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Solvent-free reactions of C_{60} with active methylene compounds, either with or without carbon tetrabromide, in the presence of bases under high-speed vibration milling conditions

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Solvent-free reactions of C_{60} with active methylene compounds, either with or without carbon tetrabromide (CBr_4), in the presence of a base under high-speed vibration milling (HSVM) conditions were investigated. The reaction of C_{60} with diethyl bromomalonate was conducted under HSVM conditions in the presence of piperidine, triethylamine or Na_2CO_3 to afford cyclopropane derivative **2**. In the presence of CBr_4, methanofullerenes **2**, **7**, **8** and **9** could be obtained by the direct reaction of C_{60} with diethyl malonate, dimethyl malonate, ethyl acetoacetate and ethyl cyanoacetate, respectively, with the aid of 1,8-diazabicyclo[5,4,0]undec-7-ene, piperidine, triethylamine or Na_2CO_3. More interestingly, 1,4-bisadducts **10** and **11** were produced by the reaction of C_{60} with diethyl malonate and dimethyl malonate in the presence of piperidine, triethylamine or Na_2CO_3 under HSVM conditions. On the other hand, dihydrofuran-fused C_{60} derivatives **18**, **19** and **20** were obtained from the reaction of C_{60} with ethyl acetoacetate, 2,4-pentanedione and 5,5-dimethyl-1,3-cyclohexanedione with the aid of a base. Under the same conditions, less activated aryl methyl ketones such as 2-acetylpyridine, 2-acetylpyrazine and acetophenone provided monocarbonylated methanofullerene derivatives **27**, **28** and **29**. Except for the Bingel reactions, all other reactions under the HSVM conditions are considered to proceed according to a single-electron-transfer mechanism.

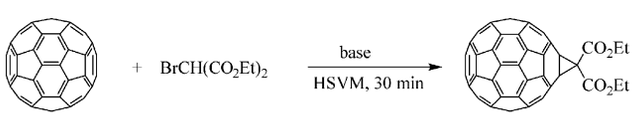
Introduction

In fullerene chemistry, the solvent-free mechanochemical reaction has particular significance in the chemical modification of fullerenes from the viewpoint of solving the problem of the low solubility of fullerenes in common organic solvents. In 1994, Braun *et al.* reported the use of ball-milling technique to prepare the γ-cyclodextrin complex of [60]fullerene (C_{60}).[1] The first C–C bond forming organic reaction of C_{60} conducted under solvent-free mechanochemical conditions was, however, realized in 1996, when a novel technique called high-speed vibration milling (HSVM) was applied to the Reformatsky-type reaction of C_{60}.[2] Following this, Diels–Alder cycloaddition reactions,[3–5] the Prato reaction[6] and the Bingel reaction[7] have been achieved with the HSVM technique. This HSVM technique is advantageous not only because it is an environmentally benign procedure eliminating the usage of harmful organic solvents but because it can occasionally promote some novel reactions that cannot be realized by liquid-phase reactions. For example, this HSVM technique has been extended to the reaction of C_{60} with various potassium salts, alkaline metals, or amines to give fullerene dimers and trimers;[8–12] the reaction of C_{60} with dichlorodiphenylsilane[13] or with dichlorodiphenylgermane[14] in the presence of lithium powder to provide novel fullerene dimers connected by a silicon or a germanium bridge, and the reaction of C_{60} with diethyl malonate with the aid of an inorganic base to give a novel 1,4-bisadduct.[7] In the continuation of our work on HSVM-promoted fullerene reactions, we recently reported preliminary results of the solvent-free mechanochemical reaction of C_{60} with active methylene compounds in the presence of Na_2CO_3.[7] In this paper we present the full account of the solvent-free reaction of C_{60} with active methylene compounds and CBr_4 or without CBr_4 in the presence of either an inorganic or organic base under HSVM conditions.

Results and discussion

Among the various known reactions in fullerene chemistry, the Bingel reaction, giving a variety of cyclopropanated fullerenes, is one of the most widely employed reactions.[15] In the Bingel reaction, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) has been most commonly used as a base to formally capture a molecule of hydrogen halide from halogenated active methylene compounds. In order to determine whether the Bingel reaction could be realized under solvent-free HSVM conditions, a mixture of C_{60}, diethyl bromomalonate (**1**) and DBU in a molar ratio of 1 : 1.5 : 1.5 was vigorously milled for 30 min under HSVM conditions. The result was no formation of the product and complete recovery of unreacted C_{60}. However, this Bingel reaction was found to proceed in the presence of other organic bases such as piperidine and triethylamine (TEA) and an inorganic base, *i.e.*, Na_2CO_3, as described below in detail (Scheme 1).

When DBU was replaced with piperidine, the desired product **2** was obtained in 10% yield (56% based on consumed C_{60}), and the use of TEA as the base increased the yield of monoadduct



1 **2**

base: piperidine, TEA, Na_2CO_3

Scheme 1

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Table 1 Yield of **2** and recovered C_{60} for the Bingel reaction of C_{60} with **1** in the presence of different bases under HSVM conditions for 30 min

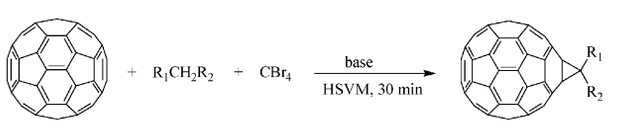
Base	Yield[a] of **2**	Recovered C_{60}
Piperidine	56%	82%
TEA	40%	48%
Na_2CO_3	78%	42%

[a] Based on consumed C_{60}.

2[15] to 21% (40% based on consumed C_{60}) along with some bisadducts. More interesting is that the expected product **2** was obtained in much higher yield when the base DBU was replaced with Na_2CO_3. Typically, an HSVM reaction of C_{60}, **1** and Na_2CO_3 in a molar ratio of 1 : 1.5 : 1.5 for 30 min afforded 45% (78% based on consumed C_{60}) of monoadduct **2** together with 8% (14% based on consumed C_{60}) of bisadduct isomers as minor products. The yields of adduct **2** and recovered C_{60} for the Bingel reaction of C_{60} with **1** in the presence of different bases are listed in Table 1. The lower yields for the reactions with organic bases may be partly ascribed to the direct reaction of organic amines with **1** to form ammonium salts under the present reaction conditions.

The reaction of C_{60} with **1** in the presence of both organic and inorganic bases is considered to follow the well-established mechanism of the Bingel reaction involving firstly the nucleophilic attack of the carbanion generated through the proton abstraction of **1** by a base. Then the anionic carbon of the C_{60} derivative produced undergoes intramolecular S_N2 reaction with bromide anion as the leaving group.[15]

It is also well known that the synthesis of methanofullerenes can be achieved by the direct reaction of C_{60} with malonate esters in the presence of CBr_4 and DBU, as first reported by Hirsch and Camps.[16] Therefore, we tested the applicability of our HSVM technique to the reaction of C_{60} with diethyl malonate (**3**) in the presence of CBr_4 and DBU, and indeed found that the expected product **2** could be obtained. Piperidine, TEA or Na_2CO_3 were also found to be utilizable in place of DBU in this reaction. When we extended this reaction to other active methylene compounds, *i.e.*, dimethyl malonate (**4**), ethyl acetoacetate (**5**) and ethyl cyanoacetate (**6**), similar reactions took place to afford methanofullerenes **7**,[17] **8** and **9**[18] under HSVM conditions (Scheme 2).



3 $R_1 = R_2 = CO_2Et$
4 $R_1 = R_2 = CO_2Me$
5 R_1 = MeCO, $R_2 = CO_2Et$
6 R_1 = CN, $R_2 = CO_2Et$

2 $R_1 = R_2 = CO_2Et$
7 $R_1 = R_2 = CO_2Me$
8 R_1 = MeCO, $R_2 = CO_2Et$
9 R_1 = CN, $R_2 = CO_2Et$

base: DBU, piperidine, TEA, Na_2CO_3

Scheme 2

The yields of methanofullerenes **2**, **7**, **8** and **9** for the reaction of C_{60} with active methylene compounds **3**, **4**, **5** and **6** in the presence of CBr_4 and different bases in a molar ratio of 1 : 1.5 : 1.5 : 1.5 for 30 min under HSVM conditions are listed in Table 2.

From Table 2 it can be seen that the use of Na_2CO_3 affords the highest yields of methanofullerenes **8** and **9** under HSVM conditions but for methanofullerenes **2** and **7** TEA gives the best results. The reason for this contrast is not clear at present.

The reaction of C_{60} with active methylene compounds in the presence of CBr_4 and base is supposed to proceed *via* the Bingel reaction mechanism, in which the brominated methylene compounds are formed *in situ* from active methylene compounds and CBr_4 with the aid of a base.

Table 2 Yields of methanofullerenes **2**, **7**, **8** and **9** for the reaction of C_{60} with compounds **3**, **4**, **5** and **6** in the presence of CBr_4 and different bases for 30 min

Base	Yield[a] of **2**	Yield[a] of **7**	Yield[a] of **8**	Yield[a] of **9**
DBU[b]	12% (60%)	14% (66%)	5% (42%)	11% (52%)
Piperidine	8% (53%)	11% (52%)	20% (71%)	—[c]
TEA	42% (76%)	39% (78%)	13% (52%)	10% (53%)
Na_2CO_3	11% (39%)	21% (62%)	36% (75%)	29% (71%)

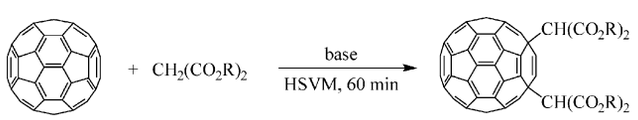
[a] Yield in parenthesis based on consumed C_{60}. [b] Reagent ratio 1:1:1:1. [c] The products were too complex to be analyzed.

Table 3 Yields of 1,4-bisadducts **10** and **11** for the reaction of C_{60} with malonates **3** and **4** in the presence of different bases under HSVM conditions for 1 h

Base	Yield[a] of **10**	Yield[a] of **11**
Piperidine	18% (25%)	16% (41%)
TEA	13% (41%)	11% (29%)
Na_2CO_3	18% (82%)	19% (77%)

[a] Yield in parenthesis based on consumed C_{60}.

Expecting the occurrence of a "non-Bingel" reaction and hoping to find some novel products by the use of an inorganic base, Na_2CO_3, we conducted the HSVM reaction using malonate **3** instead of bromomalonate **1**. Actually, a totally different product, *i.e.*, novel 1,4-bisadduct **10** was obtained in 18% yield (82% based on consumed C_{60}) after HSVM reaction for 1 h.[7] Other bases such as piperidine and TEA also gave product **10**. 1,4-Bisadduct **11**[19] was similarly obtained when the reaction was extended to malonate **4** (Scheme 3).



3 R = Et
4 R = Me

10 R = Et
11 R = Me

base: piperidine, TEA, Na_2CO_3

Scheme 3

The yields of 1,4-bisadducts **10** and **11** for the reaction of C_{60} with malonates **3** and **4** in the presence of different bases in a molar ratio of 1 : 2 : 2 under HSVM conditions for 1 h are listed in Table 3.

Compared with the use of TEA and Na_2CO_3 as the base, the reaction of C_{60} with malonate **3** was faster with piperidine as a base under HSVM conditions and resulted in recovery of C_{60} in only 28% yield. Furthermore, the reaction of C_{60} with malonate **3** and DBU was found to be extremely fast. After only 15 min vibration milling a large amount of insoluble solid was produced with the formation of only a trace of 1,4-bisadduct **10** and a small amount of methanofullerene **2**, which was absent when piperidine, TEA or Na_2CO_3 was used as the base. Eguchi and co-workers reported that no reaction took place when a mixture of C_{60}, malonate **4** and piperidine was treated in chlorobenzene.[20] In contrast, under our solvent-free HSVM conditions the bisadduct **10** or **11** was formed albeit in moderate yields from the reaction between C_{60} and malonate **3** or **4**.

The structures of bisadducts **10** and **11** were fully characterized by their MS, ^{1}H NMR, ^{13}C NMR, FT-IR and UV-vis spectra, which were totally consistent with those resulting from the radical reaction of C_{60} with malonates **3** and **4** in the presence of manganese(III) acetate dihydrate in refluxing chlorobenzene.[19]

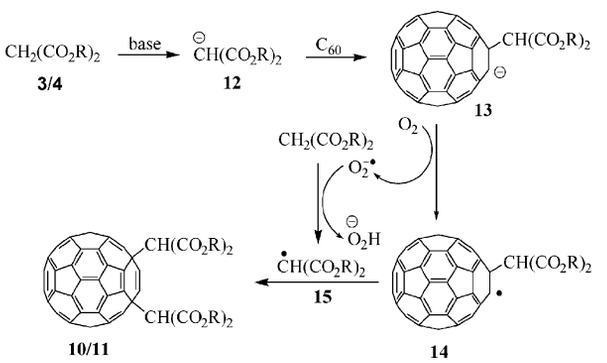
A control experiment showed that no reaction occurred when the HSVM reaction of C_{60} with a malonate ester and Na_2CO_3

Table 4 Yields of adducts **18**, **19** and **20** for the reaction of C_{60} with compounds **5**, **16** and **17** in the presence of different bases under the HSVM conditions for 30 min

Base	Yield[a] of **18**	Yield[a] of **19**	Yield[a] of **20**
Piperidine	33% (42%)	17% (45%)	22% (44%)
TEA	24% (57%)	7% (50%)	8% (23%)
Na_2CO_3	22% (49%)	Trace	10% (37%)

[a] Yield in parenthesis based on consumed C_{60}.

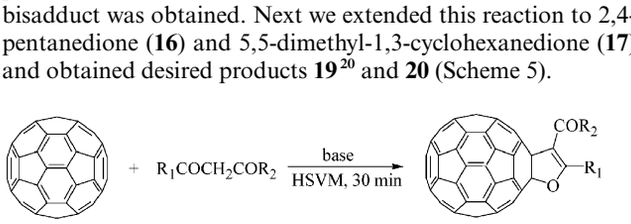
was conducted under a nitrogen atmosphere. A plausible formation mechanism for **10** and **11** in the presence of oxygen is outlined in Scheme 4.



Scheme 4

Nucleophilic addition of carbanion **12**, generated *in situ* from malonate ester **3** or **4** by a base, to C_{60} gives fullerene anion **13**, which is oxidized by O_2 to the corresponding radical **14**. Hydrogen abstraction of malonate ester **3** or **4** by previously formed oxygen radical anion affords radical **15**, which couples with intermediate **14** to give the 1,4-bisadduct **10** or **11**. The bulky $CH(COOR)_2$ group prohibits the 1,2-bisaddition due to steric hindrance, hence causing the selective formation of 1,4-bisadducts **10** and **11**, as supported by theoretical calculations.[7]

In sharp contrast, the reaction of C_{60} with ethyl acetoacetate (**5**) in the presence of a base under HSVM conditions was found to give the dihydrofuran-fused C_{60} derivative **18**.[7,20] Although an unknown compound was also isolated as a minor product in this reaction, no trace of methanofullerene or 1,4-bisadduct was obtained. Next we extended this reaction to 2,4-pentanedione (**16**) and 5,5-dimethyl-1,3-cyclohexanedione (**17**) and obtained desired products **19**[20] and **20** (Scheme 5).



5 R_1 = Me, R_2 = OEt
16 $R_1 = R_2$ = Me
17 R_1, R_2: -$CH_2C(CH_3)_2CH_2$-

18 R_1 = Me, R_2 = OEt
19 $R_1 = R_2$ = Me
20 R_1, R_2: -$CH_2C(CH_3)_2CH_2$-

base: piperidine, TEA, Na_2CO_3

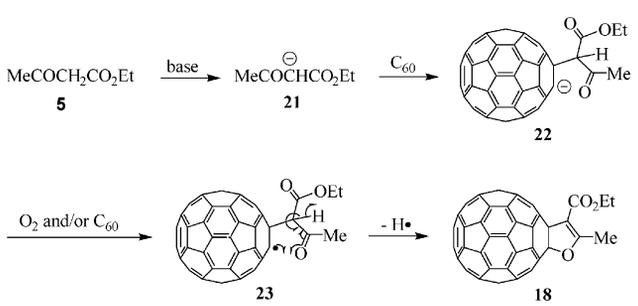
Scheme 5

The yields of dihydrofuran-fused C_{60} derivatives **18**, **19** and **20** for the reaction of C_{60} with compounds **5**, **16** and **17** in the presence of different bases in a molar ratio of 1 : 1.5 : 1.5 for 30 min under HSVM conditions are listed in Table 4.

It was reported that the reaction of C_{60} with **5** in the presence of piperidine for 35 h in chlorobenzene afforded adduct **18** in 33% yield, based on starting C_{60}.[20] Adduct **18** was isolated in a comparable yield under our HSVM conditions when piperidine was employed as the base, but in a much shorter time, *i.e.* 30 min. Na_2CO_3 and TEA gave compound **18** in over 20% yield. This result contrasts sharply with the previous report that TEA was ineffective in the liquid-phase reaction.[20]

The identification of compound **20** was made by its MS, ^{1}H NMR, ^{13}C NMR, FT-IR and UV-vis spectra. The MALDI-TOF MS spectrum of **20** showed the molecular ion peak at *m*/*z* 858. The observation of two peaks at δ 69.24 ppm and 104.82 ppm, assigned to the two sp^3 carbons of the C_{60} cage, and 30 peaks including two half-intensity ones at δ 134.48–147.79 ppm, corresponding to sp^2 carbons of the C_{60} skeleton, in the ^{13}C NMR spectrum of **20** is fully consistent with the C_s symmetry of its molecular structure. The UV-vis spectrum exhibited a peak at 428 nm, which is a diagnostic absorption of the 1 : 1 cycloadduct of C_{60} at the 6,6-junction. The ^{13}C NMR and FT-IR spectra of compound **20** match nicely with those of the dihydrofuran-fused C_{60} derivative **18**,[7] supporting the assigned structure of **20**.

In a control experiment, in which the HSVM reaction of C_{60} with **5** and Na_2CO_3 was conducted under a nitrogen atmosphere, the yield of **18** decreased from 22% to 9%. Based on this experimental result, the formation of compound **18** is supposed to involve the participation of oxygen. A possible reaction mechanism is proposed to explain the formation of dihydrofuran-fused C_{60} derivative **18** (Scheme 6).

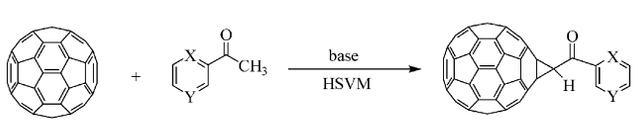


Scheme 6

Anion **21**, formed by deprotonation of **5** with a base, attacks C_{60} to give fullerene anion **22**. Anion **22** is oxidized by O_2 or partially by another molecule of neutral C_{60} to the radical **23**. The possibility of oxidation of anion **22** by C_{60} arises from the fact that the reaction of C_{60} with **5** and Na_2CO_3 was not completely suppressed under a nitrogen atmosphere. Intramolecular cyclization of radical **23** with the release of a hydrogen radical gives the dihydrofuran derivative **18**. The formation of compounds **19** and **20** is supposed to proceed *via* the same pathway.

Ethyl cyanoacetate also reacted with C_{60} with the aid of a base under HSVM conditions. However, HPLC measurement of the reaction mixture on a Cosmosil Buckyprep column showed that the reaction mixture was quite complex. Therefore, no effort was made to isolate each individual product.

Finally, three less-activated aryl methyl ketones, *i.e.* 2-acetylpyridine (**24**), 2-acetylpyrazine (**25**) and acetophenone (**26**), were selected in order to examine whether similar reactions affording dihydrofuran-fused C_{60} derivatives could occur. The 30-min reaction of 14.4 mg of C_{60} with 2.0 equivalents of ketone **24** (**25** or **26**) and 2.0 equivalents of a chosen base under HSVM conditions afforded unexpected products, *i.e.* methanofullerenes **27**, **28** and **29**,[15] instead of dihydrofuran-fused C_{60} derivatives (Scheme 7). The yields of methanofullerenes **27**, **28** and **29** for the reaction of C_{60} with methyl ketones **24**, **25** and **26** in the presence of different bases in a molar ratio of 1 : 2 : 2 are listed in the Table 5.



24 X = N, Y = C
25 X = Y = N
26 X = Y = C

27 X = N, Y = C
28 X = Y = N
29 X = Y = C

base: piperidine, TEA, Na_2CO_3

Scheme 7

Table 5 Yields of **27**, **28** and **29** for the reaction of C_{60} with methyl ketones **24**, **25** and **26** in the presence of different bases under HSVM conditions for 30 min

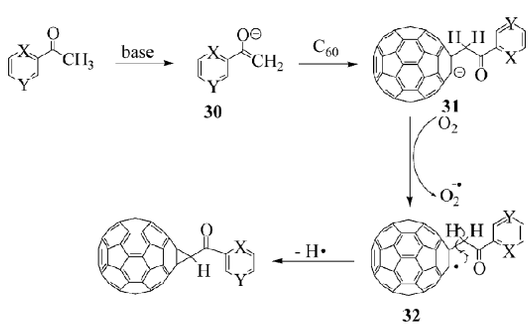
Base	Yield[a] of **27**	Yield[a] of **28**	Yield[a] of **29**
Piperidine[b]	26% (49%)	23% (42%)	16% (43%)
TEA	16% (50%)	17% (48%)	Trace
Na_2CO_3	18% (69%)	12% (48%)	Trace

[a] Yield in parenthesis based on consumed C_{60}. [b] The milling times for the reaction of C_{60} with **25** and **26** were 15 and 60 min, respectively.

The efficiency of the reactions shown in Scheme 7 was dependent on the hetero-atom contained in the aromatic ring of the methyl ketones. For example, when piperidine was used as the base in the reaction of C_{60} with **25**, milling for only 15 min was enough to obtain a satisfactory yield. However, for the reaction of C_{60} with **24** and **26**, milling times of 30 min and 60 min respectively were required to obtain a similar result. For other bases a milling time of 30 min was found to be sufficient.

The structure of **27** was determined from the spectral data as follows. The ^{1}H NMR spectrum of **27** showed a singlet signal at 6.66 ppm for the methine proton and four signals in the range from 7.70 to 8.80 ppm for the four aromatic protons. In the ^{13}C NMR spectrum the methine carbon and sp^3 carbon of the C_{60} cage were observed at 40.72 and 72.56 ppm, respectively. 26 signals between 136 and 149 ppm, including three overlapping signals, were assigned to 58 sp^2 carbons of the C_{60} skeleton, consistent with its C_S symmetry. The MALDI-TOF MS spectrum of **27** exhibited the molecular-ion peak at *m*/*z* 839. The UV-vis spectrum showed the typical absorption of a methanofullerene at 427 nm. Methanofullerene **28** was characterized by ^{1}H NMR, ^{13}C NMR, MS, IR and UV-vis spectra in the same way.

In the same manner as described above, the cyclopropanation of C_{60} with methyl ketones in the presence of a base should involve a single-electron-transfer pathway. The possible pathway is shown in Scheme 8.



Scheme 8

[60]Fullerene derivative anion **31**, formed by the attack of aryl enolate anion **30**, is oxidized by oxygen to afford [60]fullerene radical **32**. Intramolecular cyclization of radical **32** with the release of a hydrogen radical gives the methanofullerene derivatives **27**, **28** and **29**.[19,21]

It is noteworthy that C_{60} failed to react with an active methylene compound (**3**, **4**, **5** or **6**) and CBr_4 to afford a methanofullerene (**2**, **7**, **8** or **9**) in the presence of Na_2CO_3, TEA or piperidine in heated toluene. Furthermore, the novel reaction of C_{60} with a β-diester (**3** or **4**) in the presence of Na_2CO_3 and TEA or with an aryl methyl ketone (**24**, **25** or **26**) in the presence of a base could not be realized in heated toluene. These facts show the great advantage of the HSVM technique for the functionalization of fullerene.

In summary, the solvent-free HSVM reaction of C_{60} with bromomalonate **1**, with active methylene compounds **3**, **4**, **5** and **6** and CBr_4, and with aryl methyl ketones **24**, **25** and **26** in the presence of a base, afforded methanofullerenes **2**, **7**, **8**, **9**, **27**, **28** and **29** respectively. However, without the presence of CBr_4, the reaction of C_{60} with active methylene compounds having no halogen atom in the presence of a base under HSVM conditions afforded 1,4-bisadducts **10** and **11** and dihydrofuran-fused C_{60} derivatives **18**, **19** and **20**. Except for the Bingel reaction, all other reactions are considered to involve a single-electron-transfer pathway.

Experimental

General methods

^{1}H NMR and ^{13}C NMR spectra were recorded in CS_2–$CDCl_3$ at 300 MHz and 75 MHz, respectively. All intensities in the ^{13}C NMR spectral data are 2C except where indicated. MALDI-TOF mass spectroscopy was taken with 4-hydroxy-α-cyanocinnamic acid as the matrix.

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 reaction mixture along with the milling ball was fixed in a home-built vibration arm, which was vibrated vigorously at a rate of 3500 cycles per minute.[9]

C_{60} (>99.9%) was purchased from 3D Carbon Cluster Material Co. of Wuhan University in China. All other commercial available reagents are of analytical grade.

Reaction of C_{60} with bromomalonate 1 in the presence of DBU, piperidine, TEA or Na_2CO_3

A mixture of C_{60} (14.4 mg, 0.02 mmol), **1** (5.0 μl, 0.03 mmol) and 1.5 equivalents of a chosen base (DBU, piperidine, TEA or Na_2CO_3) was milled by HSVM for 30 min. The reaction mixture from three runs was combined and then separated on a silica gel column with toluene/petroleum ether as the eluent to afford unreacted C_{60} and compound **2**.[15]

Reaction of C_{60} with CBr_4 and compounds 3, 4, 5 and 6 in the presence of DBU, piperidine, TEA or Na_2CO_3

A mixture of C_{60}, (14.4 mg, 0.02 mmol), CBr_4, active methylene compound **3** (**4**, **5** or **6**) and a chosen base (DBU, piperidine, TEA or Na_2CO_3) in 1 : 1.5 : 1.5 : 1.5 molar ratio was milled by HSVM for 30 min. The reaction mixture from three runs was combined and then separated on a silica gel column with toluene/petroleum ether as the eluent to afford recovered C_{60} and methanofullerene **2** (**7**,[17] **8** or **9**[18]).

Spectral data of **8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (t, J = 7.2 Hz, 3H), 2.86 (s, 3H), 4.56 (q, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, CS_2–$CDCl_3$) δ 14.04 (1C, CH_2CH_3), 28.15 (1C, $COCH_3$), 58.93 (1C, $CCOCH_3$), 63.19 (1C, OCH_2CH_3), 72.00 (sp^3-*C* of C_{60}), 137.62, 139.00, 140.58, 140.64, 141.43, 141.45, 141.82 (4C), 142.56, 142.62 (5C), 142.69 (1C), 142.74 (1C), 143.41, 143.44, 144.17 (4C), 144.30 (6C), 144.40 (2C), 144.42 (3C), 144.66, 144.76 (4C), 144.81, 144.84 (4C), 145.08, 163.20 (1C, $CO_2CH_2CH_3$), 192.76 (1C, $COCH_3$); MS (MALDI-TOF) *m*/*z* 848; IR: 2921, 1748, 1720, 1468, 1426, 1265, 1231, 1197, 1095, 1046, 1020, 712, 576, 526; UV-vis ($CHCl_3$) λ_{max}/nm 259 (ε/dm^3 mol^{-1} cm^{-1} 97406), 326 (26651), 427 (2028).

Reactions of C_{60} with malonates 3 and 4 in the presence of piperidine, TEA or Na_2CO_3

A mixture of C_{60} (14.4 mg, 0.02 mmol), 2 equivalents of malonate ester **3** or **4** and 2 equivalents of a chosen base (piperidine, TEA or Na_2CO_3) was milled by HSVM for 30 min. The reaction mixture from three runs was combined and then separated on a silica gel column with toluene/ethyl acetate as the eluent to afford recovered C_{60} and 1,4-bisadduct **10**[7] or **11**.[19]

Reaction of C_{60} with compounds 5, 16 and 17 in the presence of piperidine, TEA or Na_2CO_3

A mixture of C_{60} (14.4 mg, 0.02 mmol), 1.5 equivalents of

compound **5** (**16** or **17**) and 1.5 equivalents of a chosen base (piperidine, TEA or Na_2CO_3) was milled by HSVM for 30 min. The reaction mixture from three runs was combined and then separated on a silica gel column with toluene as the eluent to afford recovered C_{60} and compound **18**[7,20] (**19**[20] or **20**).

Spectral data of **20**: ^{1}H NMR (300 MHz, CS_2–$CDCl_3$) δ 1.44 (s, 6H), 2.58 (s, 2H), 2.98 (s, 2H); ^{13}C NMR (75 MHz, CS_2–$CDCl_3$) δ 28.36 (*C*H_3), 33.68 (1C, *C*H_2), 38.15 (1C, *C*H_2), 51.37 (1C, *C*$(CH_3)_2$), 69.24 (1C, sp^3–*C* of C_{60}), 104.82 (1C, sp^3-*C* of C_{60}), 111.90 (1C, C=*C*CO), 134.48, 137.31, 139.31, 139.72, 140.87, 141.27, 141.69, 141.79, 141.95, 142.05, 142.16, 142.25, 142.32, 142.56, 143.57, 144.11, 144.28, 144.55, 144.70, 144.97, 145.04, 145.49, 145.52, 145.56, 145.83, 145.97, 146.39, 146.67 (1C), 147.56 (1C), 147.79, 174.45 (1C, C=*C*O), 193.28 (1C, C*C*OCH_2); MS (MALDI-TOF) *m*/*z* 858; FT-IR υ/cm^{-1} (KBr) 2924, 2854, 1640, 1460, 1375, 1236, 1179, 1062, 909, 853, 627, 572, 525; UV-vis ($CHCl_3$) λ_{max}/nm 256 (ε/dm^3 mol^{-1} cm^{-1} 82813), 316 (25898), 428 (1504).

Reaction of C_{60} with methyl ketones 24, 25 and 26 in the presence of piperidine, TEA or Na_2CO_3

A mixture of C_{60} (14.4 mg, 0.02 mmol), 2 equivalents of an aryl methyl ketone **24** (**25** or **26**) and 2 equivalents of a chosen base (piperidine, TEA or Na_2CO_3) was milled by HSVM for 30 min except for the cases of ketones **25** and **26** in the presence of piperidine, for which milling times of 15 and 60 min respectively were applied. The reaction mixture from three runs was combined and then separated on a silica gel column with toluene as the eluent to afford methanofullerene **27** (**28** or **29**[15]).

Spectral data of **27**: ^{1}H NMR (300 MHz, CS_2–$CDCl_3$) δ 6.66 (s, 1H), 7.68 (ddd, *J* = 7.8, 4.2, 1.2 Hz, 1H), 8.04 (td, *J* = 7.8, 1.6 Hz, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 8.94 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (75 MHz, CS_2–$CDCl_3$) δ 40.72 (1C, *C*H), 72.56 (sp^3–*C* of C_{60}), 122.10 (1C, aryl *C*), 127.50 (1C, aryl *C*), 136.02, 136.83 (1C, aryl *C*), 140.16, 140.31, 140.56, 141.37, 141.52, 141.68, 141.97, 142.19, 142.37 (6C), 142.51 (1C), 142.70, 143.13, 143.38, 143.75, 143.92, 143.98, 144.04 (4C), 144.27 (1C), 144.39, 144.52 (4C), 144.61, 144.68, 145.05, 145.66, 148.29, 149.01 (1C, aryl *C*), 152.16 (1C, aryl C), 190.93 (1C, *C*O); MS (MALDI-TOF) *m*/*z* 839; FT-IR υ/cm^{-1} (KBr) 2927, 2850, 1694, 1580, 1428, 1334, 1217, 1186, 994, 778, 739, 691, 617, 575, 526, 493; UV-vis ($CHCl_3$) λ_{max}/nm 259 (ε/dm^3 mol^{-1} cm^{-1} 109926), 326 (36074), 427 (2842).

Spectral data of **28**: ^{1}H NMR (300 MHz, CS_2–$CDCl_3$) δ 6.46 (s, 1H), 8.87 (d, *J* = 2.4 Hz, 1H), 8.94 (d, *J* = 2.4 Hz, 1H), 9.50 (s, 1H); ^{13}C NMR (75 MHz, CS_2–$CDCl_3$) δ 39.96 (1C, *C*H), 71.67 (sp^3-*C* of C_{60}), 135.65, 139.75, 139.95, 140.19, 140.92, 141.09, 141.25, 141.48, 141.78, 141.99 (6C), 142.12 (1C), 142.30, 142.71, 142.96, 143.42, 143.46 (aryl *C*), 143.57, 143.64 (6C), 143.79 (1C), 144.02, 144.09, 144.14, 144.17, 144.24, 144.48, 144.70, 145.96 (1C, aryl *C*), 147.40, 148.22 (1C, aryl *C*), 190.03 (1C, *C*O); MS (MALDI-TOF) *m*/*z* 840; FT-IR υ/cm^{-1} (KBr) 2924, 2854, 1693, 1633, 1504, 1461, 1422, 1178, 1052, 1006, 701, 572, 525; UV-vis ($CHCl_3$) λ_{max}/nm 259 (ε/dm^3 mol^{-1} cm^{-1} 91570), 326 (27994), 427 (2326).

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