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Addition Reaction of Benzyne to C_{60}

Minoru TSUDA, Takayuki ISHIDA, Takashi NOGAMI,* Sadamu KURONO, and Mamoru OHASHI
Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182

Benzyne generated by the reaction of 2-aminobenzoic acid and pentyl nitrite in a refluxing benzene was found to add to C_{60} in good yield. The reaction products were separated by HPLC to give $C_{60}(C_6H_4)$, $C_{60}(C_6H_4)_2$, $C_{60}(C_6H_4)_3$, and $C_{60}(C_6H_4)_4$, which were confirmed by mass spectra. ^1H NMR spectrum of $C_{60}(C_6H_4)$ is consistent with the structure of mono-addition product, whereas those of $C_{60}(C_6H_4)_2$, $C_{60}(C_6H_4)_3$, and $C_{60}(C_6H_4)_4$ indicate that they consist of the corresponding mixtures of isomers.

The studies on physics and chemistry of fullerenes[1] have been made explosively since the method of macroscopic synthesis of fullerenes was discovered in 1990.[2] Although the physical properties of fullerenes have attracted much attention in such fields as superconductivity[3] and ferromagnetism,[4] the chemistry of fullerenes is also very attractive. Several reactions of fullerenes such as hydrogenation,[5] halogenation,[6] metallation,[7] and addition reactions[8] have been reported. The reactions of fullerenes are expected to give tremendous types of new materials which may be used in various fields in the near future. Here, we report the addition reaction of benzyne to C_{60}.

The addition reaction was conducted as follows. To a refluxing benzene solution (40 ml) containing C_{60} (36 mg, 0.05 mmol) and pentyl nitrite (0.1 ml, 0.8 mmol) was added 2-aminobenzoic acid (103 mg, 0.75 mmol).[9] The purple solution immediately turned brown, and the solution was refluxed with stirring for another 30 min under nitrogen atmosphere. After cooling the solution to a room temperature, it was washed with an aqueous solution of $NaHCO_3$, and then with water, and the organic layer was concentrated to dryness by a vacuum pump. The residue obtained (40 mg) was considerably soluble to chloroform, whereas C_{60} is almost insoluble to chloroform. Thus, C_{60} is considered to be almost consumed. The residue (30 mg) was chromatographed on an HPLC (LC 908, Japan Analytical Industry, Co., Ltd) by using gel permeation columns (Jaigel 1H +1H) and chloroform as an eluent, and after two recycles we obtained four reaction products. The weights of the brown powdered products are as follows; product 1: 4.7 mg, product 2: 5.8 mg, product 3: 4.9 mg, and product 4: 3.7 mg in the order of an increasing retention time. Other C_{60} derivatives gave several minor fractions.

The FAB mass spectra of the four products were measured on a TSQ 700 (Finningan Mat. Co., Ltd). Samples were ionized from a matrix of *m*-nitrobenzyl alcohol. A xenon beam with an energy of 8 kV was used. We could observe molecular ion peaks ascribable to $C_{60}(C_6H_4)$, $C_{60}(C_6H_4)_2$, $C_{60}(C_6H_4)_3$, and $C_{60}(C_6H_4)_4$ for products 4, 3, 2, and 1 respectively. Figure 1 shows the negative ion FAB mass spectrum of $C_{60}(C_6H_4)_4$ as a typical example. Besides the molecular ion peak at *m/z* 1024, fragment ions were found at *m/z* 948, 872, 796, and 720, which could be ascribable to $C_{60}(C_6H_4)_3^{-\cdot}$, $C_{60}(C_6H_4)_2^{-\cdot}$, $C_{60}(C_6H_4)^{-\cdot}$, and $C_{60}^{-\cdot}$ respectively.[10] In the positive ion FAB mass spectra could we also observe fragment ions generated by the loss of benzyne as well

as molecular ions for these products. ^{1}H NMR spectra of these products were measured on a JNM-GX-270 (JEOL Co., Ltd.). The spectrum of $C_{60}(C_6H_4)$ showed a typical AA'BB' coupling pattern due to the *o*-phenylene moiety (δ 7.71-7.74 (m, 2H) and 7.93-7.96 (m, 2H) in $CDCl_3/CS_2$ (1:2) solution). However, those of $C_{60}(C_6H_4)_2$, $C_{60}(C_6H_4)_3$, and $C_{60}(C_6H_4)_4$ were somewhat complicated. This fact indicates that the multi-addition products consist of the corresponding mixture of isomers. Benzyne can add not only to C_{60} carbons but also to pendant *o*-phenylene rings.

We have also found that Diels-Alder type reaction occurs when a toluene solution of C_{60} and 600 molar amounts of cyclopentadiene was stirred overnight at a room temperature. After GPC separation similar to those described above, a soluble main product showed an intense molecular ion peak at *m/z* 1711 in the positive ion FAB mass spectrum, which is ascribed to a cation of an addition product $C_{60}(C_5H_6)_{15}$. Its ^{1}H NMR spectrum in $CDCl_3$ showed complicated patterns, suggesting it likewise to be a mixture of several isomers.

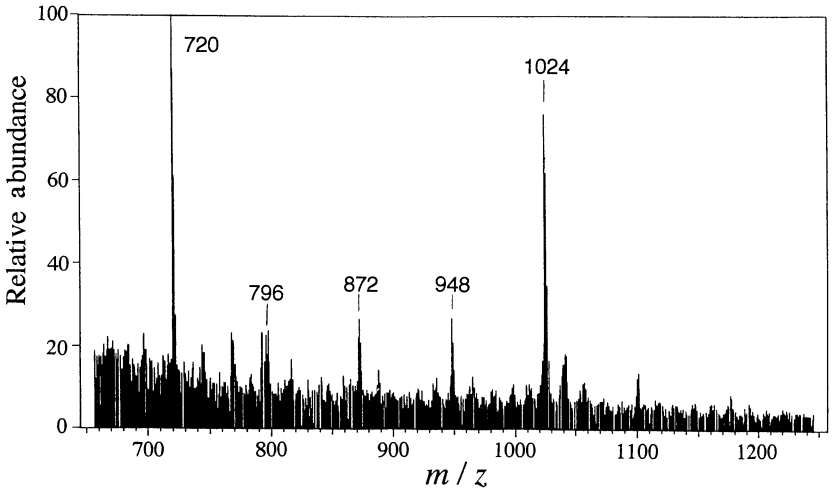

Fig. 1. Negative ion FAB mass spectrum of $C_{60}(C_6H_4)_4$ by using *m*-nitrobenzyl alcohol as a matrix.

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9) The reaction product between 2-aminobenzoic acid and isopentyl nitrite is known to generate benzyne with liberation of CO_2 and N_2 upon pyrolysis. See, F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, Coll. Vol. V, 54 (1973).

10) Figure 1 also shows the weak peaks at *m/z* 1100 and 1176 ascribable to $C_{60}(C_6H_4)_5^{-\cdot}$ and $C_{60}(C_6H_4)_6^{-\cdot}$ respectively, which are contaminated in the $C_{60}(C_6H_4)_4$ fraction.

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