Photolysis of C_{60} with Cyclic Amino Acids: Preparation of Dihydrofullerenes by Decarboxylation

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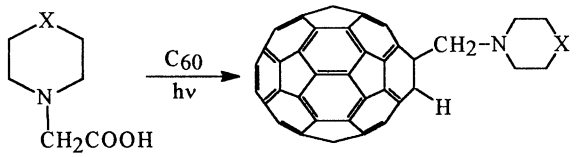
Photolysis of C_{60} with piperidinoacetic acid and morpholinoacetic acid results in the decarboxylation of the acids and formation of the 1,2-dihydrofullerenes $C_{60}(H)[CH_2N(CH_2)_5]$ **1**, $C_{60}(H)[CH_2N(CH_2CH_2)_2O]$ **2**. Under the same conditions the reactions with the methyl esters of the two cyclic amino acids give the fullerropyrrolidine derivatives $C_{60}[CH(CH_2)_4NCH\text{-}COOCH_3]$ **3**, and $C_{60}[CH(CH_2OCH_2CH_2)NCHCOOCH_3]$ **4**.

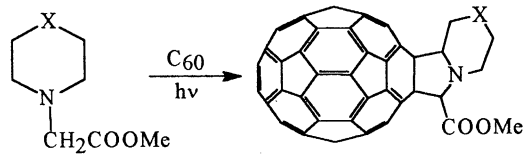
Fullerene chemistry has developed rapidly in recent years.[1,2] The combination of fullerenes with diverse heterocycles provides a variety of fullerene derivatives. Most C_{60} derivatives containing a heterocyclic five-membered ring were prepared by 1,3-dipolar cycloadditions,[1-4] We recently reported the formation of several fullerene pyrrolidine derivatives by direct photochemical reactions between C_{60} and amino acid esters.[5] In these reactions both C-N bond breaking and formation processes are involved. We have now extended the photochemical reaction from amino acid esters to amino acids. Unlike the esters, decarboxylation of amino acids takes place and dihydrofullerenes are formed. Here we report the reaction of C_{60} with two cyclic amino acids, namely piperidinoacetic acid and morpholinoacetic acid. For comparison the photolysis with the methyl esters of the two amino acids are also investigated.

The cyclic amino acids were prepared by treating the corresponding cyclic amines with bromoacetic acid. The photochemical reactions with C_{60} were carried out according to the following procedure for compound 1. Piperidinoacetic acid (715 mg, 5.0 mmol) in 50 ml methanol (pH around 8.5) was added to a solution of C_{60} (72 mg, 0.10 mmol) in toluene (200 ml). The resulting mixture (cooled with water) was irradiated under stirring with a 250 W overhead projector light bulb for 10 min. The solvent was removed. Isolation by flash column chromatography on silica gel using toluene as eluent afforded unreacted C_{60} (25 mg) and compound **1** (37 mg, 70% yield based on converted C_{60}).



X = CH_2, **1**; O, **2**

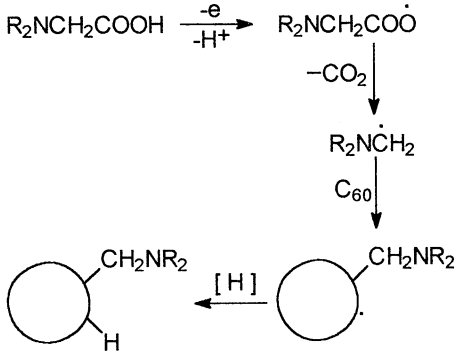
When the corresponding methyl esters of the aminoacids were irradiated with C_{60} under the same conditions as above, the fulleropyrroldine derivatives **3** and **4** were obtained. The net result is the loss of two H atoms. This is analogous to our previously reported photoreaction between iminodiacetic ester and C_{60}.[5]



X = CH_2, **3**; O, **4**

In order to make the solutions for photolysis homogeneous, about 10-20 ml methanol may be needed in addition to the cyclic amino acids methanol soltuions. When the solution changes from purple to slightly reddish, the irradiation was stopped. It took 30 min for **3**, 20 min for **4**, and only 7-10 min for **1** and **2**. Prolonged irradiation gives more multiadducts. The pH of the amino acids or esters solution before mixing with C_{60} should be no more than 9.0 to avoid hydroxylation of C_{60}.[5]

A possible path way is shown in the following scheme. The first step is electron transfer and proton loss. Under the conditions employed here, these steps are easily initiated. C_{60} may well act as the electron acceptor. The CO_2 loss from carboxyl radicals are well-known.[6] The so-formed aminomethyl radical then adds to C_{60}. The final step is the abstraction of hydrogen from the environment.



The alkylation of electron-deficient molecules by decarboxylation of carboxylic acids via photo-induced electron transfer are well known. These reactions usually give many by-products, and the yields of alkyldihydro-derivatives are less than 20%.[7,8] Several dihydrofullerenes have been reported by different methods such as Grignard reagents.[9] The above reaction reported here would provide a convenient method for the preparation of dihydrofullerenes.

The structures of the fullerene derivatives were characterized spectroscopically. In the ^1H NMR spectrum of **1**, the proton on C_{60} appeared at 6.95 ppm as a singlet, the chemical shift being in good agreement with the reported values for 1-alkyl-2-hydrofullerene-C_{60}.[10] The ^{13}C NMR of both **1** and **2** gave 32 signals for the C_{60} skeleton, indicating a C_s symmetry. DEPT

experiment of **2** located one methine peak at 58.19, two morpholine ring-carbon peaks at 55.85 (2C) and 67.14 (2C), and one methylene carbon at 72.05 ppm. Both the ^{1}H and ^{13}C NMR of **3** and **4** indicated that just one stereoisomer was isolated.

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10 **1**: ^{1}H NMR (400 MH_Z, $CDCl_3$-CS_2) δ 1.71 (m, 2H), 1.93 (m, 4H), 3.23 (m, 4H), 4.33 (s, 2H), 6.95 (s, 1H). ^{13}C NMR (100.6 MH_Z, $CDCl_3$-CS_2) δ 24.97 (CH_2), 27.39 (CH_2), 30.29 (CH_2), 57.04 ($2CH_2$), 58.37 (CH), 67.36 (sp^3 C), 72.59 (CH_2), 135.99 (2C), 136.30 (2C), 140.22 (2C), 140.40 (2C), 141.72 (2C), 141.75 (2C), 141.95 (2C), 142.08 (2C), 142.14 (2C), 142.44 (2C), 142.65 (2C), 142.66 (2C), 143.16 (3C), 143.35 (1C), 144.63 (2C), 144.78 (2C), 145.44 (2C), 145.46 (2C), 145.48 (1C), 145.55 (2C), 145.88 (2C), 146.21 (2C), 146.26 (2C), 146.43 (3C), 146.85 (2C), 147.28 (1C), 147.33 (2C), 147.41 (1C), 154.66 (2C), 155.53 (2C). Anal. Found: C, 95.87 ; H, 2.02 ; N, 1.67%. Calcd for $C_{60}H[CH_2N(CH_2)_5]0.5H_2O$: C, 95.64 ; H, 1.70 ; N, 1.69%. **2**: ^{1}H NMR (400 MH_Z, $CDCl_3$-CS_2) δ 3.28 (t, 4H), 3.99 (t, 4H), 4.38 (s, 2H), 6.97 (s,1H). ^{13}C NMR (100.6 MH_Z, $CDCl_3$-CS_2) δ 55.98 ($2CH_2$), 58.26 (CH), 66.85 (sp^3 C), 67.46 ($2CH_2$), 72.21 (CH_2), 136.09 (2C), 136.17 (2C), 140.28 (2C), 140.49 (2C), 141.76 (3C), 141.80 (2C), 141,88 (2C), 142.08 (2C), 142.17 (2C), 142.41 (2C), 142.69 (2C), 142.72 (3C), 143.38 (2C), 144.61 (2C), 144.82 (2C), 145.48 (2C), 145.50 (2C), 145.51 (2C), 145.63 (2C), 145.85 (2C), 146.27 (2C), 146.32 (2C), 146.47 (2C), 146.49 (2C), 146.68 (2C), 147.23 (2C), 147.32 (2C), 147.48 (2C), 154.36 (2C), 155.04 (2C). DEPT spectrum: 55.85 (CH_2), 58.19 (CH), 67.14 (CH_2), 72.05 (CH_2). **3:** ^{1}H NMR (400 MH_Z, $CDCl_3$-CS_2) δ 1.75 (m, 1H), 2.01 (m, 3H), 2,25 (m, 1H), 2.67 (m, 1H), 3.01 (m, 1H), 3.54 (m, 1H), 3.88 (s, 3H, OCH_3), 5.07 (q, 1H, NCH), 5.48 (s, 1H, $NCHCOOCH_3$). ^{13}C NMR (100.6 MH_Z, $CDCl_3$-CS_2) δ 24.91 (CH_2), 26.25 (CH_2), 31.57 (CH_2), 48.76 (CH_2), 51.21 (CH_3), 69.23 (CH), 71.48 (SP^3 C), 74.35 (SP^3 C), 76.17 (CH), 136.34 (1C), 136.48 (1C), 137.90 (1C), 139.66 (1C), 139.95 (1C), 140.20 (1C), 140.31 (1C), 141.72 (1C), 141.77 (1C), 141.84 (2C), 141.95 (1C), 142.06 (1C), 142.08 (1C), 142.10 (1C), 142.21 (1C), 142.23 (1C), 142.24 (1C), 142.36 (1C), 142.60 (1C), 142.70 (2C), 142.74 (1C), 143.05 (1C), 143.11 (2C), 143.13 (1C), 143.20 (1C), 144.34 (1C), 144.55 (1C), 144.65 (1C), 144.74 (1C), 145.15 (1C), 145.28 (1C), 145.31 (1C), 145.34 (2C), 145.42 (1C), 145.53 (1C), 145.54 (1C), 145.55 (1C), 145.71 (1C), 145.99 (2C), 146.08 (1C), 146.09 (1C), 146.20 (1C), 146.30 (1C), 146.32 (1C), 146.35 (2C), 146.66 (1C), 146.76 (1C), 147.26 (1C), 147.38 (1C), 150.44 (1C), 154.04 (1C), 154.11 (1C), 155.51 (1C), 170.01 ($\underline{C}OOCH_3$). Anal. Found: C, 92.81; H, 1.25; N, 1.33%. Calcd for $C_{60}[CH(CH_2)_4NCHCOOCH_3]$: C, 93.25; H, 1.50; N, 1.60%. **4**: ^{1}H NMR (400 MH_Z, $CDCl_3$-CS_2) δ 3.42 (m, 2H), 3.91 (s, 3H, OCH_3), 3.95 (m, 1H), 4.04 (t, 1H), 4.15 (m, 1H), 4.69 (m, 1H), 5.25 (q, 1H, NCH), 5.54 (s, 1H, $NCHCOOCH_3$).