Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 55–60

TETRAHEDRON

Solvent-free reactions of fullerenes and *N*-alkylglycines with and without aldehydes under high-speed vibration milling

Guan-Wu Wang,[a,*] Ting-Hu Zhang,[a] Er-Hong Hao,[a] Li-Juan Jiao,[a] Yasujiro Murata[b] and Koichi Komatsu[b]

[a]*Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*
[b]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

Received 5 September 2002; revised 23 October 2002; accepted 14 November 2002

Abstract—The solvent-free reactions of fullerenes and *N*-alkylglycines with and without aldehydes (RCHO) **2a**–**e** under high-speed vibration milling (HSVM) conditions have been investigated. Fulleropyrrolidines **4a**–**e** ($C_{60}(CH_2N(CH_3)CHR)$, R=H (**4a**), C_6H_5 (**4b**), *p*-NO_2–C_6H_4 (**4c**), *p*-CH_3O–C_6H_4 (**4d**), *p*-$(CH_3)_2N$–C_6H_4 (**4e**)) were obtained in moderate yields from reactions of C_{60} with aldehydes **2a**–**e** and *N*-methylglycine (Prato reaction). In all these solvent-free reactions, **4a** was found to be formed besides **4b**–**e**, indicating that fullerenes can react with *N*-substituted glycines in the absence of aldehyde to give fulleropyrrolidines. For this novel reaction, a possible reaction mechanism involving an electron transfer process has been proposed. Intrigued by this observation, the dependence of the yield on the reagent ratio for the reaction of C_{60} with paraformaldehyde and/or *N*-methylglycine was examined to search the optimal conditions. The reaction of C_{70} with paraformaldehyde and/or *N*-methylglycine under HSVM conditions was also studied and was found to give the positional isomers of [70]fulleropyrrolidines.

1. Introduction

Chemical modifications of fullerenes have been intensively explored because of the potential applications of fullerene derivatives in many fields.[1] Over the past ten years, numerous fullerene derivatives have been synthesized via various functionalization methods.[2] Among these methods, the 1,3-dipolar cycloaddition of azomethine ylide to fullerene, known as the Prato reaction, is one of the most investigated reactions. A number of [60]fulleropyrrolidines have been synthesized by the reaction of C_{60} with *N*-substituted glycine or other amino acid and aldehydes or ketones.[3] The reaction of C_{70} with *N*-methylglycine and paraformaldehye has also been investigated and the formation of three positional isomers of monoadducts was observed.[4]

Recently solvent-free organic reactions[5] have attracted great attention due to the increasing concern for protection of the environment.[6] On the other hand, the solubility of fullerenes in common organic solvents is so low that the use of a large amount of solvents is inevitable for their reactions. Therefore, solvent-free reaction of fullerene is an attractive and appealing method to synthesize functionalized fullerenes. Recently the mechanochemical solvent-free reactions of fullerene have been developed.[7–14] The technique called 'high-speed vibration milling (HSVM)' has been used to promote reactions of fullerenes under solvent-free conditions. In this technique, the mechanical energy caused by local high pressure, friction, shear strain, etc. can be used as a driving force for the reaction. This HSVM technique has been successfully utilized in the Reformatsky-type reaction of C_{60},[8] reactions of C_{60} to prepare fullerene dimers and trimers catalyzed by various potassium salts, alkaline metals, or solid amines,[9] [4+2] reactions of C_{60} with condensed aromatics,[10] with phthalazine[11] and with di(2-pyridyl)-1,2,4,5-tetrazine,[12] reaction of C_{60} with dichlorodiphenylsilane and lithium,[13] and reactions of C_{60} with organic bromides and alkali metals.[14] Preliminary work on 1,3-dipolar cycloadditions of C_{60} with diazo compounds and with organic azides have also been reported.[7b] It is to be noted that many of the functionalized fullerenes obtained in these studies could only be produced by the HSVM reactions and cannot be attained by conventional liquid-phase reactions.[9–11,13] We now report our study on the solvent-free HSVM reactions of fullerenes with *N*-alkylglycines and aldehydes **2a**–**e**, and more importantly, the novel reactions of fullerenes and *N*-alkylglycines without aldehyde under HSVM conditions.

2. Results and discussion

The 1,3-dipolar cycloaddition of azomethine ylide generated

Keywords: fullerenes; Prato reaction; *N*-alkylglycine; solvent-free reaction; high-speed vibration milling.

* Corresponding author. Tel.: +86-551-360-7864; fax: +86-551-360-7864; e-mail: gwang@ustc.edu.cn.

0040–4020/03/$ - see front matter
PII: S0040-4020(02)01478-3

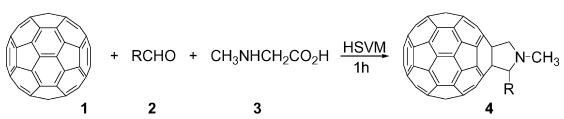
in situ from *N*-methylglycine and paraformaldehyde to C_{60} to give fulleropyrrolidine was reported at a very early stage of fullerene chemistry by Prato and co-workers.[15] Since then many fulleropyrrolidine derivatives with novel functionalities have been prepared. As a typical procedure, a mixture of C_{60}, *N*-methylglycine or other amino acids, and aldehydes or ketones was reacted at elevated temperature (refluxing toluene or chlorobenzene) to afford fulleropyrrolidine.[3,4] Then we questioned if the HSVM technique could be applied to this Prato reaction of C_{60} under solvent-free conditions. A mixture of C_{60}, 1 equiv. of *N*-methylglycine (**3**) and 1 equiv. of aldehyde **2a**–**e** was vigorously shaken by HSVM technique for 1 h, and we found that the expected fulleropyrrolidines **4a**–**e** were obtained in moderate yields (Scheme 1). The identities of the products were confirmed by comparison of their spectral data with those reported in literature.[15,16]

Noteworthy is the fact that in these solvent-free HSVM reactions we unexpectedly isolated **4a** as a minor product besides the corresponding fulleropyrrolidines **4b**–**e** in all reactions of C_{60} with **3** and **2b**–**e**. The yields of the products and recovered C_{60} for these reactions of C_{60} with **3** and aldehydes in a molar ratio of 1:1:1 are listed in Table 1.

Since the reagents commonly used for all these reactions are C_{60} and **3**, **4a** may have resulted from the direct reaction between these two. To test this hypothesis, we treated the mixture of C_{60} and **3** (1:1) under the HSVM conditions for 1 h. The reaction mixture was separated by a silica-gel column chromatography eluted with toluene to give **4a** in 19% (35% based on the consumed C_{60}). Its structure was confirmed by ^{1}H and ^{13}C NMR, HRMS, IR and UV–Vis spectra.[15] Then, as a much less soluble product, which was eluted out by *o*-dicholorobenzene, the fullerene dimer C_{120}[9a] was obtained in 23% (42% based on the consumed C_{60}) (Scheme 2). When **3** was substituted by *N*-ethylglycine, the same kind of reaction occurred, *N*-ethyl fulleropyrrolidine (**5**) and C_{120} were obtained in 16% (36% based on the consumed C_{60}) and 19% (43% based on the consumed C_{60}) yields, respectively (Scheme 2). Fulleropyrrolidine **5** exhibited 17 lines for the sp^2 carbons of the C_{60} cage in its ^{13}C NMR, which is consistent with its C_{2v} symmetry. Its ^{13}C NMR pattern for the C_{60} cage carbons and UV-vis spectrum were the same as those of **4a**.

Compound **5** was also obtained in 26% (52% based on the consumed C_{60}) from the mechanochemical HSVM reaction of C_{60} with *N*-ethylglycine and paraformaldehyde under the HSVM conditions for 1 h (Scheme 3).

To examine how the reagent ratio affects the product distribution and yield, we monitored the reaction mixtures at various reagent ratios by the use of HPLC analysis. Two series of experiments have been conducted. First, the ratio



a, R = H; **b**, R = C_6H_5; **c**, R = *p*-NO_2-C_6H_4; **d**, R = *p*-CH_3O-C_6H_4; **e**, R = *p*-$(CH_3)_2N$-C_6H_4

Scheme 1.

Table 1. Product yields and recovered C_{60} for the reactions of C_{60} with *N*-methylglycine and aldehydes

Aldehyde	**4** (Yield, %)	Recovered C_{60} (%)
2a	**4a** (30%)	43
2b	**4b** (23%)+**4a** (7%)	50
2c	**4c** (29%)+**4a** (12%)	53
2d	**4d** (24%)+**4a** (7%)	56
2e	**4e** (18%)+**4a** (9%)	58

of C_{60} and **3** was fixed at 1:1 and the amount of **2a** was varied; then the relative yields of produced **4a** and C_{120} and unchanged C_{60} at various equivalents of **2a** were determined to give the results shown in Figure 1. Second, the ratio of C_{60} and **2a** was fixed at 1:1, and the amount of **3** was varied; then the yields of **4a**, C_{60} and C_{120} were determined at various equivalents of **3** to give the result shown in Figure 2.

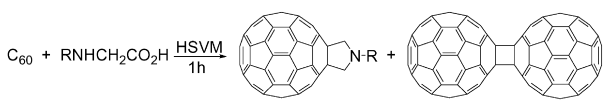
As clearly seen in Figure 1, the yield of **4a** changed little when **2a** varied from 1 to 6 equiv., and then decreased gradually with the increase of recovered C_{60}.

Meanwhile, as shown in Figure 2, the yield of **4a** increased rapidly with the change in the amount of **3** from 0.3 to 1 equiv. and was maintained nearly constant until 2.3 equiv. of **3**; then it rapidly decreased until 3 equiv. of **3** and kept gradually decreasing. In all cases, the formation of C_{120} was negligible (<10%). From these results, we conclude that the optimal amount for paraformaldehyde is 1–6 equiv. and that for **3** is 1–2 equiv. relative to C_{60} to obtain high yield of fulleropyrrolidine **4a** for the present HSVM reaction.

We have also investigated the dependence of the relative product yield on reagent ratios for the reaction of C_{60} with **3** in the absence of aldehydes. The relative yields of **4a**, C_{60} and C_{120} at various equivalents of **3** are shown in Figure 3.

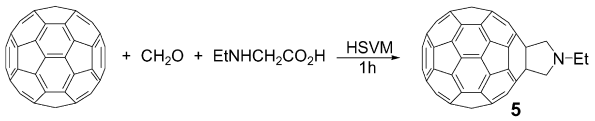
As shown in Figure 3, the fulleropyrrolidine (**4a**) was formed in the range of 0.3–4 equiv. of **3**, while C_{120} was formed at the all range of **3**. The yield of **4a** increased from 0.3 to 2 equiv. of **3**, then decreased gradually and finally dropped to zero after 4 equiv. of **3**. Meanwhile, there is a plateau for the yield of C_{120} around 20% from 1 to 2 equiv. of **3**, then the yield increased rapidly and reached nearly the maximum (~40%), and then was almost unchanged until 7 equiv. of **3**. Thus, C_{120} can be obtained selectively without contamination of **4a** when more than 5 equiv. of **3** was used. Previously, it has been reported that the HSVM treatment of C_{60} with solid amines can give 30–40% of C_{120}.[9b]

Another aspect of interest is how the mass of the reaction mixture affects the product yield in the present HSVM reaction. The reagent ratio was kept unchanged, but the total amount of the reaction mixture was altered to see how the product yield was affected. The reaction of C_{60} with *N*-methylglycine (**3**) and paraformaldehye (**2a**) was chosen for this purpose. It was found that the increase of C_{60} from 7.2



4a, R = Me; **5**, R = Et

Scheme 2.



Scheme 3.

to 28.8 mg for the reaction of C_{60} with **2a** and **3** in the ratio of 1:1:1 has almost no effect on the yield of **4a**. The same phenomenon was true for the reaction of C_{70} with **2a** and **3** (vide infra). The milling time can be made shorter, the reactions of 20–30 min gave almost the same yield of **4a** and also the functionalized C_{70}, i.e. **6**, **7**, **8**. However, the increase of the total amount for the reaction of C_{60} with **2b**–**e** and **3** decreased the yield of **4b**–**e**, and even did not give any **4b** or **4d** for the reaction of C_{60} with **2b** or **2d** and **3**. Therefore, we kept the amount of C_{60} at 7.2 mg for each run to compare the product yields for different aldehydes. The exact reason for this dependence of the product yield on the quantity of reaction mixture is not quite clear at the moment, but probably the high temperature required for these reactions is critical. When a smaller amount of the reaction mixture was used the temperature of the reaction mixture could get higher because of the greater degree of the direct contact of the milling ball with the inner surface of the capsule causing greater friction.

We have also explored the reaction of [70]fullerene with *N*-methylglycine and paraformaldehyde under HSVM conditions. This reaction gave three monoadduct isomers (Scheme 4).

A mixture of monoadducts **6**–**8**[4] was isolated by column chromatography in total yield of 41%. The relative amount of **6**–**8** was determined as 47:36:16 by ^{1}H NMR. It was reported that the above Prato reaction of C_{70} tended to produce more **7** at the expense of **8** at higher reaction temperature and under microwave irradiation.[4] The obtained ratio under the present HSVM conditions is closest to that in refluxing toluene, and quite different from that under microwave irradiation. A larger amount of monoadduct isomer **8** was obtained under HVSM conditions than that in refluxing chlorobenzene and *o*-dichlorobenzene, and under microwave irradiation. These facts hint that the local

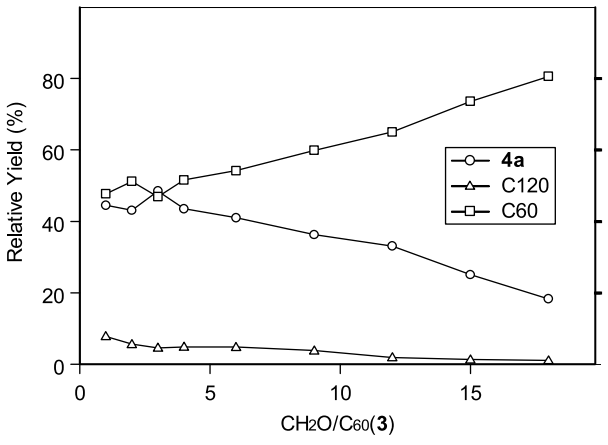


Figure 1. Distributions of **4a**, C_{60} and C_{120} at various equivalents of **2a** for the reaction of C_{60} with **2a** and **3** conducted under the HSVM conditions for 1 h.

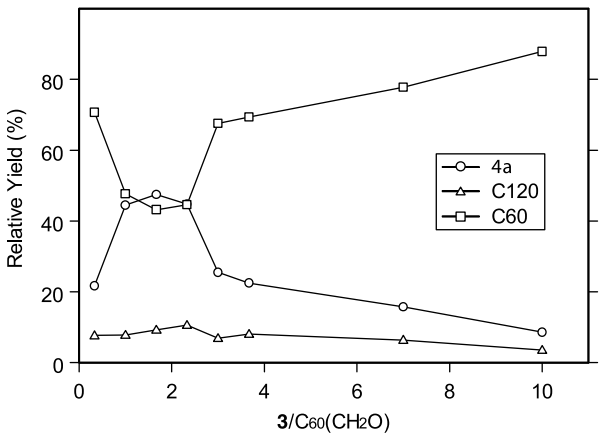


Figure 2. Distributions of **4a**, C_{60}, and C_{120} at various equivalents of **3** for the reaction of C_{60} with **2a** and **3** conducted under the HSVM conditions for 1 h.

reaction temperature under HSVM is lower than the boiling point of toluene.

To find out if a similar reaction of C_{60} with *N*-methylglycine occurs for C_{70}, a mixture of C_{70} and *N*-methylglycine was treated with HSVM. It turned out that the reaction indeed proceeded and gave monoadducts **6** and **7** in total yield of 23% with relative ratio of 1.5:1 (Scheme 5). The reason for the absence of **8** is not known.

Fulleropyrrolidines were obtained from reactions of fullerenes with *N*-alkylglycine and aldehydes under HSVM conditions most probably through the expected 1,3-dipolar cycloaddition of the azomethine ylide. To explain the formation of [60]fulleropyrrolidines and C_{120} from the direct reactions of C_{60} and *N*-alkylglycine, we propose the following reaction pathways as a possible reaction mechanism (Scheme 6).

The first step is the electron transfer from *N*-alkylglycine to C_{60} to form C_{60} radical anion and **9** ((a) in Scheme 6). Radical cation **9** loses CO_2 and a proton to afford radical **11**. The proposed formation of radical **11** from C_{60} and glycines has precedent in the literature.[17] Radical **11** adds to the 6,6-bond of C_{60} to form intermediate **12**, which undergoes intramolecular electron transfer to give **13**, and then couples

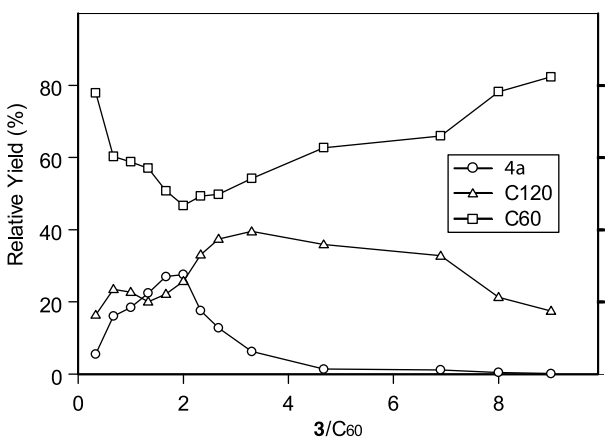
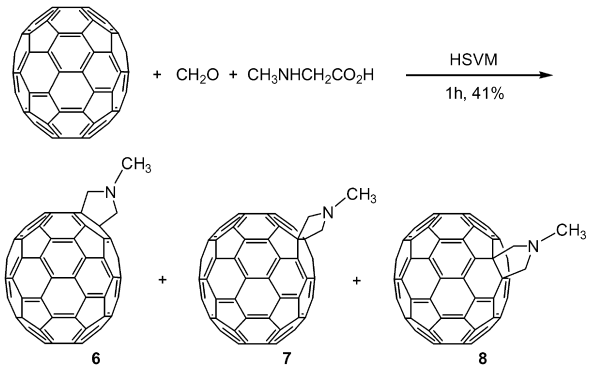


Figure 3. Distributions of **4a**, C_{60}, and C_{120} at various equivalents of **3** for the reaction of C_{60} with **3** conducted under the HSVM conditions for 1 h.



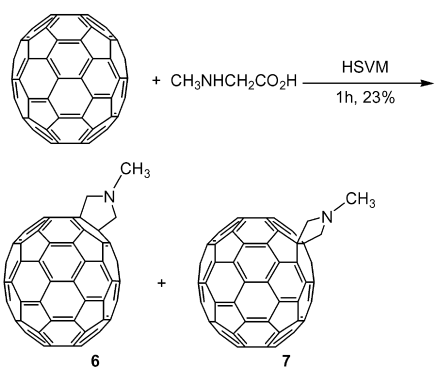
Scheme 4.

with radical **11** to afford anion **14**. Amines are known to easily transfer an electron to C_{60}.[18] The formed **14** transfers one electron to C_{60} to give intermediate **15**, which cyclizes with the loss of the alkyl amine radical to afford the fulleropyrrolidine **16** ((b) in Scheme 6). Cyclization accompanied with unusual C–N bond breaking has been noticed before.[19] Alternatively, the anion **14** can transfer one electron to C_{60} to form radical **17**, which cyclizes with the loss of alkyl amine radical to afford the fulleropyrrolidine ((c) in Scheme 6). C_{120} is supposed to be formed by the coupling of C_{60} radical anion with C_{60} to form C_{120} radical anion **18**, which transfers one electron to another molecule of C_{60} to give C_{120} diradical **19**, which couples to afford C_{120} ((d) in Scheme 6). Thus, C_{120} can be formed once the C_{60} radical anion is produced by the process (a) as has been suggested before.[9b]

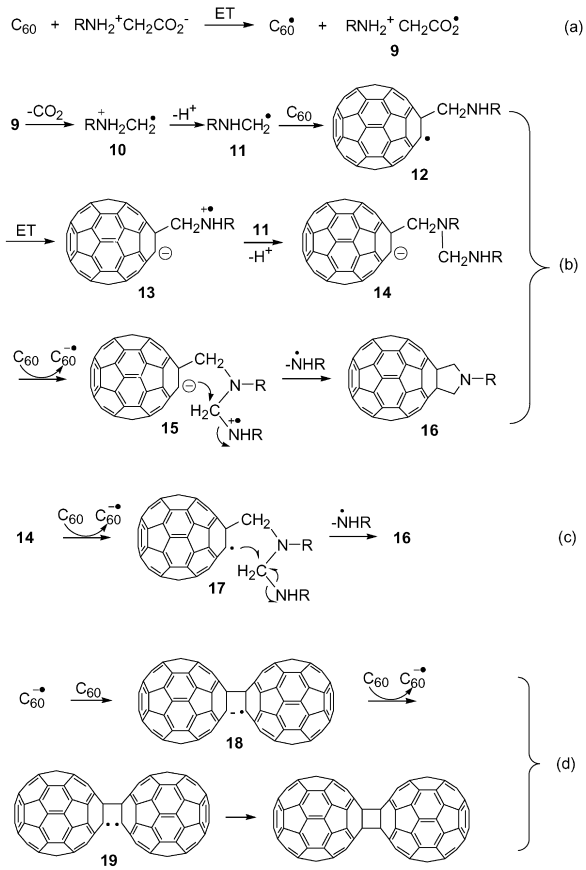
C_{70} should react with *N*-alkylglycine via the same pathway as that of C_{60} with *N*-alkylglycine to give [70]fulleropyrrolidines. It should be noted that there is no evidence of the formation of C_{70} dimer, C_{140}. This is consistent with the failure of formation of C_{140} from the reactions of C_{70} with potassium salts, metals, and amines.[9c]

The synthesized fulleropyrrolidines can be converted to the corresponding fullerene-containing amphiphiles bearing ammonium head group. These amphiphiles are water-soluble and expected to form interesting supramolecular assemblies in water and polar organic solvents. Work along this line is in progress.

In conclusion, the reactions of C_{60} with aldehydes and *N*-methylglycine (Prato reaction) under solvent-free conditions were investigated by the use of the HSVM technique. Not only the expected products **4a**–**e** were produced but the simplest *N*-methyl fulleropyrrolidine **4a** was obtained from all the reactions regardless of the type of aldehyde. From this observation, a novel reaction of C_{60} or C_{70} with *N*-alkylglycine was found. A possible reaction mechanism was proposed for the reaction of C_{60} with *N*-alkylglycine to explain the formation of fulleropyrrolidine and also the fullerene dimer, C_{120}.



Scheme 5.



Scheme 6.

3. Experimental

3.1. General procedures

^1H and ^{13}C NMR spectra were recorded at 300 or 400 and 75 MHz, respectively, in CS_2–$CDCl_3$. IR spectra were recorded on a Shimadzu 8600 FT IR spectrometer. UV-vis spectra were obtained on a Shimadzu UV-2100PC spectrometer.

High-performance liquid chromatography analysis was conducted on an Agilent 1100 liquid chromatograph with a diode-array detector using a Cosmosil Buckyprep column (4.6 mm×250 mm) with toluene as the eluent. For the reaction of C_{60} with *N*-methylglycine and paraformaldehyde, the retention time for the product, **4a**, C_{60}, and C_{120} were 6.0, 8.0 and 18.9 min, respectively, at the flow rate of 1 mL min^{-1}. For the HPLC measurements, the reaction mixture was monitored at 326 nm, and the relative ratios of C_{60} and its derivatives' peak areas were taken as the relative

amounts of C_{60} and its derivatives. Their actual amounts are slightly different due to the slightly different molar extinction coefficients for C_{60} and its derivatives at 326 nm. However, this treatment does not affect the distribution trends shown in Figures 1–3.

All solvent-free reactions were performed using a high-speed vibration mill that consists of a capsule and a milling ball made of stainless steel. The capsule containing the milling ball was fixed on a vibration arm of a home-built mill, and was vibrated vigorously at a rate of 3500 cycles per minute.

C_{60} (>99.9%) and C_{70} (98%) were purchased from 3D Carbon Cluster Material Co. of Wuhan University in China. All other reagents were commercial material.

3.1.1. Reaction of C_{60} with *N*-methylglycine and aldehydes. A mixture of C_{60} (7.2 mg, 0.01 mmol), *N*-methylglycine (0.9 mg, 0.01 mmol) and *p*-nitrobenzaldehyde (**2c**) (1.5 mg, 0.01 mmol) was vigorously shaken by HSVM for 1 h. The combined reaction mixture from six runs was separated on a silica gel column with toluene/petroleum ether as the eluent to afford recovered C_{60} (22.9 mg, 53%), **4c** (15.5 mg, 29%), and **4a** (5.6 mg, 12%). Similar results were obtained from reactions of C_{60} with *N*-methylglycine and other aldehydes. All fulleropyrrolidines **4a–e** were characterized by NMR, UV-vis, and their structures were confirmed by comparison of their spectral data with those reported in literature.[15,16]

3.1.2. Reaction of C_{60} with *N*-methylglycine. A mixture of C_{60} (7.2 mg, 0.01 mmol) and *N*-methylglycine (0.9 mg, 0.01 mmol) was vigorously shaken by HSVM for 1 h. The combined reaction mixture from six runs was separated on a silica gel column with toluene/petroleum ether as the eluent to afford recovered C_{60} (19.9 mg, 46%) and a black solid (8.9 mg, 19%), which was proven to be the same product as that from the reaction of C_{60} with *N*-methylglycine and paraformaldehyde by comparison their ^{1}H NMR, ^{13}C NMR, MS, IR, UV–Vis spectra, and was further confirmed by high-resolution mass spectroscopy as **4a**. **4a**: MS (−APCI) *m/z* 777 (M^-); HRMS (+FAB) calcd for $C_{63}H_8N$ (M+1), 778.0656, found 778.0609.

The silica gel column was further eluted with *o*-dichlorobenzene. A poorly soluble compound was obtained and was identified as C_{120} (10.0 mg, 23%) by comparison of its spectral data with those of an authentic sample.[9a]

3.1.3. Reaction of C_{60} with paraformaldehyde and/or *N*-ethylglycine. A mixture of C_{60} (7.2 mg, 0.01 mmol), *N*-ethylglycine (1.0 mg, 0.01 mmol) and paraformaldehyde (0.3 mg, 0.01 mmol) was vigorously shaken by HSVM for 1 h. The combined reaction mixture from six runs was separated on a silica gel column with toluene/petroleum ether as the eluent to afford recovered C_{60} (21.6 mg, 50%), and *N*-ethylfulleropyrrolidine **5** (12.3 mg, 26%). **5**: IR (KBr) ν 2964, 2795, 2775, 1510, 1473, 1461, 1428, 1385, 1340, 1310, 1194, 1165, 1130, 1114, 1107, 1087, 768, 597, 575, 561, 553, 527, 513, 478 cm^{-1}; UV–Vis (cyclohexane) λ_{max} 211, 256, 324, 431 nm; MS (−APCI) *m/z* 791; HRMS (+FAB) calcd for $C_{64}H_{10}N$ (M+1), 792.0813, found 792.0825; ^{1}H NMR (300 MHz, CS_2–$CDCl_3$ (2:1)) δ 4.40 (s, 4H), 3.14 (q, 2H, *J*=7.3 Hz), 1.55 (t, 3H, *J*=7.3 Hz); ^{13}C NMR (75 MHz, CS_2–$CDCl_3$ (2:1)) δ 154.70 (4C), 146.98 (2C), 145.95 (4C), 145.76 (4C), 145.75 (4C), 145.39 (2C); 145.17 (4C), 144.98 (4C); 144.28 (4C), 142.83 (2C), 142.35 (4C), 141.95 (4C), 141.80 (4C), 141.62 (4C), 139.92 (4C), 136.02 (4C), 70.31 (2C), 67.54 (CH_2N), 49.15 (NCH_2CH_3), 14.10 (NCH_2CH_3).

Compound **5** (16%) and C_{120} (19%) along with recovered C_{60} (56%) were obtained from the reaction of C_{60} with *N*-ethylglycine using the same procedure as described above.

3.1.4. Reaction of C_{70} with aldehydes and/or *N*-methylglycine. A mixture of C_{70} (8.4 mg, 0.01 mmol), *N*-methylglycine (0.9 mg, 0.01 mmol) and paraformaldehyde (0.3 mg, 0.01 mmol) was vigorously shaken by HSVM for 1 h. The combined reaction mixture from six runs was separated on a silica gel column with toluene/petroleum ether as the eluent to afford recovered C_{70} (22.7 mg, 45%) and a mixture of monoadducts **6–8**[4] (22.1 mg, 41%). The ratio of **6–8** was determined to be 47:36:16 by ^{1}H NMR. Monoadducts **6** and **7** (1.5:1) in a total yield of 23% along with 62% of recovered C_{70} can also be obtained by the reaction of C_{70} with *N*-methylglycine using the same procedure as described above.

Acknowledgements

We are grateful for financial support from the 'Hundred Talents Program' of the Chinese Academy of Sciences, National Science Fund for Distinguished Young Scholars (20125205), Anhui Provincial Natural Science Foundation (00045306), and USTC Environment and Resource Research Base Foundation.

References

1. (a) Prato, M. *Top. Curr. Chem.* **1999**, *199*, 174–187. (b) Da Ros, T.; Prato, M. *Chem. Commun.* **1999**, 663–669. (c) Guldi, D. M. *Chem. Commun.* **2000**, 321–327.
2. (a) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685–693. (b) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138–1141. (c) Hirsch, A. *Synthesis* **1995**, 895–913. (d) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317–323. (e) Hirsch, A. *Top. Curr. Chem.* **1999**, *199*, 1–65.
3. Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519–526.
4. (a) Wilson, S. R.; Lu, Q. *J. Org. Chem.* **1995**, *60*, 6496–6498. (b) Langa, F.; de la Cruz, P.; de la Hoz, A.; Espíldora, E.; Cossío, F. P.; Lecea, B. *J. Org. Chem.* **2000**, *65*, 2499–2507.
5. For recent reviews see: (a) Toda, F. *Synlett* **1993**, 303–312. (b) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480–486. (c) Loupy, P. *Top. Curr. Chem.* **2000**, *206*, 153–207. (d) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025–1074. (e) Cave, G. W. V.; Raston, C. L.; Scott, J. L. *Chem. Commun.* **2001**, 2159–2169.
6. (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998. (b) Metzger, J. O. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2975–2978.
7. (a) Braun, T. *Fullerene Sci. Technol.* **1997**, *5*, 1291–1311.

(b) Komatsu, K.; Murata, Y.; Wang, G.-W.; Tanaka, T.; Kato, T.; Fujiwara, K. *Fullerene Sci. Technol.* **1999**, *7*, 609–620.
8. Wang, G.-W.; Murata, Y.; Komatsu, K.; Wan, T. S. M. *Chem. Commun.* **1996**, 2059–2060.
9. (a) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583–586. (b) Komatsu, K.; Wang, G.-W.; Murata, Y.; Tanaka, T.; Fujiwara, K.; Yamamoto, K.; Saunders, M. *J. Org. Chem.* **1998**, *63*, 9358–9366. (c) Komatsu, K.; Fujiwara, K.; Murata, Y. *Chem. Commun.* **2000**, 1583–1584. (d) Komatsu, K.; Fujiwara, K.; Murata, Y. *Chem. Lett.* **2000**, 1016–1017. (e) Kunitake, M.; Uemura, S.; Ito, O.; Fujiwara, K.; Murata, Y.; Komatsu, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 969–972.
10. Murata, Y.; Kato, K.; Fujiwara, K.; Komatsu, K. *J. Org. Chem.* **1999**, *64*, 3483–3488.
11. Murata, Y.; Kato, K.; Komatsu, K. *J. Org. Chem.* **2001**, *66*, 7235–7239.
12. Murata, Y.; Suzuki, M.; Komatsu, K. *Chem. Commun.* **2001**, 2338–2339.
13. Fujiwara, K.; Komatsu, K. *Org. Lett.* **2002**, *4*, 1039–1040.
14. Tanaka, T.; Komatsu, K. *Synth. Commun.* **1999**, *29*, 4397–4402.
15. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.
16. Zhou, D.-J.; Gan, L.-B.; Tan, H.-S.; Luo, C.-P.; Huang, C.-H.; Pan, J.-Q.; Lü, M.-J.; Wu, Y. *Chin. Chem. Lett.* **1995**, *6*, 1033–1036.
17. Gan, L.-B.; Jiang, J.-F.; Zhang, W.; Su, Y.; Shi, Y.-R.; Huang, C.-H.; Pan, J.-Q.; Lü, M.-J.; Wu, Y. *J. Org. Chem.* **1998**, *63*, 4240–4247.
18. (a) Hirsch, A.; Li, Q. Y.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1309–1310. (b) Liou, K. F.; Cheng, C. H. *Chem. Commun.* **1996**, 1423–1424. (c) Lawson, G. E.; Kitaygorodskiy, A.; Sun, Y.-P. *J. Org. Chem.* **1999**, *64*, 5913–5920.
19. (a) Zhou, D.-J.; Tan, H.-S.; Luo, C.-P.; Gan, L.-B.; Huang, C.-H.; Lü, M.-J.; Pan, J.-Q.; Wu, Y. *Tetrahedron Lett.* **1995**, *36*, 9169–9172. (b) Gan, L.-B.; Zhou, D.-J.; Luo, C.-P.; Tan, H.-S.; Huang, C.-H.; Pan, J.-Q.; Lü, M.-J.; Wu, Y. *J. Org. Chem.* **1996**, *61*, 1954–1961.