Reaction of [60]Fullerene with Benzocyclobutenone and Benzocyclobutenedione

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Thermolysis of benzocyclobutenone in dichlorobenzene in the presence of [60]fullerene affords the *o*-phenylene(methylene)ketene–C_{60}[4 + 2] cycloadduct, while similar thermolysis of benzocyclobutenedione gives no cycloadduct; irradiation of the dione with [60]fullerene, produces a phthalide-1-ylidene–C_{60} adduct.

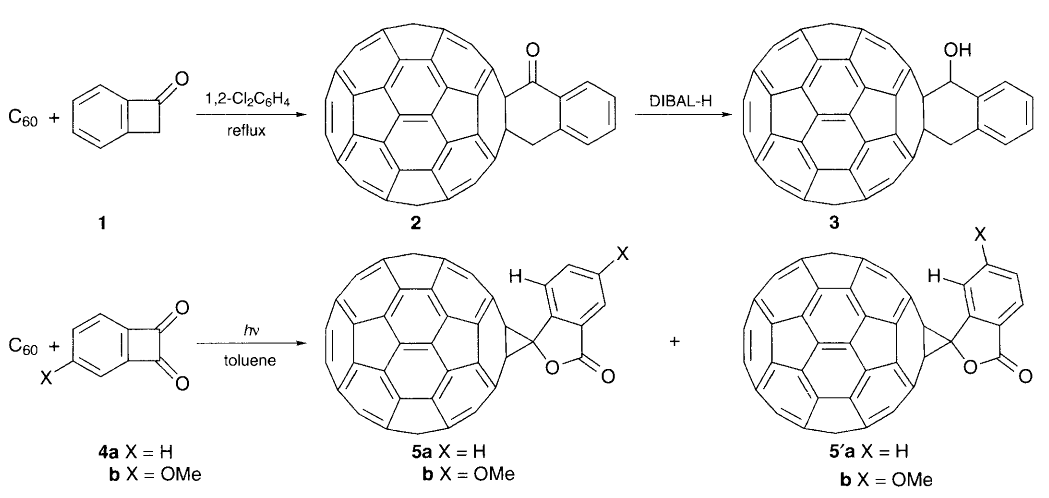
Since the discovery of the multigram synthesis of [60]fullerene (C_{60}),[1] organic chemical derivatization of this fascinating molecule continues to attract great interest.[2–4] The literature on its chemical reactivity and transformations is growing rapidly.[5] Among the derivatization methods available, cycloadditions have been particularly successful. Thus, it is now well established that fullerene molecules undergo Diels–Alder cycloaddition reactions with a variety of dienes, including cyclopentadiene, furan, isobenzofuran, anthracene and buta-1,3-diene.[2,6] Some of the adducts are thermally unstable because they undergo fast cycloreversion to their components. The adducts easily obtained by the Diels–Alder reaction of C_{60} with *o*-quinodimethane, however, are shown to be thermally stable since the stabilization energy provided by the aromatic system through a retro-Diels–Alder reaction has to be overcome to give the unstable *o*-quinodimethane.[7] A variety of modified fullerenes linked with chromophoric, electrophoric or ionophoric units have been obtained from functionalized *o*-quinodimethanes.[7b] Since benzocyclo-butenones **1** and -butenediones **4** similarly undergo ring opening to give *o*-phenylene(methylene)ketenes and *o*-phenylenebis(ketene),[8] respectively, which can be trapped by dienophiles, they are expected to be equally useful substrates for the modification of fullerenes. Thus, we studied the reactions of the ketones with C_{60} and found that, while the butenone gave the expected [2 + 4] cycloadduct, the dione afforded the oxacarbene adduct, no expected [2 + 4] cycloadducts being produced.

While refluxing a mixture of the butenone **1**[9] and C_{60} in toluene did not result in any appreciable consumption of **1**, **1** underwent smooth reaction with C_{60} in refluxing 1,2-dichlorobenzene (Scheme 1). HPLC analysis indicated the presence of two products in addition to unreacted C_{60}. C_{60} (13%) and monoadduct **2** (49%)† were easily separated by flash column chromatography. The other products, probably diadducts, could not be further purified or assigned. FABMS of **2** indicated that it is a 1 : 1 adduct, IR showed distinctive bands corresponding to the dihydrofullerene core[10] in addition to the C=O stretching bands at 1680 cm^{-1}. The UV–VIS spectrum was similar to that of most dihydrofullerenes.[11] ^1H and ^{13}C NMR spectra of the adduct are consistent with the assigned structure. Thus, ^1H NMR (270 MHz, $CDCl_3$) of **2** showed a 2 H singlet at δ 4.80 ascribable to benzyl protons, and partially resolved ABCD aromatic proton signals at δ 8.05–7.67. The ^{13}C NMR spectrum (68 MHz, $CDCl_3$–CS_2) showed one signal (δ 193.66) for carbonyl carbon, three signals for aliphatic carbons and 33 (3 coincidental) of the 36 expected signals for sp^2 carbons. The spectrum reveals C_s symmetry as a result of the addition to 6,6-junction.

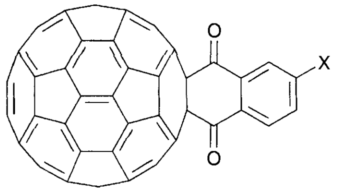
To assist in assigning structures, the adduct was reduced by treating with DIBAL-H[12] to the corresponding hydroxy fullerene **3**. The ^1H NMR spectrum of **3** thus obtained, showing two sets of signals resulting from two 'frozen' 6,6-addition benzocyclohexene conformers, is in complete agreement with that of the adduct obtained in the reaction of C_{60} with benzocyclobutenol.[7d] Thus, a C_{60} adduct bearing carbonyl group directly to the fullerene core is attained in a single step.

The reaction with the butenedione **4a**[13] gave unexpected results. Refluxing a mixture of **4a** and C_{60} either in toluene or in 1,2-dichlorobenzene did not result in any appreciable decomposition of **4a**. Photolysis (λ > 300 nm) of a solution of **4a** and C_{60} in toluene, on the other hand, afforded monoadduct **5a**† in 35% yield, along with a mixture of multiadducts and C_{60} (55%). Again C_{60} and the monoadduct were easily separated by flash column chromatography, while the other products could not be further purified or assigned. FABMS of **5** shows it to be a 1 : 1 adduct. While the UV–VIS spectrum of **5** is similar to that of most dihydrofullerenes,[12] the IR and NMR spectra cannot be explained in terms of the *o*-phenylene bis(ketene)–C_{60} adduct **6a**. Thus, IR shows the C=O bands at 1780 cm^{-1} in addition to distinctive bands corresponding to the dihydrofullerenes.[10] The C=O bands are rather high for the quinoid structure. ^1H NMR of the adduct showed ABCD patterns instead of the A_2B_2 pattern expected for **6a**.

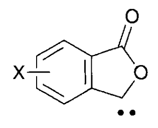
The structure which explains these data best is the spirophthalide adduct **5a**, which must be produced by the addition of okacarbene **7a**, known[8] to be generated in the photolysis of **4a**. As the spiroadduct **5a** was extremely insoluble in most organic solvents, we were not able to obtain distinct ^{13}C NMR spectra for **5a**. In order to improve the solubility, the adducts bearing appropriate substituents are desired. Thus, we reacted C_{60} with



Scheme 1



6a X = H
b X = OMe



7a X = H
b X = OMe

4-methoxybenzocyclobutenedione **4b**.[12] The adducts provided chemical as well as spectroscopic evidence supporting the spirocyclopropyl structure. Thus, NMR indicated that the monoadduct was a mixture of two isomers (**5b** and **5b′**)† in a roughly 2 : 1 ratio. One would not expect isomer formation from the C_{60}–bisketene adduct **6b**, assuming that the addition occurs across the 6,6-junction. Thus, ^{1}H NMR of the monoadducts exhibited the presence of two sets of *meta*-substituted aromatic proton signals in addition to two methoxy signals. ^{13}C NMR of **5b′** exhibited δ 55.88 (OMe), 76–77 (aliphatic), 107–127 (aromatic), 130–147 (26 resonances, 4 coincidental, fullerene sp^2 carbons) and 166.26 (ester CO). The spectrum reveals formation of cyclopropane from the signals at δ 77, and C_s symmetry from 30 (26 observed) signals in sp^2 region. One relevant feature of the ^{1}H NMR spectrum of the adduct is the striking low-field resonances of one of the aromatic protons. Inspection of the molecular model of the spiro adduct clearly reveals that one of the aromatic protons is located much closer to the fullerene sphere than the other two. Thus, the observation again is explicable in terms of the carbene adduct much better than the bisketene adduct.

It should be noted that usual dienophiles such as maleic anhydride react with **4** in its bisketene form to give diketone as an initial adduct, no carbene adducts being formed.[12] In the light of the fact that C_{60} is known to possess considerably high electron affinity and low ionization potential, it must react with the bis(ketene) more easily than with the carbene. In accord with this expectation, the reactivities of C_{60} toward **7** relative to simple a alkene, *i.e.* 2,3-dimethylbutene, was estimated to be only 1/35 per bond basis by competition experiments. It may be that C_{60} reacts with the bisketene to form the dione **6** but this adduct might undergo retroaddition to regenerate the ketene and C_{60} owing to the inherent instability under the reaction conditions.‡ Thus, C_{60} is reluctantly trapped by carbene **7**.

Thus, benzocyclobutenone is shown to be useful substrate to modify C_{60} where carbonyl group is introduced directly on the fullerene core. While benzocyclobutenedione fails to give the expected fullerene dione, it gives spirocyclopropyl adduct with interestingly aligned benzene ring, which should be useful for studying intramolecular interaction between fullerene core and functional groups. The reaction is suggestive of the limitation of reactivities of C_{60} toward enophiles.

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Footnotes

† *Spectral data* for **2**: ν_{max}/cm^{-1} (neat) 1680; ^{1}H NMR (270 MHz, $CDCl_3$–CS_2) δ 8.05 (1 H, d, *J* 7.3 Hz), 7.81 (1 H, t, *J* 7.6 Hz), 7.70 (1 H, d, *J* 7.6 Hz), 7.67 (1 H, t, *J* 7.6 Hz), 4.80 (2 H, s); ^{13}C NMR (125.65 Hz, $CDCl_3$–CS_2) δ 193.66, 156.11, 152.90, 148.39, 148.23, 147.98, 147.22, 146.98, 146.94, 146.42, 146.33, 146.22, 146.17, 146.13, 145.59, 145.33, 145.28, 143.73, 143.41, 143.35, 143.03, 142.75, 142.49, 142.34, 142.25, 141.18, 140.85, 138.60, 136.31, 136.04, 135.11, 129.36, 128.90, 128.53, 76–77, 63.18, 43.95. For **5a**: ν_{max}/cm^{-1} (neat) 1792; ^{1}H NMR (500 MHz, C_5D_5N) δ 8.54 (1 H, d, *J* 7.3 Hz), 8.25 (1 H, d, *J* 7.3 Hz), 7.98 (1 H, d, *J* 7.3 Hz), 7.79 (1 H, d, *J* 7.3 Hz). For **5b** (major isomer): ν_{max}/cm^{-1} (neat) 1780; ^{1}H NMR (270 MHz, $CDCl_3$–CS_2) δ 8.24 (1 H, d, *J* 8.6 Hz), 7.57 (1 H, d, *J* 2.3 Hz), 7.40 (1 H, dd, *J* 8.6, 2.3 Hz), 4.00 (3 H, s). For **5b′** (minor isomer): ν_{max}/cm^{-1} (neat) 1780; ^{1}H NMR (270 MHz, $CDCl_3$–CS_2) δ 8.10 (1 H, d, *J* 8.6 Hz), 7.84 (1 H, d, *J* 2.3 Hz), 7.28 (1 H, dd, *J* 8.6, 2.3 Hz), 4.02 (3 H, s); ^{13}C NMR (125.65 Hz, $CDCl_3$–CS_2) δ 166.26, 165.09, 147.06, 145.24, 145.17, 145.09, 145.04, 144.83, 144.72, 144.70, 144.58, 144.46, 144.39, 143.74, 143.54, 143.41, 143.05, 142.99, 142.96, 142.93, 142.34, 142.12, 142.04, 141.57, 141.51, 141.35, 137.60, 130.52, 127.95, 118.93, 116.61, 107.85, 77.21, 76.89, 55.86.

‡ We do not know the exact nature of this instability.

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