Cycloaddition of diazoacetates to C_{60} fullerene catalysed by Pd complexes

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An efficient catalytic method of the cycloaddition to C_{60} fullerene of the diazoacetates, containing substituents of diverse structures in ester groups, in the presence of a Pd-based three-component catalyst was developed. An influence of nature and the structure of substituent in the ester group on the activity of diazoacetates in the reaction with C_{60} was studied. Yields of respective cycloadducts were determined.

Key words: metallocomplex catalysis, C_{60} fullerene, diazoacetates, cycloaddition.

An interest in carboxy derivatives of methanofullerenes is caused by a possibility of obtaining of promising preparations for medicine and agriculture on their base.[1—5] However, a synthesis of these C_{60} derivatives containing substituents in the ester group consists in multi-stage conversion of carboxymethanofullerene which results in low yields of the target products.[1,3,6—9]

Recently, an efficient catalytic method of cycloaddition of diazoacetic ester and α-substituted ethyl diazoacetates to the C_{60} fullerene using the three-component catalyst $Pd(acac)_2—PPh_3—Et_3Al$ (20 mol.%) was suggested.[10,11] As it is noted, by a ratio of the starting components of catalytic system and the nature of the substituent in α-position to the diazo group of the initial diazoacetate, it is possible to definitely regulate a direction of the cycloaddition and to selectively obtain both methanofullerenes and homofullerenes.

In order to develop our earlier elaborated[10,11] method of the catalytic cycloaddition of the diazoacetates to the C_{60} fullerene under the action of catalysts on a basis of low-valent Pd complexes, as well as to investigate the influence of the structure of substituent in the ester group of diazoacetate on the direction and the structural selectivity of the reaction of the latters with the fullerene C_{60}, we studied the cycloaddition of diazoacetates with alkyl, cycloalkyl, allyl, and steroid substituents to the fullerene C_{60} catalysed by $Pd(acac)_2—PPh_3—Et_3Al$ (1 : 2 : 4)

Results and Discussion

It was earlier shown,[11] that the influence of nature and substituent structure in the α-substituted ethyl diazoacetates on the selectivity of formation of homo- and methanofullerenes in the reaction with C_{60} is most evident when the three-component catalyst $Pd(acac)_2—PPh_3—Et_3Al$ (components molar ratio is 1 : 2 : 4, respectively) is used. During the cycloaddition using the components molar ratio of this catalytic system equal to 1 : 4 : 4, only the methanofullerenes were formed regardless of the substituent structure in the diazo compound. Therefore, all the following experiments were carried out using the catalytic system $Pd(acac)_2—PPh_3—Et_3Al$ (1 : 2 : 4) with a purpose of more detailed study of the influence of the structure of initial diazoacetates on the composition of the cycloadducts formed.

In a reaction of isopropyl diazoacetate with the fullerene C_{60} (molar ratio 5 : 1) in the presence of 20 mol.% of three-component catalyst $Pd(acac)_2—PPh_3—Et_3Al$ (1 : 2 : 4) in 1,2-dichlorobenzene at 80 °C, in 1 h a mixture of [6,6]-closed (**1**) and two stereoisomeric [5,6]-open (**2**, **3**) adducts of C_{60} with a total yield* ~70% is formed (Scheme 1). An increasing of the reaction duration to 2 h does not result in a noticeable increasing of the total yield (~76%) of the target cycloadducts. At a higher concentration of organophosphorous ligand in the three-component catalytic system (components ratio 1 : 4 : 4), we managed to direct the mentioned reaction to the selective formation of the respective methanofullerene **1** in a ~72% yield.

Using a method of semi-preparative HPLC we isolated a mixture of the cycloadducts of mono addition **1—3**. We could not separate the compounds **1—3**. This was caused by the close physical-chemical constants and polarity of the obtained adducts, which do not allow their separation in individual forms by chromatography. One- (^1H and ^{13}C) and two-dimensional (COSY, HSQC, HMBC) NMR experiments showed that the mixture of

* Hereafter the yields are based on the starting fullerene C_{60}.

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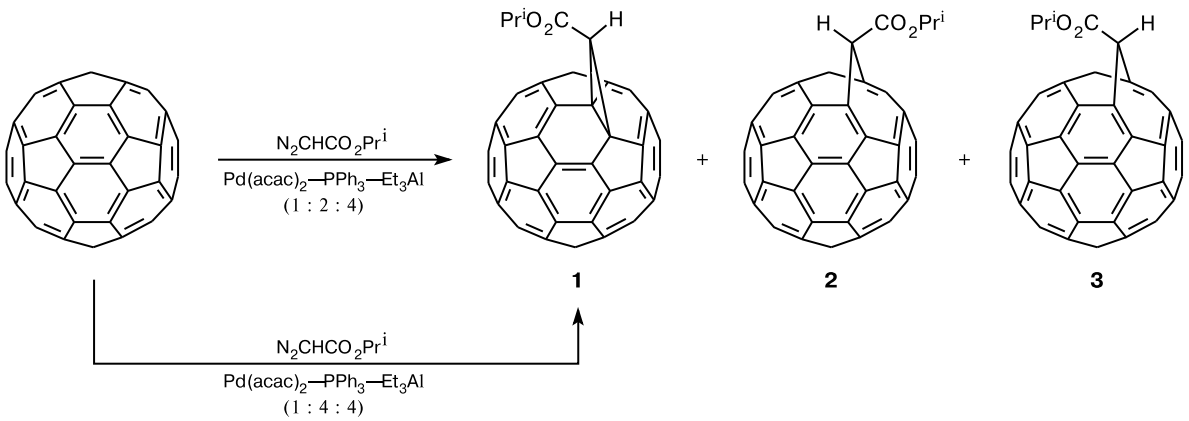
Scheme 1



[6,6]-closed (**1**) and stereoisomeric [5,6]-open (**2**, **3**) monoadducts of the fullerene was formed.

On the basis of integral curves of signals in ^1H NMR spectrum of the compounds **1**—**3**, a ratio of the cycloadducts was found: **1** : **2** : **3** = 6 : 5 : 4. Singlet signals (δ_H 4.74, 7.40, and 3.75) by analogy with the earlier obtained data[10,11] were assigned to hydrogen atoms at a bridge carbon atom of the compounds **1**—**3**, respectively. The ^1H NMR spectrum of the compounds **1**—**3** mixture also has three sets of doublets (δ_H 1.54 (J = 6.0 Hz), 1.36 (J = 6.0 Hz), and 1.49 (J = 6.0 Hz)) and septets (δ_H 5.38 (J = 6.0 Hz), 5.12 (J = 6.0 Hz) and 5.47 (J = 6.0 Hz)), pertaining to the hydrogen atoms of the isopropyl group of the ester fragment. By analogy with the earlier published data[10] for the adducts of cycloaddition of the diazoacetic ester to the fullerene C_{60} this confirms the formation of [6,6]-closed methanofullerene **1** and two stereoisomeric [5,6]-open fulleroids **2** and **3** in which the hydrogen atom is arranged at the bridge carbon atom above a plane of five- and six-membered fragment of the C_{60} molecule, respectively. In ^{13}C NMR spectrum of the mixture of adducts **1**—**3**, ten signals in a high field (δ_C 21.82, 22.03, 22.14, 39.61, 52.10, 54.45, 69.83, 70.36, 70.55, and 70.84) were observed. The analysis of HSQC spectra of the mixture of compounds **1**—**3** showed that the signals at δ_C 22.14 and 70.36 are assigned to carbon atoms of the isopropyl group, and the signal at δ_C 39.61 is assigned to the bridge carbon atom of the compound **1**. In the same way, the signals at δ_C 22.03 and 69.83 and δ_C 21.82 and 70.55 are assigned to the carbon atoms of the two isopropyl groups, and the signals at δ_C 52.10 and 54.45 are assigned to the bridge carbon atoms of the adducts **2** and **3**, respectively.

In the HMBC experiment for the mixture of isomers **1**—**3** (Fig. 1) we observed cross-peaks of the hydrogen atoms at the respective bridge carbon atoms with fullerene carbon atoms in α- and β-surrounding. Thus, typical of the [6,6]-closed adduct **1** are interactions of the hydrogen atom at the bridge carbon atom (δ_H 4.74) with sp^3-hybridized (δ_C 70.84) and sp^2-hybridized (δ_C 148.36) carbon atoms of the fullerene sphere in the α- and β-positions, and also with the carbon atom of carbonyl group (δ_C 165.43). Low-field and high-field signals of the hydrogen atoms at the bridge carbon atoms in the [5,6]-open adducts **2** and **3** (δ_H 7.40 and 3.75) have four cross-peaks, each one with bridge-head carbon atoms (δ_C 131.16 and 133.46) and the carbon atoms of the fullerene sphere (δ_C 136.64, 142.87, and 135.22, 144.07) in β-position, and also with the carbonyl carbon atoms (δ_C 165.23 and 169.09).

The formation of the mixture of [6,6]-closed and two stereoisomeric [5,6]-open adducts with a composition $C_{65}H_8O_2$ was also confirmed by MALDI TOF mass-spectrometry. Experiments were carried out in a linear (TOF)

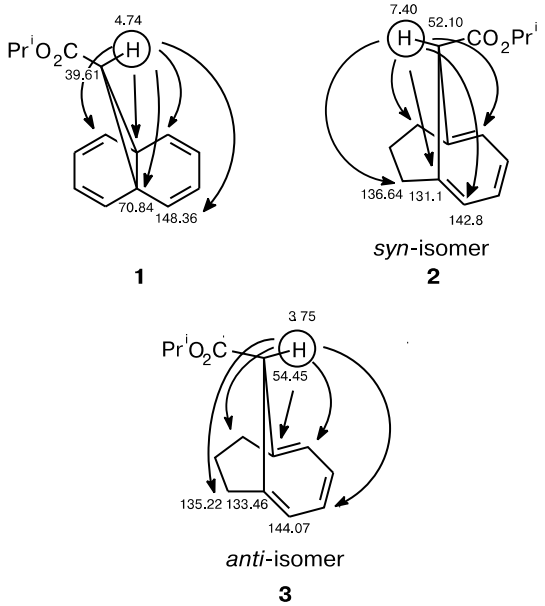


Fig. 1. Distant interactions of the hydrogen atom at the bridge carbon atom with C atoms of the fullerene cage in the HMBC experiments.

and reflector (TOF/TOF) modes with a registration of positive and negative ions, which showed the presence of a molecular ion with *m/z* 820.787 (M_{calc} = 820.758), and fragment ions with *m/z* 733.766 $[C_{60}CH]^+$ (M_{calc} = 733.662) and *m/z* 778.783 $[C_{60}CHCOO]^+$ (M_{calc} = 778.678).

In order to study the influence of a size and the structure of the substituent in the ester group of the initial diazo compound on the yield and the selectivity of the formation of homo- and methanofullerenes, *tert*-butyl, cyclohexyl, allyl, and benzyl diazoacetates (Scheme 2, Cy is cyclohexyl) were involved into the reaction with C_{60}. It was found that under the conditions we elaborated (80 °C, 1 h, $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4)), C_{60} reacts with the mentioned diazo compounds (molar ratio 1 : 5) to form respective monoadducts **4a**—**d**, **5b**,**c**, **6b**—**d**. Yields and ratios of the cycloadducts **4**—**6** are presented in Table 1.

^1H and ^{13}C NMR spectra of the compounds **4b**—**d**, **5b**,**c**, **6b**—**d** point that during the reactions stated above, the mixture of [6,6]-closed and [5,6]-open adducts of fullerene is also formed. However, the absence of the characteristic signals of the bridge carbon atom (δ_C 52.10) and bonded with it hydrogen atom (δ_H 7.40) in the ^1H and ^{13}C NMR spectra of the mixture of compounds **4d** and **6d** obtained by reaction of the C_{60} fullerene with benzyl diazoacetate shows that the stereoisomeric homofullerene, in which the ester group is arranged above the plane of the six-membered fragment of the C_{60} molecule, is not formed under these conditions. At the same time, as we have found, in the reaction of the fullerene C_{60} with *tert*-butyl diazoacetate in the presence of the three-component catalytic system $Pd(acac)_2$—PPh_3—Et_3Al (1 : 2 : 4), only the methanofullerene **4a** is formed, which is apparently explained by a spatially encumbered substituent in the ester group of the starting diazo compound.

In order to extend the scope of the method developed by us for the catalytic cycloaddition of the diazoacetates with substituents of diverse structures in the ester group to the fullerene C_{60}, we accomplished one-stage synthesis (a yield ~50%) of a methanofullerene **7** containing a cholesteryloxycarbonyl group in the methane fragment (Scheme 3). It was also found that in the mentioned reaction, the stereoisomeric [5,6]-open adducts were not formed. According to the literature data,[3,4,7,8,12] the synthesis of these carboxy derivatives of the methanofullerenes whose ester group contain bulk substituents, can be performed in five stages.

Table 1. Influence of structure of substituent (R) in ester group of initial diazo compound on yields and ratios of target cycloadducts **4**—**6**

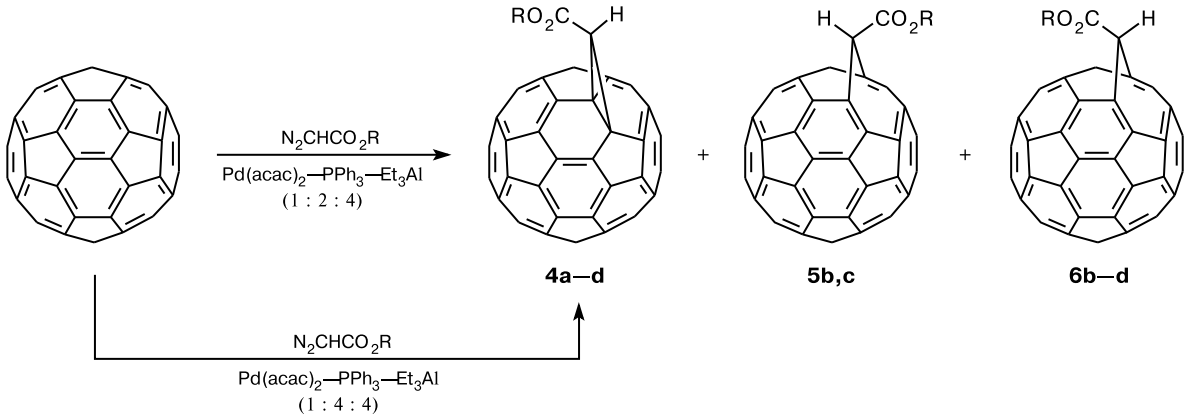
R	Total yield of cycloadducts **4**—**6** (%)	Ratio of isomers **4** : **5** : **6** (%)
Bu^t	46	1 : 0 : 0
Cy	58	2 : 2 : 3
All	48	8 : 4 : 5
Bn	45	3 : 0 : 2

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

The structure of the cycloadduct **7** was reliably identified by the methods of NMR, UV, and IR spectroscopy, as well as a high resolution mass-spectrometry.

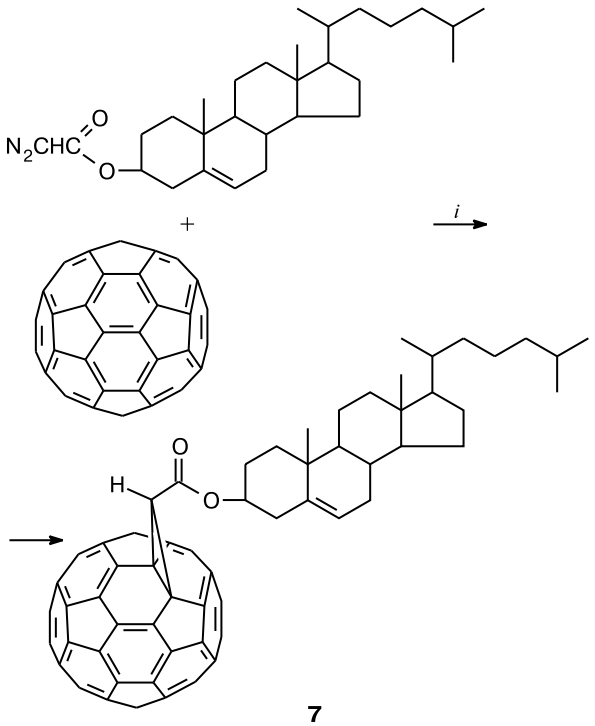
Thus, in the ^{13}C NMR spectrum, the signals of sp^3-hybridized carbon atoms of the fullerene cage (δ_C 70.87) and a methine carbon atom (δ_C 39.83) (δ_H 4.74 in the ^1H NMR spectrum) definitely point at the formation of the cyclopropane fragment of methanofullerene **7** bonded with the cholesterol residue through the carboxyl group (δ_C 164.79). The cholesterol fragment of the molecule is represented in the ^{13}C NMR spectrum by twenty four resolved signals in the high field, which is typical of sp^3-hybridized carbon atoms of the cholesterol (δ_C 12—57),

Scheme 2



R = Bu^t (**4a**); Cy (**4b**, **5b**, **6b**); All (**4c**, **5c**, **6c**); Bn (**4d**, **6d**)

Scheme 3



7

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

and also by a signal of "carbonyl" carbon atom (δ_C 76.40) and two signals of the carbon atoms at a double bond (δ_C 123.66 and 139.09). For the fullerene cage of the molecule, 17 signals in a region of sp^2-hybridized carbon atoms are observed, which points at C_2 symmetry of compound **7**.

Thus, we developed the efficient method of the catalytic cycloaddition of diazoacetates containing substituents of diverse structure in the ester group to the fullerene C_{60}. This reveals sufficiently simple and effective way to the synthesis of new practically important carboxy derivatives of the methanofullerenes with the substituents of diverse nature, including those based on steroids.

Experimental

In the experiments, a commercially accessible [60]fullerene with 99.5% purity (G. A. Razuvaev Institute of Metalloorganic Chemistry of Russian Academy of Sciences, Nizhnii Novgorod). The reaction products were analyzed by HPLC on a chromatograph Altex 330 (USA) with UV detector at 340 nm. The mixture components were separated on a metallic column Cosmosil Buckyprep Waters, 250×10 mm, at ~20 °C. A mobile phase is toluene, flow rate 2.0 mL min^{-1}. IR spectra were recorded on a Specord 75 IR spectrophotometer and IR Fourier spectrometer Bruker VERTEX 70V in KBr tablets or in $CHCl_3$. UV spectra were recorded on spectrophotometers Specord M-40 and Perkin—Elmer Lambda 750. ^1H and ^{13}C NMR spectra were recorded on a spectrometer Bruker Avance-400 (400.13 and 100.62 MHz, respectively). The solvent was a mixture $CDCl_3$—CS_2 (1 : 5). Mass-spectra were registered on a device MALDI TOF/TOF Autoflex-III Bruker without using a matrix in the linear and reflector modes with the registration of the positive and negative ions. Samples for an application on a metallic target were dissolved in toluene.

Cycloaddition of the diazoacetates to the fullerene C_{60} (general procedure). Into a glass reactor, $Pd(acac)_2$ (0.00278 mmol) in 1,2-dichlorobenzene (0.2 mL), PPh_3 (0.00556 mmol) in 1,2-dichlorobenzene (0.21 mL) were loaded, the mixture was cooled to −5—0 °C. Et_3Al (0.01112 mmol) in toluene (0.1 mL) was added under a dry argon current and stirring, the color changed from light-yellow to light-brown. To the obtained catalyst, fullerene C_{60} (0.0139 mmol) in 1,2-dichlorobenzene (1 mL) was added at ~20 °C, the solution became deep-green. The mixture was heated to 80 °C, the diazo compound (0.0695 mmol) in 1,2-dichlorobenzene (1 mL) was added dropwise during 2—3 min, the mixture was stirred for 1 h at the respective temperature. The reaction mixture was cooled to ~20 °C, treated with aqueous HCl, then 7 mL toluene was added, an organic layer passed through a column with small amount of silica gel. The reaction products and the starting fullerene C_{60} were separated by the semi-preparative HPLC, eluent was toluene. A compound **4a** was characterised in comparison with the literature data.[13]

1´-Isopropyloxycarbonyl-(C_{60}-I_h)[5,6]fullereno[2´,3´:1,9]-cyclopropane (1). IR, ν/cm^{-1}: 540, 820, 1040, 1110, 1270, 1670. UV ($CHCl_3$), λ_{max}/nm: 260, 327, 424. ^1H NMR (δ): 1.54 (d, 6 H, 2 Me, J = 6.0 Hz); 4.74 (s, 1 H, CH); 5.38 (sept, 1 H, CH, J = 6.0 Hz). ^{13}C NMR (δ): 22.14, 39.61, 70.36, 70.84 (sp^3), 136.64, 140.67, 140.99, 141.23, 142.00, 142.18, 142.32, 142.50, 142.87, 143.04, 143.11, 143.13, 143.40, 143.78, 144.02, 144.47, 144.68, 144.72, 144.92, 145.13, 145.23, 145.28, 145.63, 145.83, 148.36, 165.43. MS (MALDI-TOF), *m/z*: found: 820.787; for $C_{65}H_8O_2$ calculated: 820.758.

1´a-Isopropyloxycarbonyl-1´a-carba-1´(2´)a-homo(C_{60}-I_h)-[5,6]fullerene (stereoisomer 2). ^1H NMR (δ): 1.36 (d, 6 H, 2 Me, J = 6.0 Hz); 5.12 (sept, 1 H, CH, J = 6.0 Hz); 7.40 (s, 1 H, CH). ^{13}C NMR (δ): 22.03, 52.10, 69.83, 131.16, 134.13, 136.64, 138.76, 138.82, 140.82, 142.00, 142.33, 142.36, 142.87, 143.56, 143.87, 144.35, 144.46, 144.72, 144.92, 145.03, 145.63, 147.74, 165.23.

1´a-Isopropyloxycarbonyl-1´a-carba-1´(2´)a-homo(C_{60}-I_h)-[5,6]fullerene (stereoisomer 3). ^1H NMR (δ): 1.49 (d, 6 H, 2 Me, J = 6.0 Hz); 3.75 (s, 1 H, CH); 5.47 (sept, 1 H, CH, J = 6.0 Hz). ^{13}C NMR (δ): 21.82, 54.45, 70.55, 133.46, 134.04, 135.22, 137.87, 138.07, 138.30, 138.53, 138.54, 140.23, 141.81, 142.00, 142.21, 142.45, 142.63, 142.87, 143.05, 143.09, 143.28, 143.31, 143.42, 143.69, 143.78, 144.07, 144.68, 144.72, 144.92, 145.21, 145.28, 169.09.

1´-Cyclohexyloxycarbonyl-(C_{60}-I_h)[5,6]fullereno[2´,3´:1,9]-cyclopropane (4b). IR, ν/cm^{-1}: 570, 1040, 1060, 1220, 1480, 1660, 1750. UV ($CHCl_3$), λ_{max}/nm: 262, 326, 427. ^1H NMR (δ): 1.20—2.20 (m, 10 H, 5 CH_2); 4.75 (s, 1 H, CH); 5.05—5.16 (m, 1 H, CH). ^{13}C NMR (δ): 24.27, 25.93, 32.15, 39.79, 70.91 (sp^3), 75.25, 136.64, 140.69, 140.99, 141.25, 142.02, 142.19, 142.31, 142.50, 142.88, 143.03, 143.13, 143.40, 143.79, 144.03, 144.47, 144.69, 144.72, 144.93, 145.16, 145.23, 145.28, 145.63, 145.87, 148.36, 164.80. MS (MALDI-TOF), *m/z*: found: 860.770; for $C_{68}H_{12}O_2$ calculated: 860.822.

1´a-Cyclohexyloxycarbonyl-1´a-carba-1´(2´)a-homo(C_{60}-I_h)-[5,6]fullerene (stereoisomer 5b). ^1H NMR (δ): 1.20—2.20 (m, 10 H, 5 CH_2); 4.76—4.83 (m, 1 H, CH); 7.40 (s, 1 H, CH). ^{13}C NMR

(δ): 24.46, 25.93, 31.81, 52.15, 74.55, 131.33, 137.19, 138.74, 138.82, 140.99, 142.02, 142.31, 142.36, 142.63, 143.55, 143.92, 144.37, 144.45, 144.72, 144.93, 145.03, 145.63, 147.68, 164.38.

1´a-Cyclohexyloxycarbonyl-1´a-carba-1´(2´)a-homo(C_{60}-I_h)-[5,6]fullerene (stereoisomer 6b). ^{1}H NMR (δ): 1.20—2.20 (m, 10 H, 5 CH_2); 3.76 (s, 1 H, CH); 5.16—5.26 (m, 1 H, CH). ^{13}C NMR (δ): 24.30, 25.93, 31.99, 54.54, 75.30, 133.50, 134.04, 135.17, 137.87, 138.07, 138.30, 138.53, 138.53, 140.24, 141.81, 142.02, 142.19, 142.44, 142.63, 142.88, 143.03, 143.09, 143.30, 143.40, 143.70, 143.79, 144.03, 144.68, 144.72, 144.93, 145.21, 145.27, 147.87, 168.45.

1´-Allyloxycarbonyl-(C_{60}-I_h)[5,6]fullereno[2´,3´:1,9]cyclopropane (4c). IR, ν/cm^{-1}: 530, 760, 1090, 1150, 1180, 1420, 1640, 1740. UV ($CHCl_3$), λ_{max}/nm: 260, 330, 427. ^{1}H NMR (δ): 4.80 (s, 1 H, CH); 4.96 (d, 2 H, CH_2, J = 5.6 Hz); 5.44 (d, 2 H, CH_2, J = 10.4 Hz); 6.08—6.17 (m, 1 H, CH). ^{13}C NMR (δ): 39.80, 66.89, 70.63 (sp^3), 119.65, 131.61, 140.65, 141.10, 141.21, 142.09, 142.25, 142.36, 142.43, 142.97, 143.04, 143.12, 143.27, 143.41, 143.78, 144.23, 144.36, 144.66, 144.70, 145.00, 145.12, 145.23, 145.38, 145.61, 145.84, 148.39, 165.03.

1´a-Allyloxycarbonyl-1´a-carba-1´(2´)a-homo(C_{60}-I_h)[5,6]-fullerene (stereoisomer 5c). ^{1}H NMR (δ): 7.36 (s, 1 H, CH); 4.71 (d, 2 H, CH_2, J = 5.6 Hz); 5.38 (d, 2 H, CH_2, J = 10.8 Hz); 5.93—6.04 (m, 1 H, CH). ^{13}C NMR (δ): 51.92, 66.63, 119.14, 131.43, 134.11, 136.57, 138.76, 138.83, 140.82, 142.01, 142.33, 142.37, 142.87, 143.57, 143.87, 144.33, 144.48, 144.70, 144.89, 145.10, 145.68, 147.74, 165.18.

1´a-Allyloxycarbonyl-1´a-carba-1´(2´)a-homo(C_{60}-I_h)[5,6]-fullerene (stereoisomer 6c). ^{1}H NMR (δ): 3.81 (s, 1 H, CH); 5.00 (d, 2 H, CH_2, J = 5.6 Hz); 5.53 (d, 2 H, CH_2, J = 10.4 Hz); 6.12—6.23 (m, 1 H, CH). ^{13}C NMR (δ): 54.16, 67.10, 119.49, 131.53, 137.85, 138.03, 138.34, 138.56, 138.52, 140.27, 141.90, 142.00, 142.21, 142.45, 142.66, 142.84, 143.05, 143.12, 143.31, 143.38, 143.42, 143.69, 143.78, 144.16, 144.68, 144.81, 144.96, 145.21, 145.28, 168.76.

1´-Benzyloxycarbonyl-(C_{60}-I_h)[5,6]fullereno[2´,3´:1,9]-cyclopropane (4d). IR, ν/cm^{-1}: 545, 860, 1155, 1190, 1270. UV ($CHCl_3$), λ_{max}/nm: 260, 327, 427. ^{1}H NMR (δ): 4.81 (s, 1 H, CH); 5.53 (s, 2 H, CH_2); 7.22 (t, 1 H, CH, J = 7.2 Hz); 7.43 (t, 2 H, 2 CH, J = 7.2 Hz); 7.56 (d, 2 H, 2 CH, J = 7.2 Hz). ^{13}C NMR (δ): 39.06, 68.33, 70.72 (sp^3), 127.67 (Ph), 129.03 (Ph), 130.56 (Ph), 136.46 (Ph), 136.64, 140.67, 140.99, 141.23, 142.00, 142.18, 142.32, 142.50, 142.87, 143.04, 143.11, 143.13, 143.40, 143.78, 144.02, 144.47, 144.68, 144.72, 144.92, 145.13, 145.23, 145.28, 145.63, 145.83, 148.36, 165.43. MS (MALDI-TOF), m/z: found: 868.813; for $C_{69}H_8O_2$ calculated: 868.801.

1´a-Benzyloxycarbonyl-1´a-carba-1´(2´)a-homo(C_{60}-I_h)-[5,6]fullerene (6d). ^{1}H NMR (δ): 3.82 (s, 1 H, CH); 5.48 (s, 2 H, CH_2); 7.27 (t, 1 H, CH, J = 7.2 Hz); 7.40 (t, 2 H, 2 CH, J = 7.2 Hz); 7.45 (d, 2 H, 2 CH, J = 7.2 Hz). ^{13}C NMR (δ): 54.21, 68.16, 128.82 (Ph), 128.91 (Ph), 130.56 (Ph), 134.96 (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, 169.09.

1´-Cholesteryloxycarbonyl-(C_{60}-I_h)[5,6]fullereno[2´,3´:1,9]-cyclopropane (7). IR, ν/cm^{-1}: 527, 756, 1186, 1436, 1464, 1629, 1737, 2865, 2931. UV ($CHCl_3$), λ_{max}/nm: 259, 327, 426. ^{1}H NMR (δ): 0.74 (s, 3 H, Me); 0.90 (d, 3 H, Me, J = 6.8 Hz); 0.91 (d, 3 H, Me, J = 6.8 Hz); 0.99—2.05 (m, 27 H, 6 CH, 9 CH_2, Me); 1.14 (s, 3 H, Me); 2.06—2.11 (m, 2 H, CH_2); 2.60 (d, 2 H, CH_2, J = 8.0 Hz); 4.74 (s, 1 H, CH); 4.96 (m, 1 H, CH); 5.49 (m, 1 H, CH). ^{13}C NMR (δ): 12.17, 19.03, 19.60, 21.43, 22.87, 23.12, 24.24, 24.77, 28.42, 28.73, 30.16, 32.06, 32.39, 36.10, 36.55, 36.81, 37.36, 38.48, 39.65, 39.83, 40.11, 42.49, 50.25, 56.42, 56.95, 70.87 (sp^3), 76.40, 123.66, 139.09, 140.70, 140.95, 141.24, 142.07, 142.50, 142.81, 143.03, 143.37, 143.78, 144.02, 144.65, 144.68, 145.13, 145.22, 145.29, 145.83, 148.58, 164.79. MS (MALDI-TOF), m/z: found: 1147.542; for $C_{89}H_{46}O_2$ calculated: 1147.316.

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