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Communications

Discovery of Long Chain Hydrocarbons In The Process of Preparation Of C_{60}.[1]

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Recently, all-carbon compounds known as fullerenes are prepared by evaporating graphite in the atmosphere of helium. Huffman and co-workers[2,3] reported the macroscopic preparation of C_{60} (Buckminsterfullerene) which is expected to have 60 carbon atoms at the vertices of truncated icosahedron[4,5] having twelve five-membered rings separated by twenty six-membered benzenoid rings. Many studies on the physical properties of C_{60} such as IR[3], Raman[6], NMR[7-12] photoelectron spectroscopy[13,14], scanning tunneling microscopy (STM)[15,16], mass spectroscopy[2,8,10,17,18], ESR[19,20], photophysical[19,21], and electrochemical[22,23] studies were accomplished. The chemical properties are, however, not well known, and only a few articles[20,22] on chemical reaction of fullerenes are reported. In order to study the chemical reactions of C_{60}, we attempted to make fullerenes and the derivatives of C_{60}.[24]

We report here long chain linear hydrocarbons are also found together with fullerenes in the process of preparation of fullerenes.

For the first step to prepare fullerenes, carbon deposits were generated by evaporating graphite rods by arc in the atmosphere of helium with the method described by Haufler *et al.*[22] We modified the method using a linear motion feedthrough to keep the graphite electrodes contacted during arcing instead of using a spring which would lose its tension because of the heat from arc. Fullerenes were isolated by extraction from the carbon deposits with boiling toluene. After extraction of the carbon deposits, C_{60} and C_{70} were separated from the extracts by the column chromatography using neutral alumina with hexane/toluene (20 : 1), and identified from electronic spectra, the ^{13}C-NMR spectrum, and the mass spectrum.

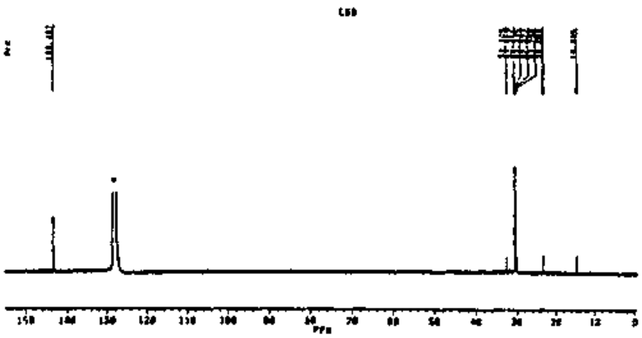

Figure 1. The ^{13}C-NMR spectrum for the fraction of C_{60}. This spectrum was recorded on a Bruker AM-300 NMR spectrometer operating at 75.13 MHz with 3 μs pulse (30° pulse) and 19 s relaxation delay (45 hours accumulation) using benzene-d_6. ▽ mark denotes solvent peak.

The UV-Vis spectrum for C_{60} shows absorption peaks at 635, 621, 598, 568, 540, 492, 404, 396, 377, 328, 256, 227, and 211 nm. For C_{70}, peaks are at 637, 624, 610, 600, 594, 544, 469, 378, 359, 331, 313, and 236 nm. These results well match the previous reports[7,9,12] The ^{13}C-NMR spectrum for the fraction of C_{60} shows a peak at 143.2 ppm assigned to C_{60}[7,9,11,12] and seven peaks between 10 ppm and 35 ppm which are assigned to linear hydrocarbons[25]. However, it is not possible to analyze the quantities of hydrocarbons and C_{60} because the relaxation times of ^{13}C atoms in two kinds of compounds are quite different.

Mass spectromery showed the presence of the linear hydrocarbons. We used the direct insertion probe method because the sublimation temperatures of fullerenes are above 400℃. In most of the spectra obtained below 250℃, as shown in Figure 2 the mass number 57 was the base peak. The intensity of peaks separated by 14 mass numbers decreased gradually as the mass number increased even over to m/z=

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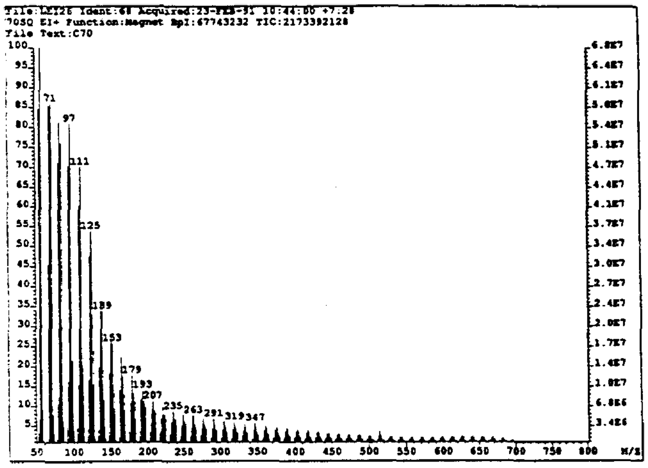

Figure 2. The mass spectrum taken with the portion of C_{70}. VG 70SQ mass spectrometer and direct probe was used and ionization energy was 70 eV. The probe temperature was 250℃.

700 which correspond to linear hydrocarbon containing up to 50 carbons. The highest mass number of the spectrum increased as the probe temperature was elevated. Though we could not confirm the exact molecular weight of the hydrocarbons, these hydrocarbons have 3 to 4 double bonds according to the results of the high resolution mass spectroscopy experiments.

This result seems to be somewhat consistent with our previous STM observation[27] that the highly oriented pyrolytic graphite(HOPG) surface was covered with long chains of carbons when carbons were deposited on the basal plane of HOPG by evaporating graphite rod in vacuum. We could observe that certain chains covered the surface of HOPG with closely packed parallel row. When we examined the line profile of the parallel row, we found every corrugation of the line scan matched carbon atom in size and height.

The explanation for the production of hydrocarbon, however, is not immediately obvious. The formation of hydrocarbon is rendered to the existence of water in the carbon deposit generator chamber or to the supply of hydrogen and/or water when the chamber is purged to the atmospheric pressure at the end of carbon deposit generation process.

Since the amount of extracts was reported not to exceed 40% of the original carbon deposit and the distribution of fullerenes are different from each other for different investigators[7,9,12,17,22,27], it would be important to know the composition of the carbon deposits for understanding the formation of C_{60} from graphite.

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24. Some new derivatives of C_{60} are already prepared. (a) S. S. Kim, I. C. Jeon, S. Y. Hwang, G. S. Bang, G. H. Lee, S. Kim, B. S. Shim. Ch. Park, Y.-S. Huh, and E.-S. Son, submitted to Bull. Kor. Chem. Soc.; (b) I. C. Jeon,

S. S. Kim, S. Y. Hwang, G. H. Lee, G. S. Bang, Ch. Park, Y.-S. Huh, S. Kim, and B. S. Shim, Abstract, Submitted to **STM'91**, 6th International Conference on Scanning Tunneling Microscopy, Interlaken, Switzerland, August 1991.
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Oxidation of Benzoylated Calix[4]arene

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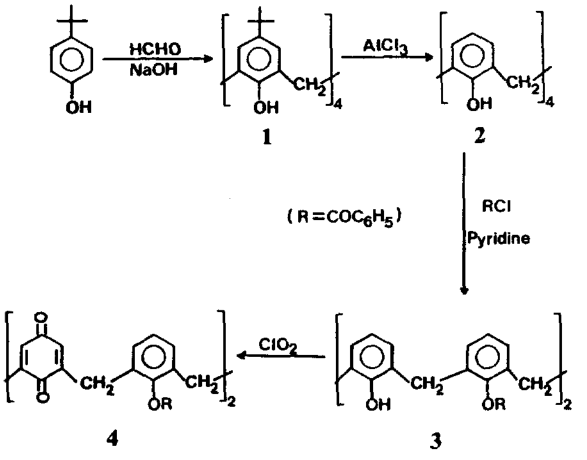
Calixarenes are cavity-containing macrocyclic compounds[1] that consist of several phenolic units in a cyclic array. Though several papers[2,3] have been reported for the preparation of functional calixarenes which can act as enzyme mimics[4], most calixarenes so obtained are symmetrically substituted. Besides the long stepwise synthesis developed by Hayes, Hunter[5] and Kämmerer[6], less symmetrical calixarenes have been synthesized by benzoylation[7] of calix[4]arene with benzoyl chloride in pyridine. Calix[4]arene yield only a tribenzoate under those conditions. Quinones are important ingredients for the biological studies[8] such as ubiquinones, alizarine and diosquinone which contain in their constitution either a 1,4- or 1,2-quinone moiety. Quinone calixarenes which contain a hydrophobic cavity as well as quinone groups could be developed into a selective guest oxidant. The purpose of present work is to exploit the benzoylation of calixarene to the preparation of less symmetrically functionalized calixarenes and to incorporate the quinone functionalities into the calixarene frame. In the present study we prepared the dibenzoylate calix[4]arene **3** under the carefully controlled conditions and oxidized it to the diquinone dibenzoyl calix[4]arene **4** with ClO_2. The tribenzoate calix[4]arene **5** which was prepared by Gutsche and Lee[7] also oxidized to the corresponding quinone calix[4]arene **6** with ClO_2.



Scheme 1

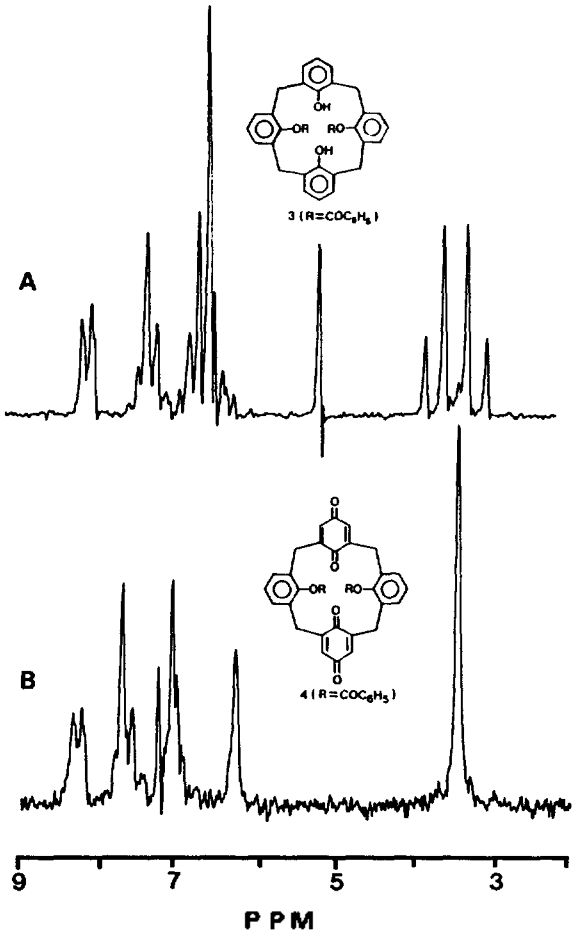


Figure 1. Proton NMR spectra of **3** and **4**.

p-tert-Butyl calix[4]arene **1** can be easily prepared in good yield by the base-induced "one-step" condensation[9] of *p-tert*-butylphenol and formaldehyde. Aluminum chloride catalyzed removal[7] of the *p-tert*-butyl groups proceeds in excellent yield, making calix[4]arene **2** a readily available starting material for the introduction of functional groups onto the calixarene framework (Scheme 1). Aroylation of calix[4]arene with **2** equivalent of benzoyl chloride in pyridine at 0℃ yields a dibenzoylate calix[4]arene **3** (85% yield) with the trace amounts of mono- and tribenzoylated calix[4]arene, which can be easily purified by recrystallization with chloroform. ^{1}H-NMR spectrum of **3** (Figure 1) shows a singlet at 5.5 ppm for two hydroxyl protons and a pair of doublet at 3.3-4.1 ppm for the bridge methylene protons, indicating that benzoylation occurred to the 1,3-position of hydroxyl groups and dibenzoylated calix[4]arene **3** exists as a rigid cone conformation[10]. No other conformations such as partical cone or alternate or 1,2-benzoylations were observed. Oxidation