Catalytic [2+1] cycloaddition of diazo compounds to [60]fullerene

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A catalytic method for the efficient synthesis of 5,6-open and 6,6-closed ($2\pi+1\pi$) fullerene adducts by [2+1] cycloaddition of ethyl 2-alkyl(hetaryl)-2-diazoacetates to [60]fullerene in the presence of a three-component catalyst $Pd(acac)_2$—PPh_3—Et_3Al have been developed.

Key words: metal complex catalysis, [60]fullerene, diazo compounds, [2+1] cycloaddition.

Substituted cyclopropafullerenes are promising compounds that could find applications in medicine and agriculture, as high energy fuel components and the heavy machinery lubricant additives.[1—13] Cyclopropafullerenes are usually obtained by cyclopropanation of fullerene with malonic acid derivatives following the Bingel procedure,[14,15] as well as by thermal[16] or catalytic[17] [2+1] cycloaddition of diazo compounds to [60]fullerene. The published data[16,17] suggest that the known synthetic methods towards cyclopropafullerenes have low effectiveness or require stoichiometric amounts of such highly expensive promoters as ruthenium complexes. Besides, the yields of the target compounds are low.

The thermal cycloaddition reaction of diazoacetates to [60]fullerene yielded 5,6-open (homofullerenes) and 6,6-closed (methanofullerenes or cyclopropafullerenes) adducts in ~35% total yield. Separation of the reaction mixture into the individual adducts is very difficult and, in some cases, is not possible.

Recently,[18] we have reported the synthesis of cyclopropafullerenecarboxylates with high yields by cycloaddition of ethyl diazoacetate to [60]fullerene in the presence of palladium complexes. In continuation of this research, in the present work we studied [2+1] cycloaddition of ethyl 2-alkyl(hetaryl)-2-diazoacetates and other substituted diazo compounds to [60]fullerene in the presence of palladium complexes. The effect of the solvents and ratio of the catalytic system components as well as the bulkiness of the alkyl substituent in starting diazo compound on the yield and selectivity have also been studied.

Results and Discussion

A three-component catalyst prepared from $Pd(acac)_2$, PPh_3, and Et_3Al turned out to be particularly efficient in the reaction under study showing the highest activity and selectivity among transition metal complexes tested. In this regard, all subsequent experiments were carried out using this catalytic system.

It has been found that the reaction of ethyl 2-methyl-2-diazoacetate with [60]fullerene (molar ratio 5 : 1) in the presence of 20 mol.% of $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4) at 20 °C (18 h, *o*-dichlorobenzene) resulted in a mixture of 6,6-closed (**1**) and 5,6-open (**2**) fullerene adducts along with the corresponding bis-cyclopropane derivatives **3** and **4** in the ratio (**1** + **2**) : (**3** + **4**) ~3 : 1 in ~77% total yield (Scheme 1). No noticeable increase in the total yield (~79%) and changes in the ratio of adducts **1**, **2** and **3**, **4** were observed when the reaction time was prolonged up to 30 h. Similar results were obtained on increase in the reaction temperature to 40 and 80 °C with concomitant reduction of the reaction time from 18 to 1.5 and 0.5 h, respectively.

The mixture of mono- (**1**, **2**) and bis-adducts (**3**, **4**) was separated using semi-preparative HPLC. The data obtained from the ^1H and ^{13}C NMR and 2D experiments (HHCOSY, HSQC, HMBC) of **1**, **2** and **3**, **4** indicated that a mixture of mono-adducts **1** and **2** along with a mixture of regioisomers of bis-adducts **3** and **4** were formed under the described conditions.

In accordance with the ^1H NMR spectral data, 5,6-open adduct **2** was the main component in the mixture **1** + **2** (signal ratio 1 : 6). The singlet signal for the methyl group of adduct **2** appeared in the lower field (δ_H 3.22) than that of **1** (δ_H 2.54). The ^1H NMR spectrum of the mixture **1** + **2** exhibited two sets of quartets (δ_H 4.53, J = 7.2 Hz, and 4.23, J = 7.2 Hz) and triplets (δ_H 1.53, J = 7.2 Hz, and 1.36, J = 7.2 Hz) assigned to the ethyl protons of the ester group. These data are in accord with previously published data[16,18] on the cycloaddition of ethyl diazoacetate to [60]fullerene, which suggests the formation of cyclopropafullerene **1** and 5,6-open adduct **2** with the methyl group arranged above the plane of a

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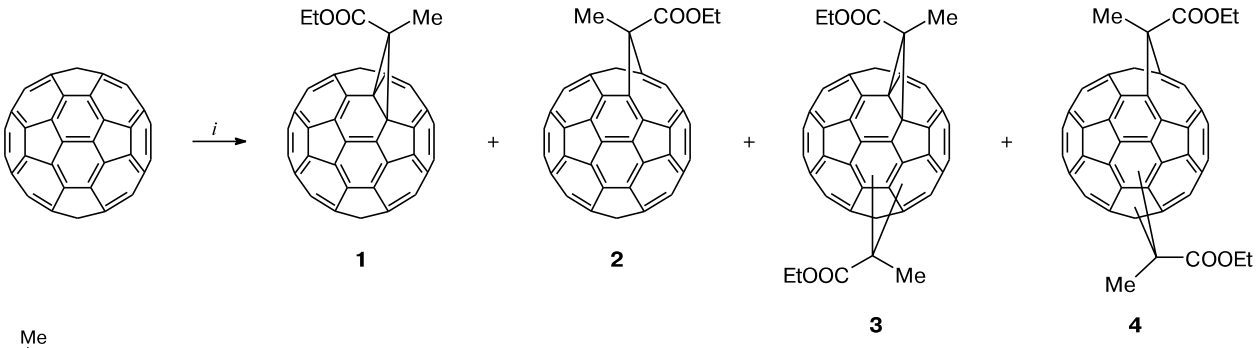
Scheme 1



i. $N_2\overset{Me}{\overset{|}{C}}COOEt$, $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4).

fullerene pentagon. Due to the low content of adduct **1** in the mixture, its ^{13}C NMR spectrum showed four signals with low intensities, which were attributed to ethyl (δ_C 62.24 and 14.39) and methyl (δ_C 15.50) carbon atoms and the bridging C atom (δ_C 44.19). The ^{13}C NMR spectrum of isomer **2** contained 28 signals in the region characteristic of fullerene at δ_C 133—148, with two of them (δ_C 135.41 and 143.65) being of double intensity. The bridging C atom (δ_C 53.44) is bound to the methyl group, which exhibited a singlet signal at δ_H 3.22 thus confirming the formation of adduct **2** of the proposed structure.

In the HMBC experiment of isomeric mixture **1** + **2** (Figs 1 and 2), the cross-peaks of the methyl hydrogens at the corresponding bridging C atoms with the fullerene β-C atoms were observed. Thus interactions of the protons of the methyl group (δ_H 3.22) with the bridgehead (δ_C 136.61) and bridging (δ_C 53.44) carbon atoms, as well as with the carbonyl C atom were observed for the main adduct **2**. The highfield signal for the methyl protons of the adduct **1** exhibited three cross-peaks with the bridging, sp^3-hybridized, and carbonyl C atoms at δ_C 44.19, 76.47, and 167.60, respectively.

Thermal isomerization of the mono-adducts **1** + **2** (refluxing in toluene for 11 h) resulted in 6,6-closed adduct **1** with quantitative yield.

The structure of the 6,6-closed adduct was confirmed using mass MALDI—TOF mass spectrometry. Thus for compound **1** the experiments operated in the linear and reflection modes with recording of positive and negative ions revealed a molecular ion with *m/z* 820.

The data from the ^{13}C NMR spectra of the bis-adducts **3** and **4** showed that the increase in the number of the isomers with respect to the arrangement of the substituents in the fullerene core resulted in the increase in the number of signals characteristic of ethyl, methyl, and carbonyl groups. The 5,6-open adduct **4** was found to be the main product in the mixture of bis-adducts **3** + **4**. The ^{13}C NMR spectrum of adduct **4** contained 7 signals at δ_C 25.08, 25.27, 25.34, 25.38, 25.60, 25.67, and 25.93 attributed to methyl groups at the bridging C atoms, which exhibited also seven signals at δ_C 52.78, 52.89, 52.96, 53.23, 53.46, 53.44, and 53.51. This pattern of the spectrum could suggest the formation of seven regioisomers regarding symmetric alignment of the methyl groups. The ^{13}C NMR spectrum of bis-adduct **4** exhibited four signals for the ethyl groups at δ_C 14.12, 14.29, 61.39, and 61.49 and four signals for the carbonyl groups at δ_C 169.09, 169.11, 169.23, and 169.34. This spectral pattern showed coincidence of the position for the signals for the ester methylene group for the most of the regioisomers of adduct **4**. The ^{13}C NMR spectrum of the mixture **3** + **4** exhibited signals for the regioisomeric 6,6-closed adduct **3**. The signals for the bridging C atoms appeared at δ_C 15.35, 15.53, and 15.66, while the signals for the ethyl C atoms coincided, as only one set of the ethyl group signals appeared

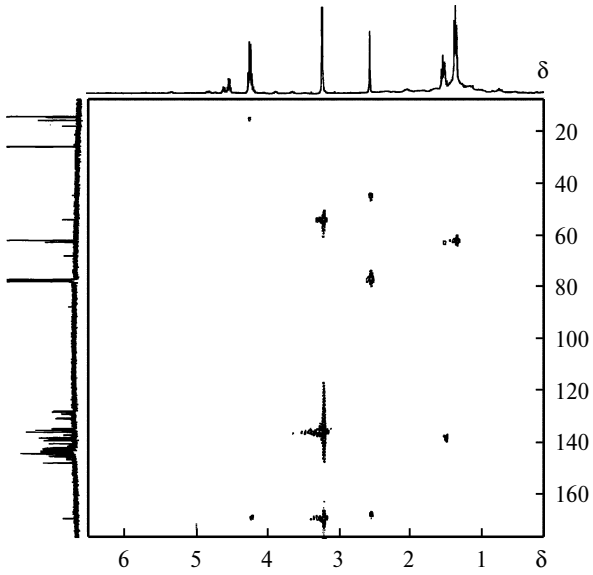


Fig. 1. HMBC Experiment for a mixture of fullerene adducts **1** and **2** (^1H at 400.13 MHz, ^{13}C at 100.62 MHz, solvent, CS_2—$CDCl_3$ (5 : 1)).

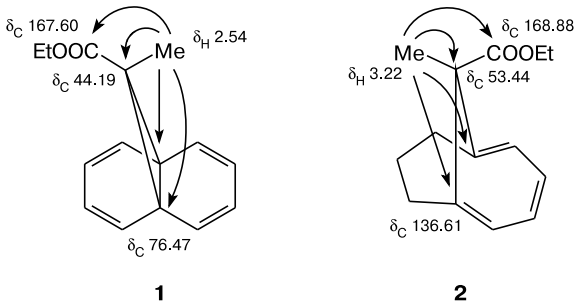


Fig. 2. Long-range interaction of methyl group protons with C atoms of the fullerene skeleton in the HMBC experiment (the chemical shifts are given in the δ scale).

(δ_C 62.20 and 14.39). Unfortunately, no signals for the carbonyl groups, bridging, and sp^3-hybridized C atoms could be detected due to their low intensity and small content of 6,6-closed bis-adduct **3** in the mixture. The fullerene skeleton of the **3** + **4** mixture exhibited 70 signals in the range of δ 130—150 (Fig. 3).

The thermal isomerization of the bis-adduct **4** in the mixture **3** + **4** into bis-adduct **3** were observed (toluene, 110 °C, 16 h).

In accordance with the ^{1}H NMR spectral data of thermal isomerization of adducts **3** + **4**, the intensity of the methyl proton signals in the range of δ_H 2.4—2.6 increased significantly due to the increase in the content of 6,6-closed isomers **3**. The ^{1}H NMR spectrum of adduct **3** exhibited nine signals (δ_H 2.43, 2.46, 2.47, 2.48, 2.49, 2.51, 2.55, 2.56, and 2.58) characteristic of the methyl groups at the bridging C atoms, which could suggest the formation of nine regioisomers of bis-adduct **3** regarding symmetric alignment of the methyl groups. The structure of the adduct **3** was confirmed by mass spectral data (*m/z* 920) that were collected in the linear mode with registration of the more informative negative ions.

With the aim at analyzing the structure of regioisomers of bis-adduct **3**, whose formation seemed more probable, we calculated the thermal effects of the model addition reaction of a carbene generated by decomposition of ethyl 2-methyl-2-diazoacetate to mono-adduct **1**. The calculations were implemented within the framework of the density functional theory at the PBE/3z level[19,20]

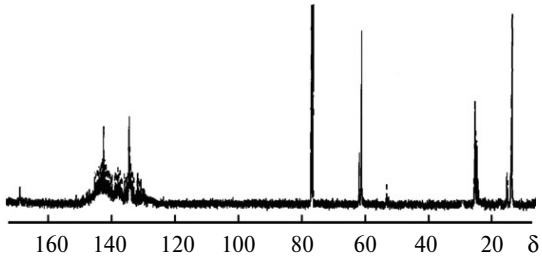


Fig. 3. ^{13}C NMR spectrum of the mixture of bis-adducts **3** and **4** (solvent, CS_2—$CDCl_3$ (5 : 1)).

(PRIRODA 2.02+ program package),[21] which correctly reproduced the energy and geometry parameters of fullerenes[22] and their derivatives.[23] Since the cyclopropanation of unsaturated hydrocarbons with carbenes exhibits high reaction rates and low activation energy,[24] the thermal effect of the reaction was chosen as a value characteristic of the reaction probability.

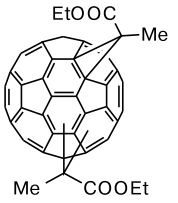
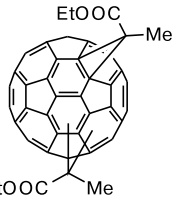
Thus the addition of the carbene to nonequivalent 6,6-bonds of mono-adduct **1** resulted in nine regioisomers (Fig. 4) depending on the relative orientation of Me and COOEt groups, each of these regioisomers could exist as two stereoisomers (*in,in* or *in,out*). The equal probability of the formation of the isomers differing in the Me and COOEt groups arrangement was confirmed by small difference in thermal effects of addition reactions leading to *in,in*- or *in,out*-isomers (Table 1).

The reactions that resulted in nine pairs of isomeric bis-adducts are exothermic with thermal effects $-\Delta_r H°$ in the range of 205.0—276.9 kJ mol^{-1}. The difference in $-\Delta_r H°$ values of the formed bis-adducts was very small. Only for *cis*-1 (*in,in* and *in,out)* isomers, the thermal effects decreased by ~50 kJ mol^{-1} in respect of the other isomeric bis-adducts due to the interaction between cyclopropane rings annulated by 6,6-bonds of the same hexagon.

The influence of the ratio of the catalytic system $Pd(acac)_2$—PPh_3—Et_3Al components (Table 2) and the solvent effects (Table 3) on the yield of adducts **1** and **2** were studied on the model reaction of [60]fullerene with ethyl 2-methyl-2-diazoacetate.

From the data presented in Table 2 followed that the increase in the concentration of PPh_3 in the three-component catalytic system resulted in the increase in the

Table 1. Calculated thermal effects ($\Delta_r H$) of addition reaction of ethoxycarbonyl(methyl)carbene to mono-adduct **1**

Bis-adduct	$\Delta_r H°$/kJ mol^{-1}	
		
	in,in	*in,out*
cis-1	205.0	215.7
cis-2	264.2	264.2
cis-3	264.3	264.6
trans-1	273.1	269.7
trans-2	272.2	272.5
trans-3	275.4	277.6
trans-4	268.4	268.8
e_{edge}	276.9	274.7
e_{face}	273.0	275.7

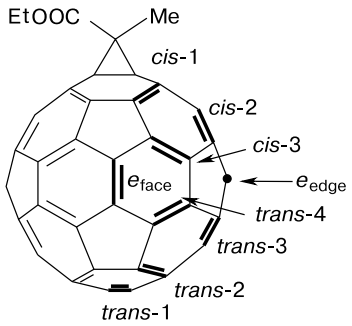


Fig. 4. Possible regioisomers of bis-adduct **3**.

6,6-closed adduct **1** yield. The same result can be obtained for the reaction carried out in 1,2,4-trichlorobenzene in the presence of the catalytic system $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4) (see Table 3). The replacement of 1,2,4-trichlorobenzene by *o*-dichlorobenzene led mainly to 5,6-open adduct **2**. The content of bis-adducts **3** and **4** did not exceed 10% in all experiments. Thus, the changes in the [Pd] : PPh_3 ratio in the three-component catalytic system or the solvent led preferably to predominant formation of 6,6-closed (**1**) or 5,6-open adducts (**2**).

The effect of the bulkiness of the α-alkyl substituent of the diazo compound on the yield and selectivity of the reaction under consideration were also studied. The reactions of [60]fullerene with ethyl 2-ethyl-, 2-isobutyl-, and 2-benzyl-2-diazoacetates were used as examples (Scheme 2). It was found that under optimum conditions (80 °C, 0.5—1.0 h, $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4)) [60]fullerene reacted with the above-mentioned diazo compounds (molar ratio 1 : 5) to give the corresponding mono- and bis-adducts.

The data from ^1H and ^{13}C NMR spectra of compounds **5—10** suggested that the reaction of [60]fullerene with ethyl 2-isobutyl-2-dizoacttate and ethyl 2-benzyl-2-diazoacetate (in contrast with ethyl 2-methyl-2-diazoacetate) yielded stereoisomers of 5,6-open adducts (**7a,b**) with alkyl substituents located above the plane of the [60]fullerene hexagon along with a mixture of mono-adducts (**5b, 6b** and **5c**, **6c**). The total yields (and ratios)

Table 2. Influence of molar ratio of the catalytic system $Pd(acac)_2$—PPh_3—Et_3Al components on the yield (Y_{1+2}) and ratio of adducts **1** and **2**

$Pd(acac)_2$—PPh_3—Et_3Al	Y_{1+2} (%)	**1** : **2**
1 : 1 : 4	52	1 : 6
1 : 2 : 4	57	1 : 6
1 : 3 : 4	50	1 : 4
1 : 4 : 4	56	2 : 1

Note. Reaction conditions: *o*-dichlorobenzene, 80 °C, 0.5 h.

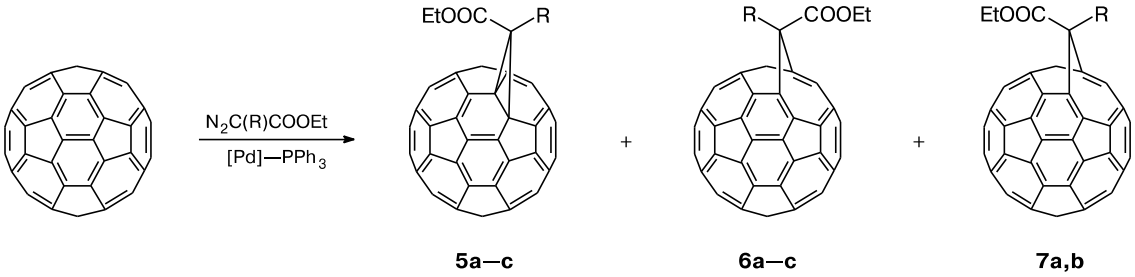
Table 3. Solvent effect on the yield (Y_{1+2}) and ratio of adducts **1** and **2**

Solvent	Y_{1+2} (%)	**1** : **2**
Benzene	47	1 : 2
Chlorobenzene	57	1 : 4
o-Dichlorobenzene	57	1 : 6
1,2,4-Trichlorobenzene	53	5 : 1
Toluene	40	1 : 3
1,3-Dimethylbenzene	49	1 : 2
1-Methylnaphtalene	50	1 : 4

Note. Reaction conditions: 80 °C, 0.5 h, $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4).

of adducts **5**, **6**, and **7** synthesized from ethyl 2-ethyl-, 2-isobutyl-, and 2-benzyl-2-diazoacetates were 54 (2 : 1 : 0), 51 (11 : 6 : 1), and 65 (4 : 4 : 1), respectively. No significant changes were observed for the reactions carried out under milder conditions (20 °C, 40 h), except for the reaction of [60]fullerene with ethyl 2-isobutyl-2-diazoacetate, where the yield of the adducts **5b**, **6b**, and **7a** decreased twofold. In the studied reactions, the bis-adducts **8—10** were also formed in minor amounts (less than 8% according to HPLC). No spectral analysis of the bis-adducts **8—10** was performed due to their low content in the mixtures. The arragenment of the alkyl substituents in stereoisomers **6a—c** and **7a,b** was assigned by comparing the spectral data of these

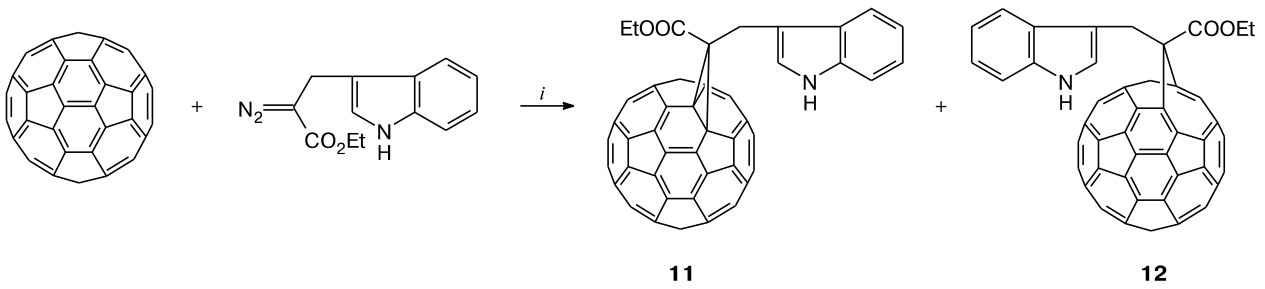
Scheme 2



5a—c **6a—c** **7a,b**

R = Et (**5a**, **6a**), Bu^i (**5b**, **6b**, **7a**), Bn (**5c**, **6c**, **7b**)

Scheme 3



11 **12**

i. 80 °C, 1 h, $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4).

compounds with those of the specimens synthesized previously by reaction of [60]fullerene with ethyl diazoacetate.[16,18]

It should be noted that under the conditions found (80 °C, 1 h, 20 mol.% $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4)) the [2+1] cycloaddition of ethyl 3-(1*H*-indol-3-yl)-2-diazopropionate to [60]fullerene occurred very selectively and resulted in mono-adducts **11** and **12** in ~40% total yield (Scheme 3). The adducts **11** and **12** could be obtained with the same yield when the reaction was carried out at ~20 °C for 21 h. In these experiments, no formation of bis-adducts was observed.

Based on the data from 1D (^1H and ^{13}C NMR) and 2D (HHCOSY, HSQC, HMBC) experiments, we found that the reactions under study yielded 6,6-closed (**11**) and 5,6-open (**12**) adducts with the indolylmethyl substituent above the plane of the five-membered ring of fullerene. The ratio of isomers **11** and **12** were determined from ^1H NMR spectral data being 6 : 1 and 2 : 1 at 80 and 20 °C, respectively.

In summary, it was experimentally shown that [2+1] cycloaddition of alkyl- and hetaryl-substituted ethyl 2-diazoacetates to [60]fullerene in the presence of a three-component catalytic system $Pd(acac)_2$—PPh_3—Et_3Al readily gives 6,6-closed or 5,6-open adducts with fairly high yields. It was shown that the structure of the products depended on the ratio of the components in the catalytic system, solvents, and reaction conditions. With the increase in the balkiness of the α-alkyl substituent in diazoacetates, their reactivity decreased, while the yield of 6,6-closed adducts increased.

Experimental

Commercially available [60]fullerene (99.5% pure, G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhniy Novgorod) was used. The reaction products were analyzed using an HPLC chromatograph Altex (model 330) (USA) equipped with a UV detector (340 nm). The mixtures were separated on metal column Cosmosil Buckyprep Waters (250×10 mm) at ~20 °C. Toluene was used as the eluent, the flow rate was 2.0 mL min^{-1}. The IR spectra were registered on a Specord 75 IR (Carl Zeiss Jena) spectrophotometer in KBr pellets, the UV spectra were recorded on a Specord M-40 and Specord M-80 instruments in $CHCl_3$. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400.13 and 100.62 MHz, respectively. A mixture of $CDCl_3$ and CS_2 (1 : 5) was used as a solvent. The negative-ion mass spectra were obtained on a MALDI TOF/TOF Autoflex-III Bruker mass spectrometer without a matrix operating in a linear mode. Samples were dissolved in toluene prior to application on a metal target.

[2+1] Cycloaddition of diazo compounds to [60]fullerene (general procedure). Solutions of $Pd(acac)_2$ (0.00278 mmol) in *o*-dichlorobenzene (0.4 mL) and PPh_3 (0.00556 mmol) in *o*-dichlorobenzene (0.42 mL) were placed in a glass reactor, cooled to −5 °C, and a solution of Et_3Al (0.01112 mmol) in toluene (0.1 mL) was added with stirring under argon. The color changed from pale yellow to pale brown. To the resulting catalyst, a solution of [60]fullerene (0.0139 mmol) in *o*-dichlorobenzene (1.0 mL) was added at ~20 °C, the color of the mixture turned to dark green. The mixture was heated to 40 or 80 °C and a solution of ethyl 2-alkyl(hetaryl)-2-diazoacetate (0.0695 mmol) in *o*-dichlorobenzene (0.5 mL) was added dropwise in 5 min. The mixture was stirred for 0.5—1.5 h at the corresponding temperature. Then the reaction mixture was cooled to room temperature and treated with aqueous HCl. After addition of toluene (7 mL), the organic layer was passed through a small layer of silica gel. The products **1—6** were separated by preparative HPLC using toluene as the eluent. Thermal isomerization of 5.6-open isomers into 6,6-adducts was carried out in accordance with the known procedure.[16,18]

1′-Methyl-1′-ethoxycarbonyl-(C_{60}-I_h)[2′,3′:1,9]cyclopropa[5,6]fullerene (1). IR, ν/cm^{-1}: 540; 820; 1040; 1110; 1270; 1660. UV, λ_{max}/nm: 260, 327, 424. ^1H NMR, δ: 1.53 (t, 3 H, Me, J = 7.2 Hz); 2.54 (s, 3 H, Me); 4.53 (q, 2 H, CH_2, J = 7.2 Hz). ^{13}C NMR, δ: 14.39, 15.50, 44.19, 62.24, 76.47 (sp^3), 138.17, 138.35, 140.92, 141.15, 142.08, 142.14, 142.24, 142.30, 142.97, 143.05, 143.12, 143.31, 143.71, 143.93, 144.29, 144.60, 144.62, 144.70, 144.83, 145.20, 145.23, 145.25, 145.58, 146.31, 147.60, 167.60 (COOEt). MS, *m/z*: 820 $[M]^+$.

1′a-Methyl-1′a-ethoxycarbonyl-1′a-carba-1′(2′)a-homo-(C_{60}-I_h)[5,6]fullerene (2). IR, ν/cm^{-1}: 520; 1080; 1120; 1200; 1740. UV, λ_{max}/nm: 262, 333. ^1H NMR, δ: 1.36 (t, 3 H, Me, J = 7.2 Hz); 3.22 (s, 3 H, Me); 4.23 (q, 2 H, CH_2, J = 7.2 Hz). ^{13}C NMR, δ: 14.08, 25.52, 53.44, 61.50, 134.06, 134.64, 135.41, 136.61, 137.65, 138.31, 138.67, 138.72, 139.91, 140.56, 141.41, 141.58, 141.75, 141.90, 142.21, 142.56, 142.59, 142.69, 142.88,

142.95, 143.15, 143.29, 143.48, 143.65, 143.83, 144.51, 144.73, 147.26, 167.60 (COOEt).

Bis-adduct 3. ^{1}H NMR, δ: 1.47—1.55 (m); 2.43, 2.46, 2.47, 2.48, 2.49, 2.51, 2.55, 2.56, and 2.58 (all s); 4.45—4.55 (m). ^{13}C NMR, δ: 14.39, 15.35, 15.53, 15.66, 44.26, 44.49, 45.26, 45.55, 50.02, 62.20, 138—147, 167.54 (COOEt), 167.61 (COOEt), 167.63 (COOEt), 167.76 (COOEt). MS, *m/z*: 920 $[M]^+$.

Bis-adduct 4. ^{1}H NMR, δ: 1.29—1.38 (m); 3.03, 3.05, 3.12, 3.17, 3.19, 3.21 and 3.25 (all s); 4.18—4.29 (m). ^{13}C NMR, δ: 14.12, 14.29, 25.08, 25.27, 25.34, 25.38, 25.60, 25.67, 25.93, 52.78, 52.89, 52.96, 53.23, 53.46, 53.44, 53.51, 61.39, 61.49, 128—147, 169.09 (COOEt), 169.11 (COOEt), 169.23 (COOEt), 169.34 (COOEt).

1´-Ethyl-1´-ethoxycarbonyl-(C_{60}-I_h)[2´,3´:1,9]cyclopropa-[5,6]fullerene (5a). IR, ν/cm^{-1}: 530; 1130; 1180; 1200; 1230; 1730. UV, λ_{max}/nm: 261, 327, 425. ^{1}H NMR, δ: 1.53 (t, 3 H, Me, *J* = 7.2 Hz); 1.58 (t, 3 H, Me, *J* = 7.2 Hz); 2.96 (q, 2 H, CH_2, *J* = 7.2 Hz); 4.54 (q, 2 H, CH_2, *J* = 7.2 Hz). ^{13}C NMR, δ: 11.63, 14.44, 23.18, 50.93, 62.13, 76.20 (sp^3), 137.36, 137.79, 140.53, 140.79, 141.71, 141.84, 141.87, 141.92, 142.60, 142.66, 142.74, 142.87, 143.33, 143.53, 143.92, 144.23, 144.32, 144.47, 144.83, 144.85, 144.87, 144.90, 145.27, 145.81, 147.78, 166.75 (COOEt). MS, *m/z*: 834 $[M]^+$.

1´a-Ethyl-1´a-ethoxycarbonyl-1´a-carba-1´(2´)a-homo-(C_{60}-I_h)[5,6]fullerene (6a). IR, ν/cm^{-1}: 520; 1200; 1220; 1730. UV, λ_{max}/nm: 262, 333. ^{1}H NMR, δ: 1.35 (t, 3 H, Me, *J* = 7.2 Hz); 1.46 (t, 3 H, Me, *J* = 7.2 Hz); 3.89 (q, 2 H, CH_2, *J* = 7.2 Hz); 4.25 (q, 2 H, CH_2, *J* = 7.2 Hz). ^{13}C NMR, δ: 10.58, 14.34, 32.18, 59.13, 61.40, 134.23, 134.85, 135.44, 137.73, 138.42, 138.70, 139.04, 139.99, 141.28, 141.88, 142.00, 142.07, 142.21, 142.65, 142.74, 142.80, 142.88, 142.94, 143.02, 143.19, 143.68, 144.04, 144.34, 144.96, 147.38 168.84 (COOEt).

1´-Isobutyl-1´-ethoxycarbonyl-(C_{60}-I_h)[2´,3´:1,9]cyclopropa[5,6]fullerene (5b). IR, ν/cm^{-1}: 520; 1120; 1170; 1220; 1460; 1620; 1730. UV, λ_{max}/nm: 260, 328, 425. ^{1}H NMR, δ: 1.36 (d, 6 H, 2 Me, *J* = 6.4 Hz); 1.52 (t, 3 H, Me, *J* = 7.2 Hz); 2.25—2.31 (m, 1 H, CH); 2.84 (d, 2 H, CH_2, *J* = 7.2 Hz); 4.52 (q, 2 H, CH_2, *J* = 7.2 Hz). ^{13}C NMR, δ: 14.88, 22.94, 28.03, 37.71, 49.27, 62.39, 75.88 (sp^3), 137.65, 138.09, 140.92, 141.16, 142.09, 142.20, 142.27, 142.96, 143.02, 143.10, 143.22, 143.76, 143.94, 144.35, 144.59, 144.67, 144.69, 144.85, 145.22, 145.25, 145.27, 145.35, 145.52, 146.82, 148.08, 166.96 (COOEt). MS, *m/z*: 862 $[M]^+$.

1´a-Isobutyl-1´a-ethoxycarbonyl-1´a-carba-1´(2´)a-homo-(C_{60}-I_h)[5,6]fullerene (6b). IR, ν/cm^{-1}: 520; 740; 1120; 1200; 1430; 1460; 1620. UV, λ_{max}/nm: 263, 330. ^{1}H NMR, δ: 1.23 (d, 6 H, 2 Me, *J* = 6.8 Hz); 1.36 (t, 3 H, Me, *J* = 7.2 Hz); 1.94—2.02 (m, 1 H, CH); 3.79 (d, 2 H, CH_2, *J* = 7.2 Hz); 4.21 (q, 2 H, CH_2, *J* = 7.2 Hz). ^{13}C NMR, δ: 14.59, 23.89, 27.71, 47.27, 57.81, 61.62, 134.51, 134.98, 135.14, 135.23, 137.91, 138.67, 138.75, 139.34, 140.27, 141.34, 141.76, 141.92, 142.17, 142.42, 142.61, 142.88, 143.17, 143.19, 143.46, 143.71, 143.86, 143.99, 144.03, 144.89, 147.64, 168.82 (COOEt).

1´a-Isobutyl-1´a-ethoxycarbonyl-1´a-carba-1´(2´)a-homo-(C_{60}-I_h)[5,6]fullerene (7a). ^{1}H NMR, δ: 1.05 (d, 6 H, 2 Me, *J* = 6.4 Hz); 1.69 (t, 3 H, Me, *J* = 7.2 Hz); 1.75—1.81 (m, 1 H, CH); 2.93 (d, 2 H, CH_2, *J* = 7.2 Hz); 4.59 (q, 2 H, CH_2, *J* = 7.2 Hz). ^{13}C NMR, δ: 14.79, 23.89, 26.63, 46.18, 54.25, 62.13, 135.14, 135.23, 136.55, 137.21, 138.04, 140.46, 141.68, 142.17, 142.36, 142.45, 142.97, 143.17, 143.19, 143.46, 143.57, 143.71, 144.16, 144.54, 144.79, 145.23, 147.64.

1´-Benzyl-1´-ethoxycarbonyl(C_{60}-I_h)[2´,3´:1,9]cyclopropa-[5,6]fullerene (5c). IR, ν/cm^{-1}: 520; 1180; 1210; 1430; 1630; 1730. UV, λ_{max}/nm: 260, 329, 425. ^{1}H NMR, δ: 1.34 (t, 3 H, Me, *J* = 7.2 Hz); 4.25 (s, 2 H, CH_2); 4.37 (q, 2 H, CH_2, *J* = 7.2 Hz); 7.21 (t, H, CH, *J* = 7.2 Hz); 7.43 (t, 2 H, 2 CH, *J* = 7.2 Hz); 7.60 (d, 2 H, 2 CH, *J* = 7.6 Hz). ^{13}C NMR, δ: 14.53, 35.26, 50.20, 62.45, 76.01 (sp^3), 127.67 (Ph), 129.03 (Ph), 129.23 (Ph), 136.55 (Ph), 138.09, 140.27, 141.16, 141.57, 142.08, 142.21, 142.27, 142.96, 143.06, 143.14, 143.21, 143.74, 143.96, 144.38, 144.61, 144.68, 144.71, 144.88, 145.25, 145.27, 145.30, 145.35, 145.51, 146.82, 147.88, 166.31 (COOEt). MS, *m/z*: 896 $[M]^+$.

1´a-Benzyl-1´a-ethoxycarbonyl-1´a-carba-1´(2´)a-homo-(C_{60}-I_h)[5,6]fullerene (6c). IR, ν/cm^{-1}: 510; 680; 720; 1180; 1720. UV, λ_{max}/nm: 262, 333. ^{1}H NMR, δ: 1.12 (t, 3 H, Me, *J* = 7.2 Hz); 3.98 (q, 2 H, CH_2, *J* = 7.2 Hz); 5.16 (s, 2 H, CH_2); 7.22 (t, H, CH, *J* = 7.2 Hz); 7.44 (t, 2 H, 2 CH, *J* = 7.2 Hz); 7.46 (d, 2 H, 2 CH, *J* = 7.6 Hz). ^{13}C NMR, δ: 14.15, 44.61, 60.39, 61.56, 127.73 (Ph), 128.71 (Ph), 129.62 (Ph), 134.54, 134.82, 134.93, 135.49, 135.86 (Ph), 137.90, 138.67, 138.76, 139.41, 140.27, 141.57, 141.75, 141.97, 142.13, 142.39, 142.56, 142.93, 143.25, 143.32, 143.49, 143.72, 143.89, 144.05, 144.06, 144.88, 147.64, 167.30 (COOEt).

1´a-Benzyl-1´a-ethoxycarbonyl-1´a-carba-1´(2´)a-homo-(C_{60}-I_h)[5,6]fullerene (7b). ^{1}H NMR, δ: 1.23 (t, 3 H, Me, *J* = 7.2 Hz); 3.09 (s, 2 H, CH_2); 4.32 (q, 2 H, CH_2, *J* = 7.2 Hz); 7.24 (t, H, CH, *J* = 7.2 Hz); 7.32 (t, 2 H, 2 CH, *J* = 7.2 Hz); 7.35 (d, 2 H, 2 CH, *J* = 7.6 Hz). ^{13}C NMR, δ: 14.32, 36.94, 62.32, 64.89, 127.55 (Ph), 128.46 (Ph), 130.01 (Ph), 136.91 (Ph), 135.49, 136.55, 137.07, 138.04, 138.27, 138.97, 139.29, 140.46, 141.54, 142.24, 142.30, 142.50, 142.97, 143.21, 143.25, 143.49, 143.51, 143.62, 143.70, 144.20, 144.60, 144.73, 145.14, 147.59, 171.25 (COOEt).

1´-(1*H*-Indol-3-ylmethyl)-1´-ethoxycarbonyl-(C_{60}-I_h)-[2´,3´:1,9]cyclopropa[5,6]fullerene (11). IR, ν/cm^{-1}: 500; 710; 1180; 1410; 1440; 1620; 1720. UV, λ_{max}/nm: 260, 329, 425. ^{1}H NMR, δ: 1.28 (t, 3 H, Me, *J* = 7.2 Hz); 4.31 (q, 2 H, CH_2, *J* = 7.2 Hz); 4.39 (s, 2 H, CH_2); 7.16 (t, H, CH, *J* = 6.8 Hz); 7.21 (d, H, CH, *J* = 6.0 Hz); 7.22 (d, H, CH, *J* = 6.0 Hz); 7.43 (d, H, CH, *J* = 8.0 Hz); 7.55 (t, H, CH, *J* = 8.0 Hz); 9.81 (s, 1 H, NH). ^{13}C NMR, δ: 14.49, 25.86, 50.83, 62.55, 76.61 (sp^3), 111.30, 111.41, 119.00, 120.20, 122.93, 127.65, 133.07, 137.92, 138.25, 140.96, 141.26, 141.58, 142.09, 142.18, 142.25, 142.32, 143.01, 143.06, 143.15, 143.22, 143.29, 143.75, 143.93, 144.04, 144.35, 144.66, 144.73, 144.87, 145.23, 145.27, 145.59, 146.49, 147.80, 166.75 (COOEt). MS, *m/z*: 935 $[M]^+$.

1´a-(1*H*-Indol-3-ylmethyl)-1´a-ethoxycarbonyl-1´a-carba-1´(2´)a-homo(C_{60}-I_h)[5,6]fullerene (12). IR, ν/cm^{-1}: 520; 1180; 1210; 1430; 1630; 1730. UV, λ_{max}/nm: 263, 330. ^{1}H NMR, δ: 1.03 (t, 3 H, CH_3, *J* = 7.2 Hz); 3.87 (q, 2 H, CH_2, *J* = 7.2 Hz); 5.35 (s, 2 H, CH_2); 7.11 (t, H, CH, *J* = 6.8 Hz); 7.21 (d, H, CH, *J* = 6.0 Hz); 7.37 (d, H, CH, *J* = 6.0 Hz); 7.43 (d, H, CH, *J* = 8.0 Hz); 7.55 (t, H, CH, *J* = 8.0 Hz); 9.76 (s, H, NH). ^{13}C NMR, δ: 14.05, 35.04, 61.73, 62.43, 111.59, 111.22, 118.82, 120.10, 122.69, 130.60, 135.20, 135.72, 135.93, 136.20, 137.92, 138.09, 138.75. 138.96, 139.42, 140.24, 141.58, 141.80, 141.95, 142.18, 142.32, 142.50, 142.56, 143.48, 143.60, 143.71, 143.88, 144.04, 144.87, 147.62, 167.83 (COOEt).

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