀러린과 에탄올아민의 반응: 물에 녹는 풀러린 유도체

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Reaction of [C_{60}]Fullerene with Ethanolamine: A Derivative of Fullerene Soluble in Water

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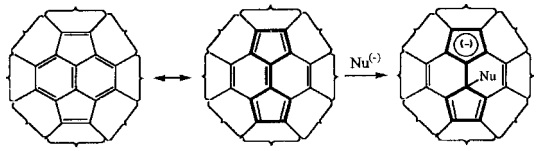
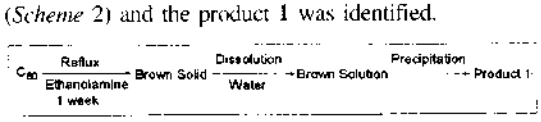
The chemical reactivities of fullerenes becomes a great interest topic since the structure and physical properties of fullerenes are unveiled.[1-19] Buckminsterfullerene (C_{60}), a kind of fullerene, possesses reactive double bonds located in 6-6 ring junctions which exhibit the character of an electron deficient alkene and show relatively high electron affinity. Wudl suggested that this high electron affinity was originated from the structure of fullerenes.[20] The close examination of C_{60} model revealed that there were a number of pyracyclene units in it as shown in *Scheme* 1.[20] Therefore, C_{60} is easily attacked by nucleophiles.[8,21-30] Especially, due to their high nuclephilicity, primary and secondary aliphatic amines undergo nucleophilic additions with electron deficient C_{60} easily.[8,21-23]

While chemical and physical application of fullerene derivatives is an interesting topic in the field of high temperature superconductor, electric conductor, catalyst, medicals and etc, for the purpose of industrial and medical applications, preparation of water soluble fullerene derivatives is an important thing. We performed the reaction of C_{60} with ethanolamine to get a water soluble derivatives of C_{60} because hydroxyl group has a great hydrophilicity. This reaction was based on the reaction of C_{60} with ethylenediamine by Wudl et al., which resulted in formation of the hexaaza-adduct.[8,21] Because C_{60} is a



Scheme 1

multi-functional molecule and the available quantities of C_{60} are limited, excess amount of ethanolamine was used in this preparation according to the following procedure (*Scheme* 2) and the product **1** was identified.



Scheme 2

EXPERIMENTAL

Reagent. All chemicals and solvents used in the synthesis were of reagent grade and used without further purification. Reagents for spectrochemical measurements were purified according to the literature procedure.[31]

Physical Measurements. IR spectra were obtained by using a Midac Prospect FT-IR spectrometer. Electronic absorption spectra were obtained with a SLM DW-2000 spectrophotometer. NMR spectra were recorded on a JEOLJMN EX 400 MHz spectrometer. Elemental anal-

yses were performed at the Korea Basic Science Institute, Korea. FAB-MS spectrum was recorded at Korea Research Institute of Chemical Technology, Korea.

Preparation. A mixture of C_{60} (50 mg) and excess amount of ethanolamine (20 mL) was refluxed until the C_{60} was dissolved. Finally, brown solution was obtained after a week. The brown solution was evaporated under reduced atmosphere and isolated solids were washed with methanol. The solids were dissolved in water (30 mL) and insoluble solids were filtered off. Methanol (10 mL) was added to the solution. Brownish yellow solids were obtained after several days. The solids were washed with methanol and dried under vacuum. Yield: ~30%. Anal. Calcd for $C_{68}H_{28}N_4O_4$: C; 84.64, H; 2.92, N; 5.83%. Found: C; 85.12, H; 2.79, N; 5.78%. IR (cm^{-1}): 3400 (s, br), 2950 (s), 2920 (m), 1760 (m), 1460 (m), 1380 (w), 1300 (w), 1075 (s), 710 (w), 650 (w) and 550 (w). ^{1}H-NMR (DMSO-d_6): δ1.2 and 2.1 (-OH and -NH), 3.6 (-$CH_{fullerenyl}$), and 4.1 and 4.4 (-OCH_2CH_2N-). FAB-MS: m/z=964.

RESULTS AND DISCUSSION

The product **1** was insoluble in toluene, benzene, dichloromethane etc. in which C_{60} is soluble and was soluble in DMSO and water with considerable amounts, and slightly soluble in methanol.

Electronic absorption spectrum (*Fig.* 1) of **1** in water shows a strong absorption band at 232 nm together with three shoulders (289, 342 and 540 nm). The presence of shoulders in this spectrum indicates that conjugation of C_{60} is removed by the addition of ethanolamine and the absence of any peak beyond 540 nm indicates that C_{60} is multi-functionalized by the reaction with an excess amount of ethanolamine.[8]

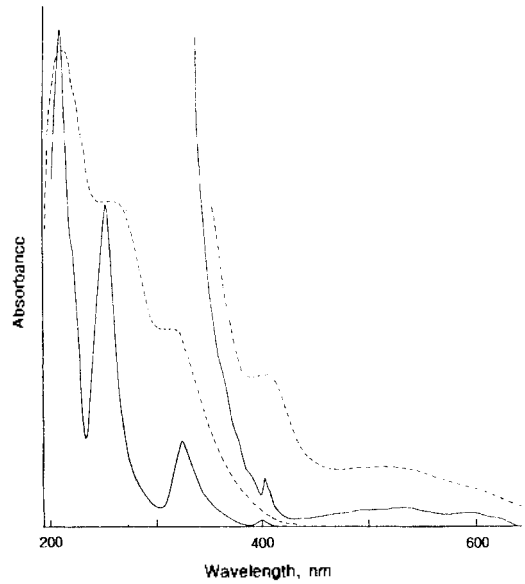


Fig. 1. Electronic absorption spectra of C_{60} (solid line) in n-hexane and the product **1** (dashed line) in water.

Spectroscopic data of the product **1** are listed in *Table* 1. IR spectrum of **1** shows a strong band at 3400 cm^{-1}, which is so strong and broad that we can't identify the ν(N-H) band. The ν(C-H) bands are shown at 2950 cm^{-1} (s) and 2920 cm^{-1}(m). ^{1}H-NMR spectrum (DMSO-d_6) shows fullerenyl proton at δ 3.6 in DMSO-d_6. The electron withdrawing influence of fullerene can make the fullerenyl proton of this product acidic.[25] Fagan *et al.* reported that the HC_{60} *t*-Bu is the strongest acids consisting exclusively of carbon and hydrogen.[26] However, this fullerenyl proton peak of **1** doesn't disappear in D_2O

Table 1. Spectrochemical data for the amine compounds of C_{60}

Compound	IR, cm^{-1}	^{1}H-NMR, δ (fullerenyl proton)	ref
1	ν (O-H); 3400 (s, br) ν (C-H); 2950 (m), 2920 (m)	3.6[a,b]	This work
$C_{60}(en)_6$[c]	ν (N-H); 3250 (m) ν (C-H); 2980 (w), 2960 (w), 2940 (sh)	3.0[b]	8
$C_{60}(NH_2C_3H_7)_6$	ν (N-H); 3300 (vw) ν (C-H); 2950 (w), 2920 (w), 2870 (m)	3.8-2.4[d]	8
$C_{60}(NH_2C_4H_9)_6$	ν (N-H); 3250 (m) ν (C-H); 2950 (w), 2920 (w), 2850 (m)	1.8[d]	8

[a]In DMSO-d_6. [b]In D_2O. [c]en: ethylenediamine. [d]In CD_3Cl.

solvent. The FAB-MS of the product shows parent peak at m/z = 964. By these spectrochemical data together with elemental analytical data, we can identify **1** as a quartet-addition product, H_4C_{60}-$(NHCH_2CH_2OH)_4$. It should be considered that many kinds of addition products such as H_nC_{60}-$(NCH_2CH_2OH)_n$ (n=1, 2, 3, etc.), might be produced in the reaction between C_{60} and excess amount of ethanolamine. Thus, the products were dissolved in water and only water soluble product was isolated (*Scheme* 2). From this procedure, quartet-addition product was obtained as the major product. There is a possibility that the product **1** may have a number of geometric isomers because there are six interconnected pyracylene moieties in C_{60}. Seperation of each addition-product and study on the stereochemistry of the product **1** are in progress.

We can conclude that the primary amine in ethanolamine is able to attack the alkene-like functional group of C_{60} and solubility of the product in water is derived from a great hydrophilicity of the hydroxy groups in multi-functionalized C_{60}.

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