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REACTION OF FULLERENE WITH BENZOCYCLOBUTENE HOMOLOGS

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Abstract: Fullerene was easily converted to its derivatives by the treatment with benzocyclobutene homologs for 20 h at 140 °C. The spectroscopic analyses clearly indicate mono-[4 + 2]-cycloadduct structures of its derivatives. Isolated yields of mono- and di-adducts were from 4.4 to 15.6% and from 8.1 to 5.3%, respectively.

Fullerene is reactive to most reagents and at the same time so stable that the adduct can easily undergo the reverse reaction to reproduce fullerene even at room temperature.[1] Concerned with the reactions of *ortho*-quinodimethane and its derivative, the adducts have been proved stable enough, because the cleavage of the adducts is an up-hill reaction due to the generation of unstable *ortho*-quinodimethane species.[2,3] Two research groups have reported the kind of reactions to form the appropriate adducts and have disclosed the expected stability of adducts. They have used decarbonylation[2] to aromatize the first Diels-Alder adduct or debromination[3] in order to generate the required *ortho*-quinodimethane species. Recently we have successfully carried out the addition reaction of fullerene with *ortho*-quinodimethane-type species, simply using the thermally allowed conrotatory [σ2 + π2] electrocyclic ring opening of benzocyclobutene homologs. In this communication, we would like to report the detailed reaction and the structural elucidation.

The benzocyclobutene homologs, **1**,[4] **2**,[5] and **3**,[6] were prepared by the reported methods with minor modifications. Fullerene C_{60} was purified from the commercially available soot by the method reported by Tour.[7] The [4 + 2] cycloaddition of benzocyclobutene homologs and fullerene was carried out in *m*-xylene at 140 °C.[8] After the evaporation of solvent, the adducts were separated by column chromatography (SiO_2, hexane/benzene). Isolated yields of mono-adducts **4** and **5** were 4.4% and 15.6%, respectively, and di-adducts **6** and **7** were 8.1% and 5.3%, respectively.[9] The mass spectroscopic and NMR spectroscopic data of these adducts are listed in Table 1.

Molecular weights were determined by FAB MS (see Table 1). Since di-adducts gave complex ^{1}H NMR spectra which apparently suggest the presence of isomers, the further detailed structural elucidation by NMR spectroscopy was done only for mono-adducts, as mentioned below. ^{1}H NMR spectra clearly give the resonance peaks of quinodimethane-homolog-residues; especially low-field-shifted aromatic proton Hb signals[10] and methylene proton Ha singlet broadened by the flipping motion[2,3] are seen and these peaks strongly suggest the adduct formation. As known in the ^{1}H NMR spectra of many fullerene-carbene adducts,[10] the protons of the carbons attached to the fullerene, such as Ha, are influenced by its anisotropic deshielding field and appear at the lower field than those of parent compounds. In Table 2 such deshielded Ha resonances are listed, compared with those of adducts **8** and **9**. The aromatic protons Hb also resonate at the lower field,

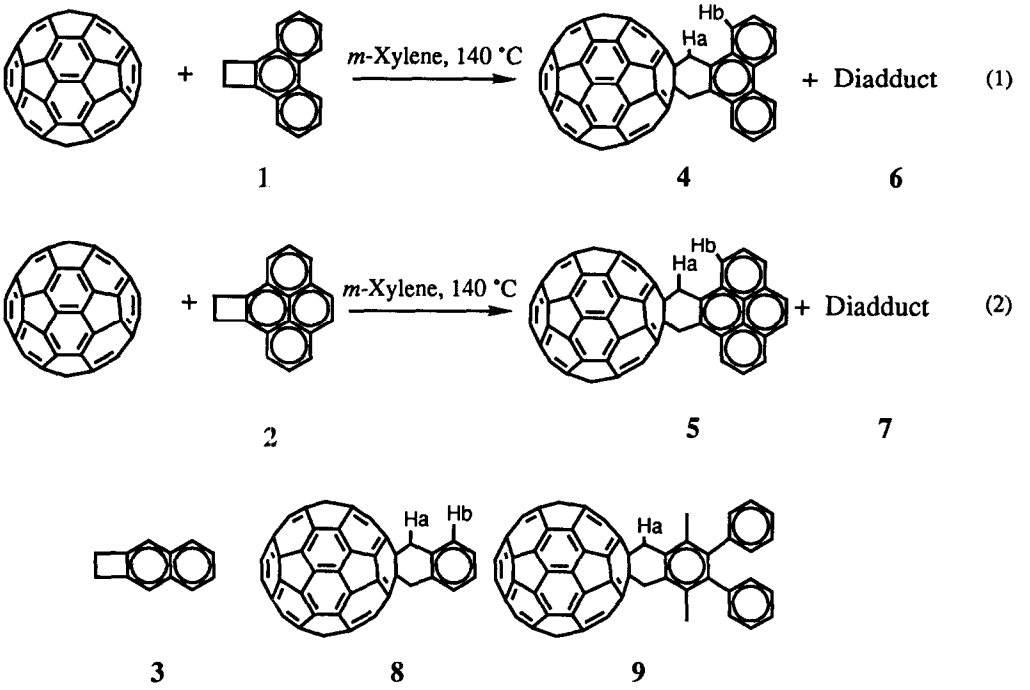

Table 1 Mass spectroscopic and NMR Spectroscopic Data of Adducts[a)]

Adduct	MS (m/z); ^{1}H NMR, δ (integral, multiplicity, *J* in Hz); ^{13}C NMR, δ (assignment).
4	924 (M^+); 5.15 (4H, bs), 7.78 (4H, m), 8.52 (2H, m), 8.95 (2H, m); 40.16 (benzylic), 66.23 (aliphatic quaternary carbon), 123.43 (aromatic C-H carbon), 123.61 (aromatic C-H carbon), 126.59 (aromatic C-H carbon), 127.32 (aromatic C-H carbon), 128.28, 130.02, 130.19, 133.23, 140.19, 141.64, 142.05, 142.24, 142.57, 143.05, 144.66, 145.43, 146.21, 146.45, 156.25.
5	948 (M^+); 5.31 (4H, bs), 8.16 (2H, t, 7.7), 8.19 (2H, s), 8.31 (2H, d, 7.7), 8.75 (2H, d, 7.9); 40.27 (benzylic), 66.15 (aliphatic quaternary carbon), 120.49 (aromatic C-H carbon), 125.57 (aromatic C-H carbon), 126.30 (aromatic C-H carbon), 127.78 (aromatic C-H carbon), 124.31, 129.27, 131.77, 133.91, 140.14, 141.55, 141.95, 142.11, 142.48,142.95, 144.56, 145.32, 146.10, 146.35, 147.51, 156.06.
6	1128 (M^+); 4.80 (4H, bm), 5.11 (4H, bm), 7.80 (8H, m), 8.26-8.65 (4H, m), 8.92 (4H, m).
7	1176 (M^+); 4.65-5.27 (8H, bm), 7.90-8.31 (12H, m), 8.50-8.91 (4H, m).

a) ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini FT-200 NMR spectrometer and a JEOL JNM-α500 NMR spectrometer, respectively. The solvent was the mixture of CS_2 and $CDCl_3$. FAB MS data were cordially obtained by Prof. Dr. Masahiko Iyoda, Tokyo Metropolitan University.

compared with the corresponding arenes or alkylarenes. Since the definite *o*-proton chemical shifts of alkylarenes are often hardly known, the differences are given with some ranges. These proton peaks, however, clearly shift to the down field by the deshielding effect of the fullerene nucleus. As these protons are more apart from the fullerene surface than protons Ha, the extent of the differences apparently becomes smaller than that of Ha.

Variable temperature NMR experiments reveal that their ring flipping above mentioned has the activation energy of around 55 kJ/mol at the coalescence temperature (see Table 2). The motion actually becomes more facile than that of **9**. At this moment we believe that this lower activation energies would come from a steric hindrance of the *o*-methyl groups and/or an electronic repulsive interaction between the fullerene surface and the larger aromatic nucleus like phenanthrene and pyrene rings.

Table 2 ^{1}H NMR Data of Selected Protons Ha and Hb (Recorded by 500 MHz Spectrometers)

Adduct	Ha, δ[a]	Δδa[b]	$\Delta G^{\neq}_c$[c] (T_c)[d] kJ/mol	Hb, δ	Δδb[b]	Remarks
4	5.15	1.80[e]	55.2±0.4 (21 °C)	8.52	0.52-1.09	This work
5	5.31	1.71[f]	55.0±0.4 (20 °C)	8.75	0.59	This work
8	4.46[g]	1.29[h]	- (>28 °C)	7.57-7.71	0.4-0.54	Ref. 2
9	4.73[g]	1.56[h]	61.1±0.4 (35 °C)	-	-	Ref. 3

a) Broad singlet due to the flipping motion. b) The differences of benzyl-proton and *ortho*-proton chemical shifts are from those of benzocyclobutene homologs and arenes or alkylarenes. c) The activation energy (at the coalescence temperature) of the flipping motion of quinodimethane-homolog-residue which is determined by D NMR spectra of Ha. d) The coalescence temperature. e) Ref. 4. f) Ref. 5. g) The chemical shift difference of adduct **9** seems to be unreasonably large, compared with that of **8**. This may be due to the steric compression of Ha by *o*-methyl group. h) Based on benzocyclobutene.

Generally the fullerene position where the addition occurs is proved by ^{13}C NMR spectroscopy, because the spectra often clearly reflect the molecular symmetry. The mono-adducts, formed by the attack of *ortho*-quinodimethane-type species at a [6,6] junction of C_{60} framework, became C_{2v} symmetric as a result of the rapid flipping motion of quinodimethane-homolog-residues which is mentioned above. Thus, mono-adducts **4** and **5** should give 23 and 24 aromatic peaks, respectively. The spectrum of **4** shows 19 aromatic peaks out of the theoretical 23 ones, and that of **5** does 20 aromatic peaks out of the theoretical 24 ones. Actually several peaks overlap each other, although they are not specified at this moment. Hence we could determined the structures of mono-adducts as depicted in equations (1) and (2).

Benzocyclobutene is known to lower its ring-opening activation barriers to *ortho*-quinodimethane when some functional group(s) is added at benzyl position(s); phenyl-, bromo-, hydroxyl-, and amino-groups reduce the temperature of ring-opening so remarkably from 200 °C to 25 °C for the extreme case.[11] Moreover, some benzocyclobutene homologs like **1**[4] and **2**[5] also lower the activation energies of the ring-opening to quinodimethane species, even though the extent is not so remarkable as that of benzylic substitution: the activation free energies of the ring opening ($\Delta G^{\neq}$) at 200 °C decreased in the order of **3** (167 kJ/mol), benzocyclobutene (155.2 J/mol),[12] **2** (142 kJ/mol), and **1** (136 kJ/mol).[13] Since fullerene itself is not so inert at rather high temperatures, it is recommended to carry out its reactions at lower temperatures. In fact, we found that its reaction with **3** at 180 °C for 20 h gave complex mixtures and no desired products with the low conversion of **3**.

So it is stressed that in this work, the quinodimethane precursors **1** and **2** were first proved useful for the modification of fullerene. These precursors reacted with fullerene in *m*-xylene at 140 °C. As the result, the work-up procedure as well as the reaction procedure is simple enough.[8)]

The reactions with difunctional benzocyclobutene homologs such as tetrahydrobiscyclobuta[*e,l*]pyrene[5)] are expected to produce bucky-dumbbells and also bucky-pearl-necklace polymers. Moreover, we speculate that the phenanthrene- and pyrene-modified fullerenes would disclose some intriguing properties connecting to functional materials. This kind of research is now under progress and will be reported elsewhere.

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8) Fullerene (31.6 mg, 0.0438 mmol) and dihydrocyclobuta[*e*]pyrene **2** (10 mg, 0.0438 mmol) were dissolved in *m*-xylene (0.22 ml) and sealed in an ampule (2 ml) in vacuum. The mixture was heated for 20 h at 140 °C. Then the solvent was evaporated and mono- and di-adducts were separated from the residue by column chromatography (SiO_2, benzene/ hexane=3:7).

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