Synthesis of Fullerene Amino Acid Derivatives by Direct Interaction of Amino Acid Ester with C_{60}

Liangbing Gan,*,† Dejian Zhou,† Chuping Luo,† Haisong Tan,† Chunhui Huang,† Mujian Lü,‡ Jinqi Pan,‡ and Yi Wu§

State Key Laboratory of Rare Earth Material Chemistry and Applications, Peking University, Beijing 100871, China, Center of Instrumental Analysis, Department of Chemistry, Peking University, Beijing 100871, China, and Beijing Institute of Microchemistry, Beijing 100091, China

Received October 31, 1995⊗

Amino acid esters react with C_{60} both thermally and photochemically to give different products. Refluxing a mixture of C_{60} and glycine ethyl ester afforded $C_{60}(Me_2CHNHCHCOOEt)$ **1**, whereas irradiation of the same mixture produced C_{60}(EtOOCCHNHCHCOOEt) **2b** as the main product. Photochemical reactions between C_{60} and sarcosine esters yielded two pyrrolidine derivatives C_{60}-($CH_2N(Me)CHCOOR$) **3** and C_{60}(ROOCCHNHCHCOOR) **2** (R = Me, Et, CH_2Ph). Compound **2a** is also prepared from the photochemical reaction between C_{60} and iminodiacetic methyl ester in high yield. These ester derivatives are difficult to hydrolyze in excess mineral acids. The fullerene dicarboxylic acid C_{60}(HOOCCHNHCHCOOH) **5** is synthesized from the *tert*-butyl derivative C_{60}(^{t}-BuOOCCHNHCHCOO^{t}Bu) **4**. A possible radical reaction mechanism for the photochemical reactions is proposed which involves an unprecedented C−N bond breakage.

Chemical modification of fullerenes have been intensively explored because of their potential applications in many fields.[1] Among them amino acid fullerene derivatives are of special interest as biologically active compounds.[2] A few methods have been developed for the synthesis of C_{60} amino acid derivatives. Esterification of the alcohol group in 1,9-(4-hydroxycyclohexane)buckminsterfullerene gave α-amino acid derivatives in high yields.[3] Acetylation of peptide by a fullerene carboxylic acid afforded the first fullerene peptide.[4] Diazoamides add directly to C_{60} to form amino acid and amido derivatives.[5] Amidation of methanofullerene-61-carboxylic acid gave the glycine and phenylalanine derivatives.[6] All these amino acid fullerene derivatives are prepared by indirect methods, either by further derivatization of certain fullerene derivatives or by employing active precursors formed through the reaction of amino acids with other agents. Since amino acids have an amino group, it should be possible for them to directly react with fullerenes. We have recently reported that amino acids add directly to C_{60} in the presence of sodium hydroxide and have prepared highly water-soluble amino acid fullerene derivatives.[7] Like many other aminofullerene derivatives, only the multiaddition products are obtained from these reactions. Isomerically pure amino-fullerene derivatives are still rare despite the fact that a wide range of amines have been reported to react with C_{60}.[8,9] Monoadducts are obtained from the reaction between C_{60} and diamines, which are actually the dehydrated C_{60} derivatives.[10] The net result of these diamine additions is a loss of H_2 and formation of two N−C(fullerene) bonds. Leigh et al. reported the first monoaminated fullerene derivatives C_{60}-azacrown ether as an inseparable mixture of 1,2 and 1,4-adducts.[11] The structure of these adducts agrees with the original proposed mechanism by Wudl et al.[8] Here we report the direct reaction between amino acid esters and C_{60} and the characterization of several fullerene pyrrolidine derivatives.[12] The formation of these compounds are unexpected based on previous reports. An novel air-assisted radical reaction mechanism is proposed, in which both C−N bond breaking and bond formation processes are involved.

Thermal Reaction between C_{60} and Glycine Ethyl Ester

Amino acids exist as the zwitterion. They are soluble in water but insoluble in organic solvents such as toluene and CS_2 which are good fullerene solvents. Direct addition of amino acids to a fullerene in a homogeneous

† State Key Laboratory of Rare Earth Material Chemistry and Applications.
‡ Center of Instrumental Analysis.
§ Beijing Institute of Microchemistry.
⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1996.

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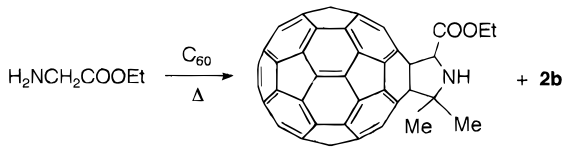
solution is thus not possible. Our previous work using a toluene/CH_3OH/H_2O ternary solvent only resulted in a mixture of products.[7,10] Amino acid esters are ideal alternatives to the amino acids. They are soluble in common polar organic solvents, and the carboxyl group is protected leaving the amino group exposed to react with the electrophilic fullerene.

The commercially available glycine ethyl ester hydrochloric acid was neutralized with 1 equiv sodium hydroxide in ethanol. The byproduct sodium chloride may be easily separated by centrifuging, but this step was not necessary as its presence had no noticeable effect on the subsequent reaction. The concentration of C_{60} in toluene is dilute so that addition of the glycine ester solution would not result in precipitation. We initially stirred the solution at room temperature for several days. Since the reaction proceeded sluggishly, we changed to refluxing, which led to the disappearance of the C_{60} purple color and the formation of a red solution. Chromatography on silica gel with toluene afforded a mixture containing mainly **1** and **2b**, which was then separated on neutral alumina with toluene. The products are further purified by crystallization in CH_2Cl_2/petroleum ether as crystalline solids.



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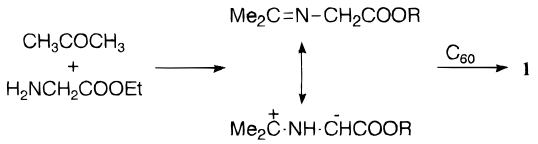
The ^1H NMR spectrum of **1** showed three methyl resonances. One of which is a triplet attributable to the ethoxyl group. Its coupling constant matches the quartet signals of the CH_2 at 4.3 ppm. Due to the presence of the chiral carbon on the five-membered ring the two methylene protons are nonequivalent. They appear as AB multiplets (J_{AB} = 12 Hz). For the same reason the two methyl groups on the pyrrolidine ring are nonequivalent at 2.14 and 2.16 ppm. The signal at 5.70 ppm is assigned to the only ring proton. The influence of the fullerene is evident from the downfield shifts of both the methyl and the ring protons. In accordance with the ^1H NMR spectrum, the ^{13}C NMR spectrum of **1** showed three methyl carbons at 14.27, 28.03, and 29.30 ppm. For the C_{60} skeleton, there are more than 44 signals some of which are overlapped. The carboxyl carbon appeared at 169.04 ppm as a singlet. FDMS (field desorption MS) and FABMS data provided another strong evidence for the structure of **1** as shown above. In the FDMS spectrum the molecular ion peak with 85% relative intensity is the only peak beside the C_{60} fragment. The FABMS is less indicative; the molecular ion peak is weak.

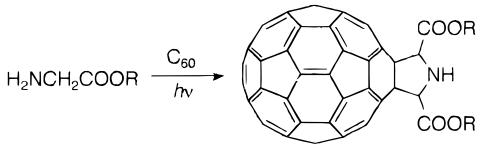
Compound **1** is the main isolated product in the above thermal reaction. The yield of **2b** is only about one-fourth of that of **1**. The isolation of **1** is unexpected. It seems to suggest the presence of acetone in the ethanol, and the acetone reacts with glycine ester to form a 1,3-dipolar intermediate as in the following equation. The addition of the intermediate to C_{60} is analogous to Prato's method, where glycine *tert*-butyl ester and paraformaldehyde was refluxed with C_{60}.[13] Our work shows acetone is active enough and may be used in place of paraformadehyde in Prato's reaction. However, the yield of **1** and the reaction rate showed almost no change when some acetone was added to the glycine ethyl ester reaction solution. Perhaps acetone is not the limiting reagent, or compound **1** is formed through other mechanisms without the involvement of acetone. Since the overall yield of **1** is less than 5%, formation of other unidentified products may have provided the reactive species leading to compound **1**. Our effort to isolate all the products have so far been unsuccessful. The ^1H NMR spectrum of the mixture is rather complex, suggesting the presence of at least five products.



Photochemical Reactions

C_{60} is highly photosensitive and has a rich photochemistry.[14] In the above thermal reaction the container flask was wrapped with aluminum foil. During several different runs, it was noticed that when the flask was unwrapped and exposed to lab light, the reaction proceeded much faster. Intrigued by this observation we next explored the photolysis of the reaction mixture.

The C_{60} and glycine ester solution was mixed using the same procedure as the thermal reaction. The solution was then irradiated starting at room temperature. No cooling was applied to the reaction flask. The heat from the lamp was found to accelerate the reaction. Under the same conditions a previously ice-cooled solution changed color at a much slower rate. At the end of the reaction the temperature of the solution is close to reflux. Depending on the irradiation source and the amount of reactants, the reaction time varies slightly. Usually the reaction was stopped after the color had changed to red for 5−10 min. Prolonged irradiation gave more byproducts.



2a R = Me
2b R = Et
2c R = CH_2Ph

Various light sources may be used for the reaction. Placing the solution in an Erlenmeyer flask on top of an overhead projector is very effective. This is a good experiment for class demonstration purposes. The starting solution mixture is stable enough to be carried around, and there is a readily visible change of color at a reasonable speed. Likewise an ordinary household tungsten light bulb is also efficient. But the luminescent energy-saving light tube gave poor results. We normally use two 500 W luminescent high pressure Hg light bulbs, which produces mainly visible light. Both the heat and light intensity from these bulbs are very strong.

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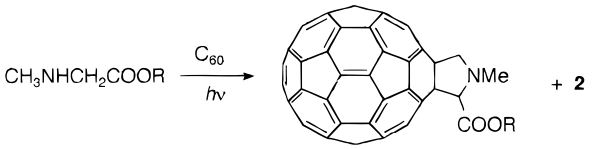
Separation of the products is straightforward, much easier than the thermal reaction. Chromatography on a short silica column afforded compound **2b** in 60% yield (based on converted C_{60}). In this photochemical reaction, compound **2b** is the only isolated product. No compound **1** was observed on the silica column. Obviously the thermal and the photochemical reactions follow different mechanisms.

The photochemical reaction may be extended to other amino acids. The glycine methyl ester reacts similarly and gave an even better result. The reaction is faster and the yield is higher. When C_{60} was irradiated with the benzyl ester, the reaction was slower than that of the ethyl ester. This order of reaction rate matches their steric hindrance increasing from methyl to benzyl. All the three glycine derivatives can yield crystalline solids upon slow evaporation in CH_2Cl_2/petroleum ether. The crystallization tendency of the methyl derivative **2a** is higher than the ethyl derivative **2b** which in turn is higher than the benzyl derivative **2c**. More crystals may be produced for **2a** than **2b** and **2c** from a certain amount of the powder material.

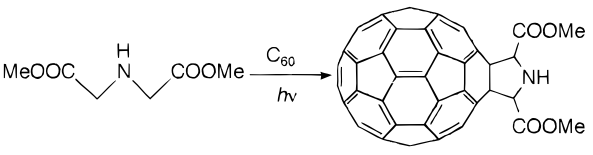
Sarcosine has one more methyl group than glycine. Due to the presence of the methyl group, its amino group is more basic and also more crowded. The two factors have opposite effects when the sarcosine reacts with C_{60}. A mixture of sarcosine methyl ester and C_{60} was prepared in exactly the same way as the glycine analog. The solution was irradiated also under the same conditions. The color of the solution changed in about 15 min, and the reaction was stopped after another 5 min. This is about twice as fast as the glycine ester reaction. So the methyl group on the nitrogen had a more positive than negative effect on the reaction rate.



3a R = Me
3b R = Et
3c R = CH_2Ph

Separation of the products afforded two compounds which are easily separated on a short column. Compound **3a** is eluted before compound **2a**, which is understandable since there are two carboxyl groups in **2**. The sarcosine reaction was also extended to the ethyl and the benzyl esters. As in the case of the glycine esters, the methyl ester gave the best results in terms of reaction rate and yield.

The photochemical addition of iminodiacetic methyl ester to C_{60} provides a third route for the synthesis of **2a**.



Spectroscopic Data and the Structure of the Pyrrolidine Derivatives 2

The structure of the pyrrolidine derivatives are determined by MS, IR, UV-vis, and ^1H and ^{13}C NMR spectroscopy. Various attemps were made to obtain the mass spectra such as EI, FAB, and FD. In most cases FDMS gave the best result for these fullerene derivatives. It generates moderately intense molecular ion signals and the expected fragmentation product C_{60}. The two peaks appear to be the only apparent signals on the spectra. Other peaks are very weak and hardly noticeable. FABMS gave a poor noise/signal ratio. The IR spectra were obtained by the microscope IR method, which can measure the crystalline solid directly without any matrix. The N−H stretching is the only band in the 3000−4000 cm^{-1} region on the IR spectrum. The carbonyl vibration of the ester group is the most prominent band at around 1746 cm^{-1} (Figure 1).

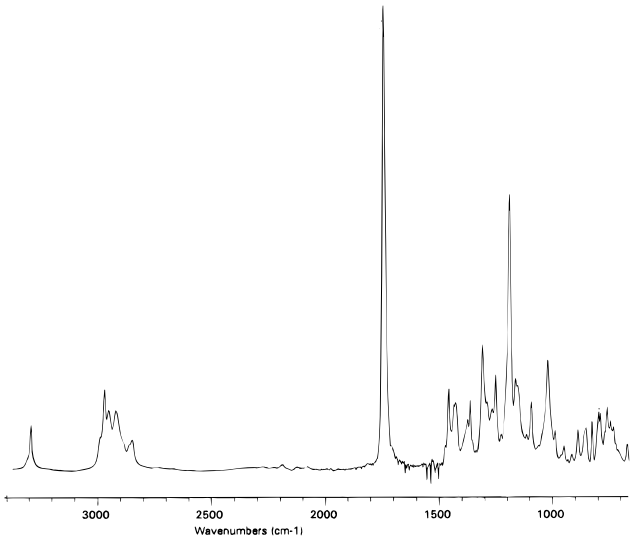
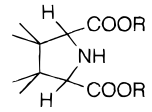
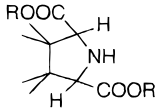


Figure 1. FTIR spectrum of C_{60}(MeOOCCHNHCHCOOMe) **2a**.

The ^1H NMR spectrum of **2a** showed three resonances at 3.89, 5.55, and 6.06 ppm in a 3.54:1:0.19 ratio (Figure 2). The first peak at 3.89 is obviously due to the methyl group, and the one at 5.55 is due to the methine proton. But the ratio between the two remained as 3.54:1 instead of the expected 3:1 for several different samples from different reaction runs. It is not due to an NMR integration deviation. It rather is a result of the cis- and trans-isomers in compound **2a**. For the trans-isomer, the methine proton is at 5.55 ppm, and for the cis-isomer it is at 6.06 ppm. The methoxy groups of the two superimposed at 3.89 ppm. Thus the integral appears reasonable. For the trans-isomer the methyl to methine ratio is 3:1, and for the cis-isomer 0.54:0.19 (also roughly 3:1).



Cis-isomer of **2a**



Trans-isomer of **2a**

Separation of the two is quite difficult. Normal chromatography on silica gel or alumina and repeated recrystallization did not produce any change on the ratio between the two. But the two isomers are not an equilibrium mixture. Preparative HPLC on a Synchropak silica column gave a cis-isomer-enriched sample. This sample consists of slightly more cis- than trans-isomer. The ratio between the two methine peaks at 5.55 and 6.06 ppm is 0.57:0.48 (Figure 2). This result further supports the existence of two isomers.

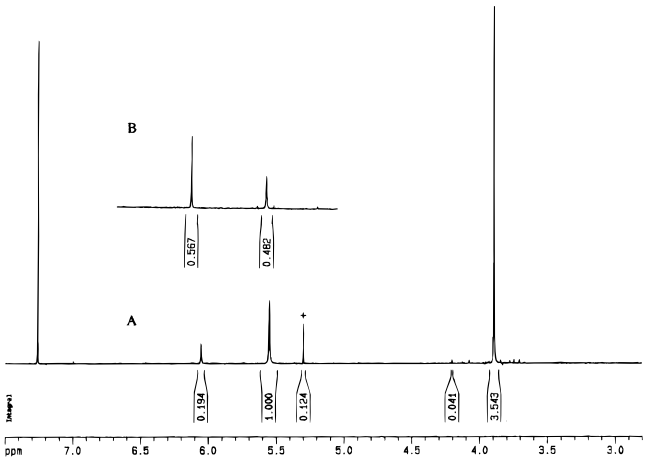


Figure 2. ^{1}H NMR spectrum of C_{60}(MeOOCCHNHCHCOOMe) **2a** in $CDCl_3$ (A) before HPLC separation, (B) after HPLC separation and + due to CH_2Cl_2.

The ^{13}C NMR spectrum of **2a** also indicates a cis- and trans-isomer mixture. All the major peaks are coupled with a small peak or shoulder. There are two methoxy carbons at 52.68 and 52.96 ppm, two methine carbons at 73.85 and 73.88 ppm, two fullerene sp^3 carbons at 77.16 and 76.15 ppm, and two carbonyl carbons at 169.18 and 170.91 ppm. The intensity ratio is about 5:1, in agreement with the ^{1}H NMR integral ratio. A total of 29 peaks could be counted for the major species in the 130−160 ppm region. Adding the one on the 6,6-junction, the total is 30, thus suggesting a C_2 symmetry. This confirms the assignment of the major species as the trans-isomer which has a C_2 symmetry. The cis-isomer has a C_s symmetry. For the C_s symmetry there should be 32 fullerene carbon peaks. Since the peaks of the minor species are weak and some are buried in the major peaks, it is not possible to locate all the 32 signals for the cis-isomer.

The spectra of **2b** and **2c** are more complex due to the increased size of the alkoxy groups. In both cases pure isomers are obtained as is evident from the ^{1}H and ^{13}C NMR spectra. On the ^{1}H NMR spectrum of **2b**, there are two methylene proton resonances at 4.29 and 4.21 ppm. They appear as a doublet of quartets due to coupling to the methyl group and geminal coupling between them. Similarly the two methylene protons of the benzyl group in compound **2c** are also nonequivalent. In this case they appear as two doublets at 5.28 and 5.39 ppm. The coupling constants for the two methylene protons, 10.8 Hz for **2b** and 12.0 Hz for **2c**, are within the range for geminal coupling. The methine protons of **2b** and **2c** exhibit almost the same chemical shift at 5.48 and 5.52 ppm, respectively. These values are rather close to the trans-isomer of **2a** (5.55 ppm). So these two compounds are likely to be the trans-configuration. The ^{13}C NMR spectra also supports this conclusion. The total number of fullerene skeleton peaks is 30 in both compounds, indicating the C_2 symmetry.

Compounds 3: Methanofullerene or Fulleropyrrolidine?

Both the two structures depicted below are compatible with all the spectroscopic data. The two structures, methanofullerene **A** and fulleropyrrolidine **B**, are constitutional isomers. Since they both attach to the C_{60} skeleton at the 6,6-junction, their UV-vis spectra would be similar. In addition they have the same functional groups. Even though the three-menbered ring and the five-menbered ring should exhibit different IR stretching bands, these bands are weak and cannot be used as a strong evidence. So elemental analysis data, FDMS, UV-vis, and FTIR could not differentiate the two structures.

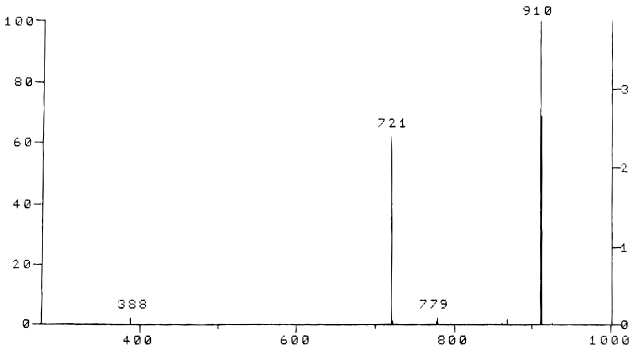
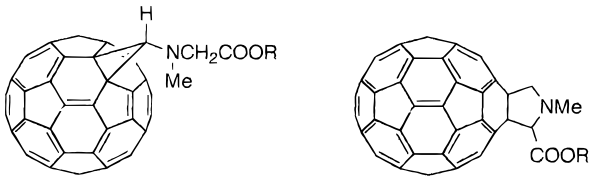


Figure 3. FD mass spectrum of $C_{60}(CH_2N(Me)CHCOOCH_2$-Ph) **3c**.



A **B**

The UV-vis spectra are almost identical for all the three monoadducts **3**. They all exhibit a sharp band at 429 nm, which is characteristic for the 6,6 adducts. Unlike those of the compounds **2**, the IR spectrum of **3** showed no N−H band. There are two carbonyl stretching bands for compounds **3**. This is probably due to rotational isomers in the solid state. The FT-Raman spectrum of **3a** shows only the C_{60} skeleton signals as would be expected. The most intensive band at 1461 cm^{-1} is assigned to the totally symmetric pentagonal pinch mode. Compared to the FT-Raman spectrum of **2a** and pure C_{60} there is negligible change, so the different substituent does not affect the vibration of the C_{60} skeleton significantly. The FDMS spectra of **3** showed an interesting pattern. The relative intensity of the molecular ion signals increases from the methyl **3a** (Figure 3) to ethyl **3b** and to benzyl **3c**. For the methyl derivative **3a**, the molecular ion peak is only 9% (relative to the base peak of C_{60}), for the ethyl it is 95%, and for the benzyl it becomes the base peak. The same pattern is also observed in the compounds **2**.

The two structures are also expected to exhibit a similar pattern and chemical shifts on the NMR spectra. For the fulleropyrrolidine structure **B**, the spectra are assigned as the following. The two methyl resonances at 3.03 and 3.88 ppm on the ^{1}H NMR spectrum of **3a** are due to the NCH_3 and OCH_3, respectively. The methine proton appears at 4.85 ppm as a singlet. The methylene protons are nonequivalent due to the chiral carbon on the five-membered ring and appear as AB quartet at 4.28 and 4.97 ppm (J_{AB} = 9.6 Hz). The ^{1}H NMR spectra of **3b** and **3c** show a similar pattern. Changing from the methyl to benzyl esters, the steric hindrance increases. In case of the ethyl derivative **3b**, the two methylene protons of the ethyl group are equivalent due to the rapid rotation about the O−CH_2CH_3 bond. Whereas in com-

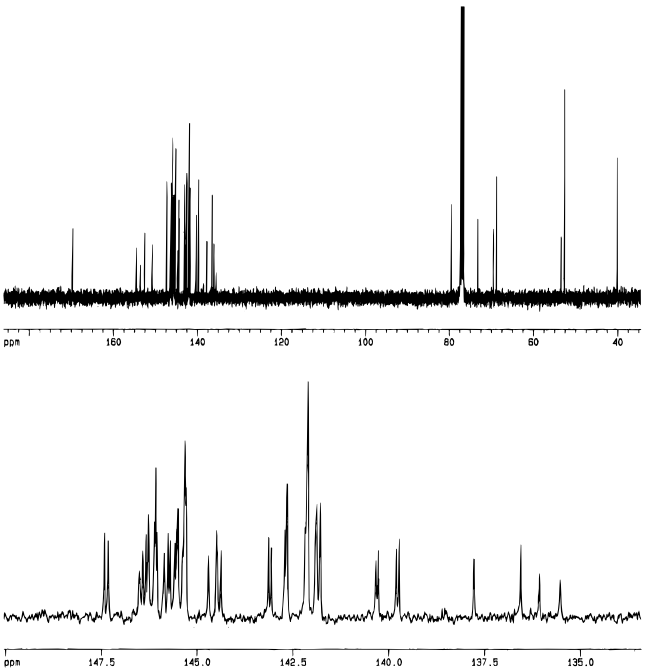


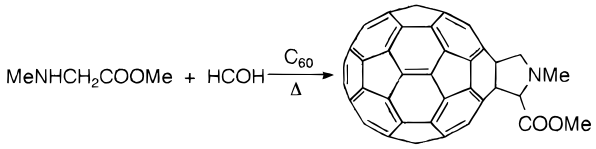
Figure 4. ^{13}C NMR spectrum of $C_{60}(CH_2N(Me)CHCOOMe)$ **3a** (top). Expanded spectrum of $C_{60}(CH_2N(Me)CHCOOMe)$ **3a** (bottom).

pound **3c**, the same rotation about the O−CH_2Ph bond is hindered and the two methylene protons on the benzyl group become nonequivalent at 5.30 and 5.37 ppm.

The methanofullerene structure **A** could also account for all the resonances on the same spectra. First, the two methyl groups here should be quite close to the above structure **B**. Second the chemical shift of the methine proton of methanofullerene derivatives has been reported to be in the range from 3.9 to 5.1 ppm.[15,16] For example the chemical shift of the methine proton of C_{60}(HCCONHCH(CH_2Ph)COOMe) is 4.69 ppm.[6] Thus the singlet at 4.85, 4.73, and 4.85 for **3a**, **3b** and **3c** could be assigned in both structures as the only methine proton. The two methylene protons in structure **A** would be equivalent if both the inversion on the nitrogen and the rotation around N−CH (methanocarbon) bond are fast on the NMR time scale. Structure modeling indicates the inversion is probably possible, but the rotation is severely hindered, so the nitrogen acts as a virtual chiral center, leading to the two nonequivalent methylene protons. Therefore ^1H NMR could not differentiate the two structures.

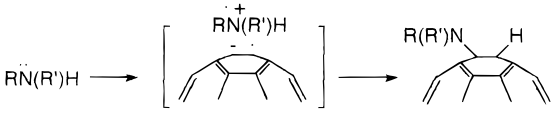
The situation in the ^{13}C NMR spectra is the same. The ester carbonyl of **3a** appears at 169.7 ppm as a single peak, indicating the presence of just one carboxyl group (Figure 4). This supports the interpretation of the two carbonyl stretching bands on the solid state IR spectrum as a result of rotational isomers rather than constitutional isomers. A DEPT experiment located two CH_3 peaks at 40.1 (NCH_3), 52.6 (OCH_3), one CH_2 at 68.8, one CH at 79.5, and two quaternary carbons at 69.5 and 73.2 ppm. This assignment is augmented by a COSY experiment, which indicates the two doublets at 4.28 and 4.97 ppm in the ^1H NMR spectrum of **3a** correlate to just one carbon at 68.8 ppm. There are 45 well-separated peaks in the 130−160 ppm region integrating as 58 fullerene carbons. This suggests a C_1 symmetry in agreement with the presence of the chiral carbon in the fulleropyrrolidine structure **B**, which is also true for the methanofullerene structure **A** since the above mentioned virtual chiral center nitrogen interrupts any symmetry in the molecule.

It seems only a molecular crystal structure could establish the structure for compounds **3**. Unfortunately the crystals we obtained are not suitable for X-ray analysis. To solve the problem we carried out the following reaction, which provides an indirect evidence that strongly favors the fulleropyrrolidine structure **B**. The mechanism of this reaction has been well studied, and a host of derivatives has been reported by the method.[13] The product obtained here exhibits the same spectroscopic data as those of **3a**.



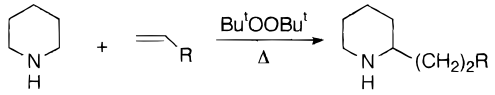
Mechanism Consideration

To explain the formation of the products a possible pathway is shown in Scheme 1. The first step generates three radicals. The aminium radical results from a single electron transfer from the amino group to C_{60}. When they first reported the C_{60} amine addition reaction, Wudl et al. proposed that the addition to C_{60} is stepwise and involves the electron transfer and radical formation.[8] The formation of the aminium radical reflects this idea.



The two carbon-centered radicals CH_2NHCH_2COOR and $CH_3NHCHCOOR$ formed in the first step are quite likely to be produced by singlet oxygen, which could be generated by C_{60} in very high yield.[17] Since our reaction was carried out without the excursion of air, enough oxygen is present. The involvement of oxygen is confirmed by a comparative study. Under exactly the same conditions the sample under atmosphere changed color in 20 min, the N_2-bubbled sample changed color in about 40 min and the air-free sample did not react. The solution wrapped in dark remained almost unchanged after 3 days.

Amines have been reported to form α-carbon-centered radicals selectively under certain conditions. Urry et al. found that the reaction of terminal olefins with amines in the presence of radical initiator gives the 1:1 adduct resulting from α-abstraction.[18] This supports the formation of the two carbon-centered radicals in step i.



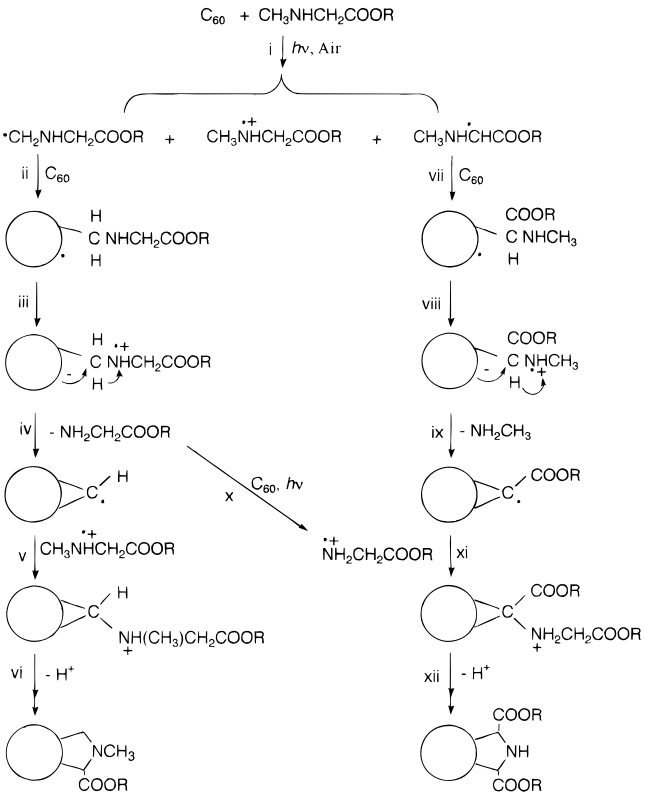
(15) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Golgschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492. Reviw of methanofullerenes: Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243.

(16) Wudl, F. *Acc. Chem. Soc.* **1992**, *25*, 157.

(17) Tokuyama, H.; Yamago, S.; Nakamura, E.;Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918. Orfanopoulos, M.; Kambourakis, S. *Tetrahedron Lett.* **1994**, *35*, 1945.

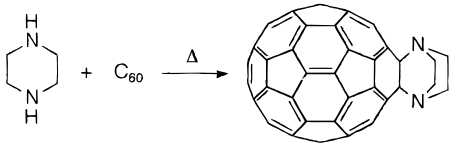
(18) Kochi, K. J. *Free Radicals*; John Wiley & Sons, Inc.: New York, 1973; Vol 2, Chapter 21, Urry, W. H.; Juveland, O. O.; Stacey, F. W. *J. Am. Chem. Soc.* **1952**, *74*, 6155.

Scheme 1



In steps ii and vii the carbon-centered radicals add to the electrophilic C_{60}. The same addition of the aminium radical to C_{60} is not observed (judging from the isolated products), presumably due to its unfavorable positive charge and the strong electrophilicity of C_{60}. Step iii is another electron transfer from the amine to the C_{60} fragment to form the zwitterion radical. The C−N bond cleavage and the release of glycine at step iv is unusual. Many pathways of radical fragmentation are known. To our knowledge there is no other process similar to step iv. Its unprecedented nature may be related to the unique properties of C_{60}. The reaction is very slow at room temperature and moderate heating is required. Perhaps it is in this endothermic C−N bond breaking step that heating is necessary. The driving force for the rearrangement at steps vi and xii may be the more stable five-menbered ring. Several other products are likely to be produced based on the steps in Scheme 1 such as the proton abstraction products by the intermediate radicals, the known methanofullerenes $C_{60}(CH_2)$[15] and $C_{60}(HCCOOR)$,[6] and the amine addition product $C_{60}(H)(CH_3NCH_2COOR)$ as we initially expected. We noticed indeed other minor species on the silica column, but their yields are very low. The combined yield of **2** and **3** is about 64% in the sarcosine reaction, representing a major portion. The formation barrier for the two must be much lower compared with others', or other products are thermally less stable and they may even undergo further reactions in the photochemical conditions.

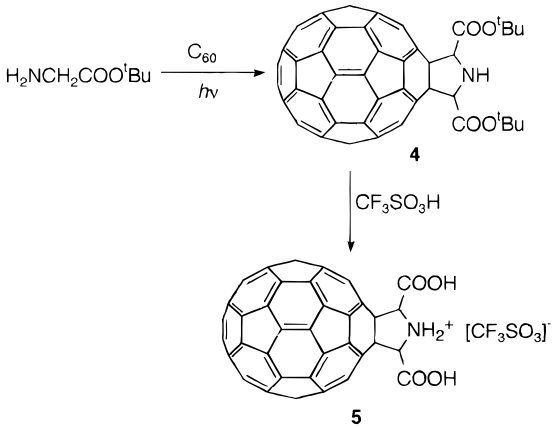
The yield of compounds **2** is much less than that of **3** in the sarcosine reaction. This is reasonable considering that its formation depends on the glycine ester released at step iv. The pyrrolidine derivative **2** can also be prepared from the reaction between glycine ester and C_{60}. Photolysis of C_{60} with iminodiacetic methyl ester $HN(CH_2COOMe)_2$ provides a third route to compound **2a**. Pathways similar to those in Scheme 1 can be envisioned for the two reactions. In case of the iminodiacetic methyl ester, a diradical centered on the two ethylene carbons can add to C_{60} and form **2a** in one step. But in the actual process it is more likely that the reaction is still stepwise, i.e., an ethylene carbon-centered monoradical adds to C_{60} and then the other ethylene carbon becomes a radical and adds to the adjacent C atom on C_{60}. There is no C−N bond-breaking process involved, and the reaction results in a net loss of H_2, reminiscent of the addition of piperazine to C_{60} (reaction below).[10] Free radical addition to C_{60} has been extensively studied by EPR.[19]



Preparation of Fullerene Dicarboxylic Acid

Fullerene carboxylic acid is of great interest in the investigation of the biological activity of fullerenes. The carbonyl group can be easily attached to other functional groups or fragments producing specific tailor-made fullerene derivatives for different investigation purposes. Synthesis of such compounds is usually achieved through the hydrolysis of its ester precursor. Since C_{60} reacts with hydroxide to form fullerols, saponification is not suitable for the hydrolysis process. Hirsch et al. employed NaH in toluene and successfully hydrolyzed malonic ester derivatives of C_{60}.[20] Prato and co-workers hydrolyzed the *tert*-butyl ester with excess trifluoromethane sulfonic acid.[4] Isaacs and Diederich used BBr_3 and toluene-4-sulfonic acid.[6]

Hydrolysis of compounds **2** and **3** is difficult under normal conditions. All the mineral acids gave poor results. For this reason we prepared the *tert*-butyl ester analog of compounds **2** according to basically the same procedure. Compared to the derivatives with less bulky groups, the *tert*-butyl derivative **4** needs more vigorous conditions. The reaction was heated at 60 °C besides irradiation, and it took more than 2 h for the solution to change from purple to red. Despite this the yield is still satisfactory at 60% based on converted C_{60}.



As in the methyl derivative **2a**, there are two isomers for compound **4**, namely the cis- and trans-isomers. The ^1H NMR showed strong methyl resonances at 1.46 ppm

(19) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Wasserman, E. J. *J. Chem. Soc., Perkin Trans. 2*, **1992**, 1425 and refereneces cited therein.

(20) Lamparth, I.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1727.

integrating as 18 protons, coupled with a small peak at 1.47 ppm. There are also two methine peaks at 5.26 and 5.75 ppm. The ratio between the two is about 4:1. The IR spectrum exhibits a carbonyl stretching band at 1731 cm^{-1}.

The *tert*-butyl ester **4** was hydrolyzed in a mixture of CS_2 and dioxane with excess trifluoromethyanesulfonic acid. The solution remained clear throughout the reaction with no visible change. The dicarboxylic acid **5** is moderately soluble in ether, dioxane, and acetone. It is very soluble in dimethyl sulfoxide. The ^1H NMR spectrum of **5** in deuterated DMSO showed the disappearance of the *tert*-butyl group. There are two singlets at 5.68 and 6.91 ppm corresponding to the trans- and cis-isomers. The ratio between the two is about 5:1. This is slightly different from the ratio in the esters, probably as a result of repeated purification processes after the hydrolysis. Because the deuterated solvents are different in measuring the ^1H NMR spectra, the small chemical shift of the methine protons before and after hydrolysis are insignificant. The ^{13}C NMR spectrum of **5** shows a similar pattern to that of **2a**, and the chemical shifts exhibit little change. For the trans-isomer the two fullerene sp^3 carbons appear at 77.03 ppm, the C-H carbon at 72.7 ppm, and the carboxyl carbon at 170.37 ppm. There are 29 fullerene skeleton carbon signals in the range from 135 to 153 ppm.

Experimental Section

General. Reagents were all reagent-grade commercials. C_{60} includes traces of solvents. All the reactions were carried out under atmosphere without any special caution to exclude air except in the mechanistic study to determine the role of oxygen.

Preparation of 1. Glycine ethyl ester hydrochloric acid (476 mg, 3.41 mmol) and sodium hydroxide (137 mg, 3.43 mmol) was added to 40 mL of ethanol (95%), and the mixture was treated with an ultrasonic cleaner for 2 min. The suspended solution (pH around 8.5) was added dropwise to a C_{60} (120 mg, 0.17 mmol) toluene solution (120 mL). The resulting mixture was refluxed under stirring for 24 h. The red solution was evaporated, and the residue was added to a silica gel column (10 cm long, 1.5 cm in diameter). Toluene first eluted unreacted C_{60}. Then a mixture of toluene/ethanol (3:1) eluted a red band. The red portion was evaporated and rechromatographed on neutral alumina. Toluene first eluted compound **1**, followed by compound **2b**. Chloroform could wash out another band, the structure of which is yet to be defined. Crystallization of **1** from CH_2Cl_2/petroleum ether gave a crystalline solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.25 (q, 3H), 2.14 (3H), 2.16 (3H), 4.26 (d of q, 1H), 4.41 (d of q, 1H), 5.70 (1H). FT-IR (microscope) 3295, 3281, 2973, 2955, 2928, 1737, 1473, 1457, 1438, 1429, 1383, 1371, 1329, 1294, 1263, 1248, 1233, 1217, 1196, 1150, 1123, 1095, 1072, 1029, 849, 821, 804, 795, 782, 760, 744, 734, 721, 674 cm^{-1}. FDMS (*m*/*z*) 865 (86%), 721 (100%, C_{60}^+ + H). Anal. Calcd for C_{60}[Me_2-CNHCHCOOMe]: C% 93.15; H% 1.52; N% 1.62; found: C% 92.10; H% 1.33; N% 1.45.

General Procedure for the Photochemical Reactions. All the photochemical reactions are carried out in a similar way. The following describes the sarcosine methyl ester reaction as an example. Sarcosine methyl ester hydrochloric acid $MeHNCH_2COOMe{\cdot}HCl$ (279 mg, 2.0 mmol) and sodium hydroxide (80 mg, 2.0 mmol) were added to 15 mL of methanol, and the mixture was treated with an ultrasonic cleaner until all the sarcosine ester crystals disappeared. The suspended solution (pH around 8.5) was added to a C_{60} (72 mg, 0.10 mmol) toluene solution (60 mL) in a normal one-neck flask (probably equivalent to a Pyrex flask). The resulting mixture was irradiated with a luminescent high pressure Hg light bulb (500 W, ordinary street light bulb). The solution was stirred continuously during the photolysis. No cooling was applied, and the solution was allowed to warm up from the heat of the light bulb. After 20 min, the solution changed from purple to red (similar to the mixture of C_{60} and C_{70} in toluene). The solution was evaporated on a rotavapor. The residue was extracted with toluene and added onto a silica gel chromatography column (8 cm long and 2.4 cm in diameter). Toluene first eluted 0.03 mmol of unreacted C_{60} (30%) and then 0.035 mmol of **3a** (35% overall, 50% yield based on converted C_{60}). Compound **2a** was followed in about 10% overall yield. Finally a mixture of toluene/methanol (2:1) eluted several other unidentified products. The bands are all well separated. Both compound **2a** and **3a** were crystallized as black crystalline solids from CH_2Cl_2/petroleum ether by slow evaporation in air.

The amount of sodium hydroxide is important and the pH of the sarcosine ester solution before mixing with C_{60} should be no more than 9.0 to avoid hydroxylation of C_{60}. The glycine ester reactions were carried out according to the same procedure, the reaction was stopped when the solution changed from purple to red. All of the isolated products were obtained as crystalline solids from slow evaporation in CH_2Cl_2/petroleum ether.

Determination of Singlet Oxygen Involvement. A reaction mixture containing C_{60} and H_2NCH_2COOMe was prepared as described above and then divided into four equal aliquots and placed in four similar glass tubes. Two tubes were wrapped in dark, one was bubbled with N_2 for 25 min, and one was degassed by a repeated freeze-pump-thaw sequence. One of the two wrapped tubes was then unwrapped and irradiated with the two N_2-filled tubes side by side. The air-containing tube changed color in 20 min, the N_2 bubbled tube in 40 min, and the tube degassed by freeze-pump-thaw sequence showed hardly any change after 1 h. This air-free tube was then opened, swirled in air, and reirradiated. It changed color in 20 min. The another wrapped tube showed no observable change after stored at rt for 3 days.

2a. ^1H NMR (400 MHz, $CDCl_3$): δ 3.89 (3.54H), 5.55 (1H), 6.06 (0.19H) (due to about 5:1 inseparable trans−cis isomers). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.18 (COO), 152.18 (2C), 149.83 (2C), 147.17 (2C), 146.42 (2C), 146.35 (2C), 146.16 (2C), 146.05 (4C), 145.54 (2C), 145.47(2C), 145.41(2C), 145.30 (2C), 145.04 (2C), 144.43 (2C), 144.29 (2C), 143.08 (2C), 143.21 (2C), 142.77 (2C), 142.75 (2C), 142.33 (4C), 142.18 (2C), 142.08 (2C), 142.00 (2C), 141.81 (2C), 139.96 (2C), 139.86 (2C), 136.79 (2C), 135.61 (2C), 77.16 (2C), 73.88 (HC−N), 52.96 (OMe). FT-IR (microscope): 3297, 2975, 2956, 2924, 1746, 1459, 1437, 1430, 1378, 1377, 1366, 1312, 1292, 1270, 1254, 1191, 1164, 1094, 1021, 855, 829, 799, 792, 761, 747, 733 cm^{-1}. FT-Raman: 1571, 1463, 523, 488, 463, 271, 255 cm^{-1}. FABMS (*m*/*z*): 817 (32%, M^+ − 2OMe), 720 (100%, C_{60}^+). Anal. Calcd for C_{60}-[$NH(CHCOOMe)_2$]·$0.5H_2O$: C% 89.19; H% 1.11; N% 1.56; found:C% 89.15; H% 0.90; N% 1.63.

2b. ^1H NMR (400 MHz, $CDCl_3$): δ 1.26 (t, 3H), 4.28 (d of q, 1H), 4.41 (d of q, 1H), 5.48 (1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 168.71 (COO), 152.32 (2C), 149.84 (2C), 147.11 (2C), 146.40 (2C), 146.30 (2C), 146.00 (4C), 145.60 (2C), 145.50 (2C), 145.44 (2C), 145.35 (4C), 145.24 (2C), 144.40 (2C), 144.26 (2C), 143.17 (2C), 143.05 (2C), 142.73 (4C), 142.32 (2C), 142.13 (2C), 142.00 (2C), 141.98 (2C), 141.75 (2C), 139.83 (2C), 139.61 (2C), 136.75 (2C), 135.75 (2C), 77.24 (2C, SP^3), 73.63 (2CH), 62.33 ($2CH_2$), 14.31 ($2CH_3$). (DEPT data): 14.31 ($2CH_3$), 62.33 ($2CH_2$), 73.63 (2CH), 77.24 (2C). FT-IR (microscope): 3297, 2975, 2957, 2926, 1747, 1541, 1459, 1437, 1430, 1378, 1366, 1358, 1312, 1292, 1270, 1254, 1229, 1191, 1164, 1155, 1115, 1094, 1021, 990, 890, 856, 828, 799, 792, 773, 761, 746, 744, 733, 723 cm^{-1}. FDMS (*m*/*z*): 908 (8%, M^+ + 1), 721 (100%, C_{60}^+ + H). UV-vis: 257.0, 311.4, 428.0, 690.4 nm. Anal. Calcd for C_{60}[$NH(CHCOOEt)_2$]·($1.5H_2O$): C% 87.37; H% 1.81; N% 1.33; found: C% 87.84; H% 1.77; N% 1.15.

2c. ^1H NMR (400MHz, $CDCl_3$): δ 5.28 (d, 1H), 5.39 (d, 1H), 5.52 (1H), 7.20−7.26 (m, 2.5H), 7.27−7.30 (m, 2.5H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 168.62 (COO), 152.06 (2C), 149.42 (2C), 147.04 (2C), 146.32 (2C), 146.29 (2C), 146.26 (2C), 145.96 (2C), 145.91 (2C), 145.52 (2C), 145.48 (2C), 145.34 (2C), 145.28 (2C), 145.17 (2C), 144.96 (2C), 144.29 (2C), 144.17 (2C), 142.90 (2C), 142.62 (4C), 142.23 (2C), 142.15 (2C), 142.05 (2C), 141.96 (2C),

141.83 (2C), 141.55 (3C), 139.56 (2C), 136.63 (2C), 135.48 (2C), 134.53 (2C), 129.43 (Ar, 2CH), 128.94 (Ar, CH) , 128.66 (Ar, 2CH), 77.12 (SP^3, 2C), 73.14 (2CH), 68.12 ($2CH_2$). (DEPT data): 68.05 ($2CH_2$), 73.14 (2CH), 128.66 (2CH), 128.94 (1CH), 129.43 (2CH). FDMS (*m*/*z*): 1032 (33%, $M^+ + 1$), 721 (100%, $C_{60}^+ + H$). Anal. Calcd for $C_{60}[NH(CHCOOCH_2Ph)_2]\cdot H_2O$: C% 89.23; H% 1.81; N% 1.33; found: C% 89.42; H% 1.77; N% 1.15.

3a. ^1H NMR (400 MHz, $CDCl_3$): δ 3.03 (3H), 3.88 (3H), 4.28 (d, 1H, $J = 9.6$ Hz), 4.85 (1H), 4.97 (d, 1H, $J = 9.6$ Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.82 (COO), 154.59, 153.63, 152.63, 150.81, 147.43, 147.33, 146.51, 146.43, 146.35, 146.29, 146.26, 146.13, 146.10 (2C), 146.06, 145.87, 145.77, 145.71, 145.59, 145.55 , 145.51 (2C), 145.38, 145.34 (3C), 145.30 (2C), 144.71, 144.50, 144.47, 144.38, 143.14 (2C), 143.07, 142.72, 142.65 (3C), 142.19, 142.15, 142.12 (4C), 141.91, 141.89 (2C), 141.79 (2C), 140.34, 140.28, 139.80, 139.73, 137.78, 136.55, 136.06, 135.53, 79.55 (CH), 73.24 (sp^3, C), 69.54 (sp^3, C), 68.84 (CH_2), 53.44 (CH_2Cl_2), 52.63 (OMe), 40.09 (NMe). FT-IR (microscope): 2947, 2839, 2783, 1755, 1737, 1463, 1451, 1431, 1371, 1344, 1335, 1284, 1248, 1216, 1182, 1127, 1110, 1095, 1065, 1032, 997, 951, 939, 921, 910, 901, 856, 773, 769, 764, 749, 739, 713, 697, 677, 668 cm^{-1}. FT-Raman: 1570, 1461, 511, 488, 452, 272, 255 cm^{-1}. FDMS (*m*/*z*): 835 (9%, M^+), 720 (100%, C_{60}^+). Anal. Calcd for $C_{60}CH_2(Me)NCHCOOMe\cdot 0.5H_2O$: C% 92.41; H% 1.19; N% 1.66; found C% 92.43; H% 1.12 ; N% 1.52.

3b. ^1H NMR (400 MHz, C_6D_6/CS_2): δ 1.00 (t, 3H), 2.77 (3H), 3.90 (d, 1H), 4.12 (q, 2H), 4.64 (d, 1H), 4.73 (1H). ^{13}C NMR (100.6 MHz, C_6D_6/CS_2): δ 169.06(COO), 155.41, 154.94, 153.98, 151.69, 147.77, 147.68, 147.15, 146.80, 146.72 (2C), 146.68, 146.62, 146.49, 146.44 (3C), 146.31, 146.16, 146.10, 146.05 (3C), 145.91, 145.89, 145.79, 145.71 (2C), 145.67, 145.11, 144.94 (2C), 144.87, 143.53 (3C), 143.15, 143.09 (3C), 142.67, 142.62 (2C), 142.54 (3C), 142.40, 142.33, 142.21 (3C), 140.72, 140.66, 140.11, 139.94, 138.33, 137.06, 136.56, 136.00, 79.05 (CH), 73.86(C, SP^3), 70.14 (C, SP^3), 68.29 (CH2), 61.36 (CH_2), 39.13 (N-CH_3), 14.52 (C-CH_3). FT-IR (microscope): 2975, 2951, 2920, 2842, 2780, 1751, 1728, 1490, 1465, 1463, 1458, 1452, 1438, 1430, 1485, 1374, 1367, 1344, 1295, 1264, 1248, 1214, 1182, 1165, 1127, 1110, 1093, 1064, 1055, 1031, 769 cm^{-1}. FDMS (*m*/*z*): 850 (95%, $M^+ + H$), 721 (100%, $C_{60}^+ + H$). UV-vis: 255.1, 307.2, 429.2, 696.4 nm. Anal. Calcd for $C_{60}CH_2(Me)NCHCOOEt \cdot 0.5H_2O$: C% 92.31; H% 1.41; N% 1.63; found: C% 92.32; H% 1.53; N% 1.60.

3c. ^1H NMR (400 MHz, $CDCl_3$): δ 3.04 (3H), 4.27 (d, 1H), 4.85 (1H), 4.97 (d, 1H), 5.30 (d, 1H), 5.37 (d, 1H), 7.2−7.3 (m, 5H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.28 (COO), 154.57, 153.79, 152.63, 150.68, 147.38, 147.28, 146.72, 146.36, 146.33, 146.25 (2C), 146.11, 146.07, 146.04, 146.01, 145.86, 145.75, 145.68, 145.58, 145.53, 145.48 (2C), 145.41, 145.35, 145.30 (2C), 145.25 (2C), 144.66, 144.46 (2C), 144.34, 143.08 (2C), 142.99, 142.68, 142.63, 142.59 (2C), 142.16, 142.11 (4C), 142.07, 141.85 (2C), 141.80, 141.75, 141.63, 140.28, 140.22, 139.57 (2C), 137.69, 136.57, 135.98, 135.47, 134.80, 129.34 (2CH), 128.71 (CH), 128.59 (2CH), 78.98 (CH), 73.28 (sp^3, 1C), 69.58 (sp^3, 1C), 68.78 (CH_2), 67.67 (CH_2), 40.00 (CH_3). DEPT spectrum: 39.99 (CH_3), 67.73 (CH_2), 68.63 (CH_2), 78.81 (CH), 128.59 (ArCH), 128.73 (ArCH), 129.34 (ArCH). FT-IR (microscope): 3032, 2951, 2920, 2864, 2840, 2781, 1751, 1729, 1464, 1463, 1460, 1456, 1429, 1378, 1334, 1272, 1250, 1230, 1213, 1178, 1142, 1126, 1110, 1060, 971, 898, 771, 769, 752, 739, 696 cm^{-1}. FDMS (*m*/*z*): 910 (100%, $M^+ - H$), 721 (62%, $C_{60}^+ + H$). Anal. Calcd for $C_{60}CH_2(Me)NCHCOOCH_2 - Ph\cdot 0.5H_2O$: C% 92.60; H% 1.53; N% 1.52; found: C% 92.42; H% 1.82; N% 1.60.

4. ^1H NMR (400 MHz, $CDCl_3$): δ 1.46 (18H), 1.47 (4.70H), 5.26 (1.96H), 5.75 (1.47H). The sample is not soluble enough for ^{13}C NMR analysis. FT-IR (KBr pellet): 3290, 3280, 2974, 2926, 1731, 1473, 1462, 1454, 1428, 1391, 1367, 1314, 1276, 1258, 1214, 1154, 1092, 889, 847, 828, 799, 774, 766, 760, 752, 729, 641, 575, 563, 553, 527, 477.

5. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 5.68 (integral, 1.0), 5.91 (0.18). ^{13}C NMR (100.6 MHz, $(CD_3)_2SO$): δ 170.37, 152.98, 151.43, 146.51, 145.82, 145.80, 145.75, 145.42, 145.34, 145.13, 144.80, 144.78, 144.75, 144.65, 143.95, 143.83, 142.61, 142.55, 142.19, 142.17, 141.88, 141.82, 141.68, 141.57, 141.45, 141.24, 139.10, 138.81, 135.85, 135.69, 77.03, 76.50, 72.71. FT-IR (KBr pellet): 3244, 2956, 2918, 2853, 1740, 1631, 1429, 1384, 1253, 1228, 1181, 1118, 1080, 1031, 870, 763, 641, 575, 563, 553, 527. FDMS (*m*/*z*): 850 (2%, $M^+ - H_2$(cation of the salt)), 720 (100%, C_{60}^+). Anal. Calcd for $C_{60}[NH_2(CHCOOH)_2]CF_3SO_3\cdot 3H_2O$: C% 73.93; H% 1.14; N% 1.32; found: C% 73.57; H% 1.02; N% 1.71.

Acknowledgment. L.B.G. thanks Dr. Y. Rubin of University of California at Los Angeles for suggestions on the possible mechanism, Dr. G. C. Jia of Hong Kong University of Science and Technology for helpful discussion, Prof. E. Larsen of the Royal Veterinary and Agricultural University in Denmark for HPLC analysis when this project was just started, and NSFC and The Climbing Program—A Fundamental Research Program of China for financial support.

JO951933U