

Palladium-catalyzed selective cycloaddition of diazo compounds to [60]fullerene

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Dedicated to Professor Usein M. Dzhemilev on the occasion of his 65th birthday

Abstract

The effective catalytic method for cycloaddition of higher diazoalkanes and diazoacetates to [60]fullerene in the presence of the three-component catalytic system Pd(acac)₂-PPh₃-Et₃Al has been developed. The yield and selective formation of the target homo- and methanofullerenes are dependent upon the structure of the original diazo compounds.

Keywords: [60]Fullerene, diazo compounds, cycloaddition, metal complex catalysts, homofullerene, methanofullerene

Introduction

Homofullerenes and methanofullerenes, synthesized via the 1,3-dipolar cycloaddition between diazo compounds and [60]fullerene or obtained by the Bingel-Hirsch reaction, appear to be one of the most perspective classes of fullerene derivatives as novel materials for various fields of science and technology as evidenced by the numerous reviews^{1,2} of both methods for a synthesis of these cycloadducts¹ and their possible applications.²

The Bingel-Hirsch reaction for the synthesis of methanofullerenes is the most cited in the scientific literature. In our view, the reaction of fullerenes with diazo compounds due to its great synthetic potential is regarded as a very promising method to synthesize methanofullerenes and also allows, together with the [6,6]-closed adducts, obtaining the [5,6]-open isomeric ones.

Analysis of domestic and foreign literature has shown that cycloaddition between diazo compounds and [60]fullerene under thermal conditions appears to be nonselective. It is accompanied by the formation of a mixture of [6,6]-closed (methanofullerenes) and stereoisomeric [5,6]-open (homofullerenes) adducts.³ While exploiting Rh₂(OAc)₄ as a promoter,

this reaction selectively affords methanofullerenes.⁴ But the use of stoichiometric quantities of expensive Rh compounds is considered to be the substantial limitation of this method.

Taking the above into consideration, there is an important and urgent need to study and develop the catalytic cycloaddition methods for the effective synthesis of homo- and methanofullerenes, containing different functional groups, from diazo compounds and carbon clusters.

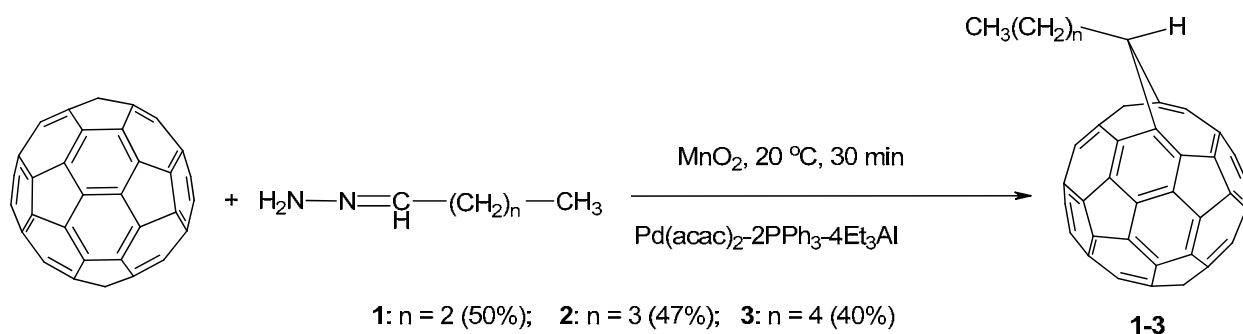
Over the past 5–10 years, we have been actively engaged in research of the cycloaddition reaction between diazo compounds and [60]fullerene under catalytic conditions and found that among the tested complexes and salts of Cu, Pd and Rh a three-component catalytic system Pd(acac)₂-PPh₃-Et₃Al has the greatest efficiency and selectivity in the reactions of C₆₀ with the simplest diazoalkanes,⁵ diazoacetates,^{6,7} and diazoketones⁸ to promote the selective formation of the corresponding homo- or methanofullerenes.

Herein, we attempted to explore the application boundaries of the cycloaddition reaction of diazo compounds to C₆₀ in the presence of Pd(acac)₂-PPh₃-Et₃Al catalyst on the example of symmetric and asymmetric diazoalkanes and also higher diazoacetates of various structure.

Results and Discussion

Recently, we have implemented selective cycloaddition between [60]fullerene and diazoalkanes generated *in situ* through oxidation of hydrazones of acetaldehyde, benzaldehyde and acetone mediated by Ag₂O or MnO₂ in the presence of 20 mol% Pd(acac)₂-PPh₃-Et₃Al (1:2:4) catalyst (20°C, 30 min) leading to the exclusive formation of homofullerenes in 55–70% yields.⁵

In continuation of these studies and also to examine the effect of alkyl substituent size in the original diazoalkanes upon the selectivity of the reaction, we have carried out catalytic cycloaddition between C₆₀ and diazoalkanes generated *in situ* by oxidation of hydrazones of butiric, valeric and caproic aldehydes. The above reaction was found to provide the formation of the corresponding homofullerenes **1–3** (Scheme 1), while the yield of target [5,6]-open adducts decreases slightly with increasing the alkyl chain length of diazoalkane.



Scheme 1. Catalytic cycloaddition of mono substituted diazomethanes to fullerene[60].

The chemical structure of **1–3** was proven by means of one-dimensional (^1H , ^{13}C) and two-dimensional (HSQC, HMBC, HH COSY) NMR spectroscopy as well as IR, UV spectroscopy and MALDI TOF/TOF mass spectrometry.

Thus, the formation of homofullerene **1** containing the hydrogen atom at the bridging C atom above the plane of a six-membered ring of C_{60} has been proven on the basis of the characteristic triplet signal of the methine hydrogen atom at $\delta(\text{H})$ 2.78 ppm ($J = 7.6$ Hz).

The ^1H NMR spectrum of **1** (Figure 1) is also characterized by a set of signals: triplet [$\delta(\text{H})$ 1.26 ppm ($J = 7.6$ Hz)], quartet [$\delta(\text{H})$ 3.49 ppm ($J = 7.6$ Hz)] and sextet [$\delta(\text{H}) = 1.95$ ppm ($J = 7.6$ Hz)], belonging to the hydrogen atoms of the propyl group at the bridging carbon atom.

In the ^{13}C NMR spectrum the bridging C atom resonates at $\delta(\text{C})$ 49.06 ppm, while the sp^2 -hybridized C atoms of the fullerene skeleton are manifested in the field of 134–148 ppm. Similarly, we proved the structure of compounds **2** and **3**.

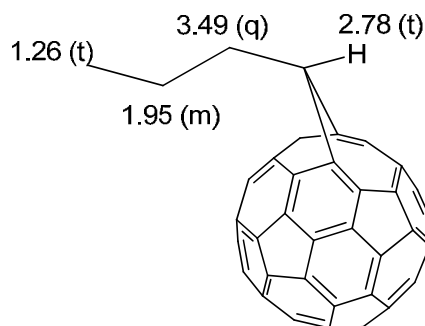


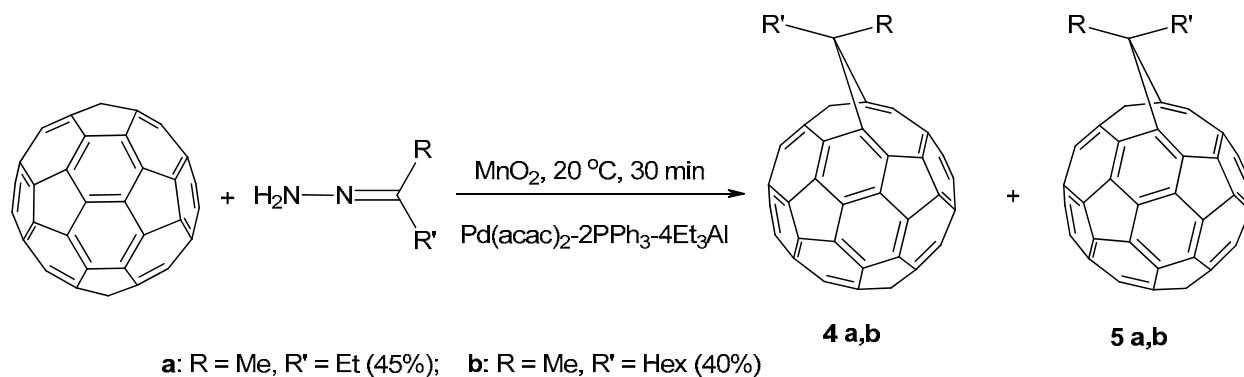
Figure 1. ^1H NMR data for compound **1**.

In contrast to mono-substituted diazoalkanes, the reaction of [60]fullerene with diazoalkanes, *in situ* generated from hydrazones of methyl ethyl ketones or methyl hexyl ketones, under optimized conditions (20 mol% $\text{Pd}(\text{acac})_2$ – 2PPh_3 – $4\text{Et}_3\text{Al}$, 20 °C, 30 min) gave rise to a mixture of stereoisomeric homofullerenes **4a,b** and **5a,b** (Scheme 2).

Apparently, the decrease in the selectivity of the reaction is conditioned by the presence of the second alkyl substituent at the bridging C atom of the cycloadduct raising the probability of the stereoisomeric [5,6]-open adduct formation.

It was noted that if negligible difference between substituents in the initial hydrazones, for example, hydrazone of methyl ethyl ketone, the ratio of stereoisomeric homofullerenes tends to unity.

The increase in alkyl chain length of the substituent leads to the predominant formation of the energetically more stable homofullerene with the more bulky substituent located above the plane of the five-membered ring of the C_{60} molecule (Scheme 2).



Scheme 2. Interaction of fullerene[60] with asymmetrical diazoalkanes in the presence of Pd-complex.

The mixtures of products **4,5a,b** and fullerene were isolated by preparative HPLC. 1D (^1H and ^{13}C NMR, DEPT, 135°C) and 2D (HHCOSY, HSQC, HMBC) experiments demonstrated that compounds **4,5a,b** consisted of a mixture stereoisomers of 5,6-open fullerene monoadducts. We failed to separate adducts **4** and **5** since their physicochemical constants and polarity at chromatography were too close.

The ratio of stereoisomeric homofullerenes **4a** and **5a** as well as **4b** and **5b** was 3:2 and 3:1, respectively, and was estimated on the basis of integral curves of the characteristic singlet signals of the methyl group at the bridging C atom the ^1H NMR spectrum of corresponding mixtures.

The location of the methyl group at the bridging C atom above the plane of the five-membered or six-membered ring of the fullerene molecule in compounds **4a,b** and **5a,b** was defined by comparison between the characteristic singlet signals of the methyl hydrogen atoms in the ^1H NMR spectrum and the known analogues.^{3a}

Thus, the characteristic singlet signal of the methyl hydrogen atoms at the bridging C atom in the ^1H NMR spectrum of homofullerene **4a** resonates at the higher field [$\delta(\text{H})$ 1.16 ppm] than that of the stereoisomer **5a** [$\delta(\text{H})$ 3.12 ppm] (Figure 2). In turn, the methylene [$\delta(\text{H})$ 3.72 ppm ($J = 7.2\text{Hz}$)] and methyl [$\delta(\text{H})$ 1.54 ppm ($J = 7.2\text{Hz}$)] hydrogen atoms of the ethyl substituent in [5,6]-open adduct **4a** manifest themselves at the lower field as compared with the similar signals at $\delta(\text{H})$ 1.50 ppm ($J = 7.2\text{ Hz}$) and $\delta(\text{H})$ 1.00 ppm ($J = 7.2\text{Hz}$) for compound **5a**.

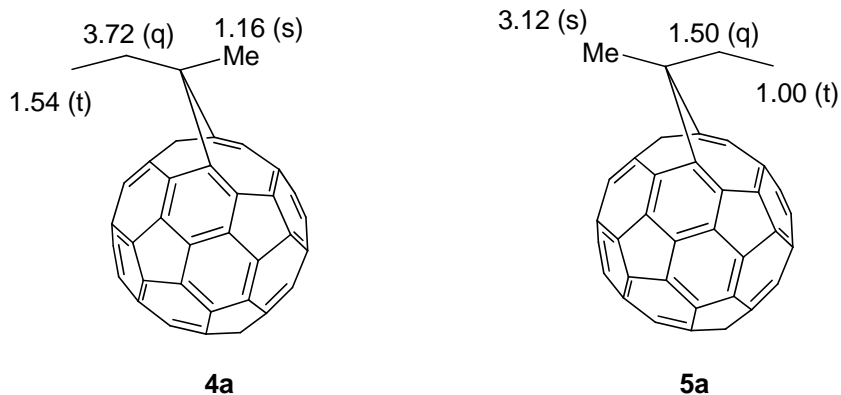
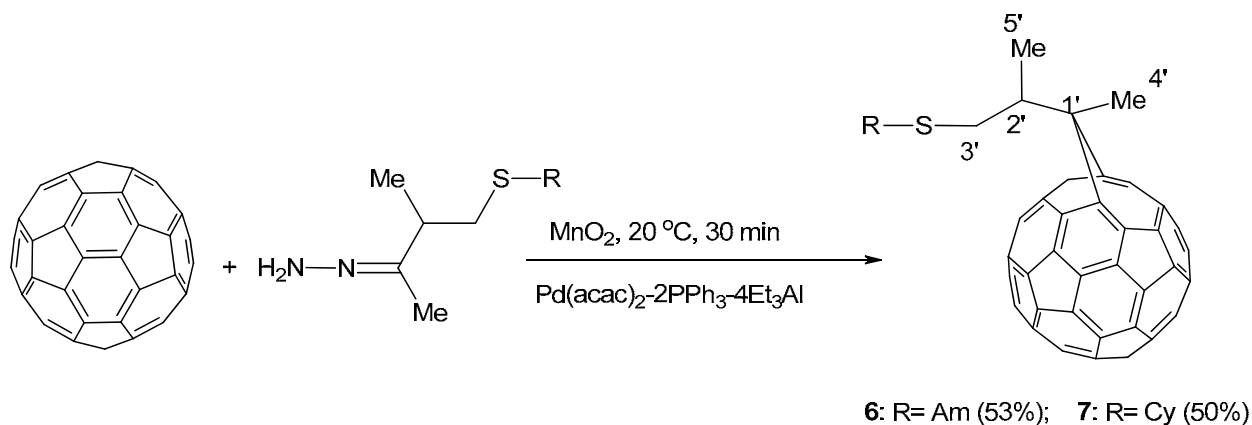


Figure 2. ^1H NMR data for compounds **4a** and **5a**.

In order to study the possibility of the selective synthesis of homofullerenes containing heteroatoms, we have carried out cycloaddition between C_{60} and sulfur-containing asymmetric diazoalkanes generated by oxidation hydrazones of ketosulfides. Thus, the interaction between [60]fullerene and diazoalkanes, generated *in situ* by oxidation of hydrazones of 3-(pentylthiomethyl)- and 3-(cyclohexylthiomethyl)-2-butanones with MnO_2 , in the presence of 20 mol% three-component $\text{Pd}(\text{acac})_2\text{-2PPh}_3\text{-4Et}_3\text{Al}$ catalyst was found to afford predominantly the corresponding homofullerenes **6** and **7** in 50% yield (Scheme 3).



Scheme 3. Catalytic synthesis of sulfur-containing homofullerenes.

Their structure has been confirmed by means of negative ion MALDI TOF/TOF MS, one- and two-dimensional (^1H , ^{13}C , COSY, HSQC and HMBC) NMR experiments and also by analysis of UV and IR spectra.

Thus, the molecular peak m/z 892.984 corresponding to empiric formula $\text{C}_{70}\text{H}_{20}\text{S}$ was observed in the mass spectrum of compound **6** recorded in the negative-ion mode in the absence of a matrix (unionized molecules of original homofullerene as matrix).

The ^1H NMR spectrum of **6** (Figure 3) reveals ABX spin system of the methine hydrogen atom with a chemical shift δ ($\text{HC}^{2'}$) 5.21 ppm and two diastereotopic hydrogen atoms of methylene groups [δ ($\text{H}^{\text{a}}\text{C}^{3'}$) 2.78 and δ ($\text{H}^{\text{b}}\text{C}^{3'}$) 3.16 ppm] coupled to each other through the combination of geminal spin-spin [$^2J^{\text{H}^{\text{a}}\text{H}^{\text{b}}} = 12.8$ Hz] and vicinal [$^3J^{\text{H}^{\text{a}}\text{H}_2} = 9.2$ and $^3J^{\text{H}^{\text{b}}\text{H}_2} = 4.8$ Hz] interactions.

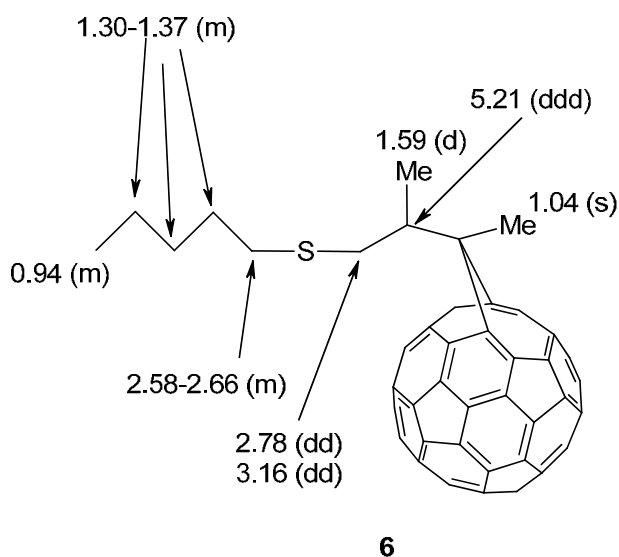


Figure 3. ^1H NMR data for compound **6**.

The thiopentyl fragment is described by five carbon signals correlated with five groups of signals of hydrogen atoms in HSQC experiment. The methyl group at δ ($\text{H}_3\text{C}^{5'}$) 1.59 ppm [δ ($\text{C}^{5'}$) 29.64 ppm], directly linked with the chiral center $\text{C}^{2'}$, can be observed as the doublet signal in ^1H NMR spectrum ($^3J = 6.8$ Hz), while the methyl group at δ ($\text{H}_3\text{C}^{4'}$) 1.04 ppm (δ ($\text{C}^{4'}$) 13.96 ppm) is represented by a singlet signal in the high field.

The high-field shielding of the methyl group at $\text{C}^{4'}$ in both ^1H and ^{13}C spectra evidenced of its location above the plane of the fullerene six-membered ring unlike the low-field shift of the methine proton [δ ($\text{HC}^{2'}$) 5.21 ppm] above the plane of the fullerene five-membered ring in [5,6]-open adduct **6**.

Increasing a number of signals of the fullerene carbon atoms up to 40 due to anisotropic influence on the chiral centre at $\text{C}^{2'}$ atom leads to the diastereotopic splitting of signals of the carbon atoms in the α , β and γ environments towards the bridging $\text{C}^{1'}$ atom.

The presence of the minor signals in the ^1H and ^{13}C NMR spectra (1:10 ratio) indicate the presence of stereoisomer of homofullerene **6** with the methyl group at the bridging C atom located above the plane of the five-membered ring of fullerene C_{60} molecule. But the low content of this isomer in the reaction mixture has not allowed characterizing it reliably.

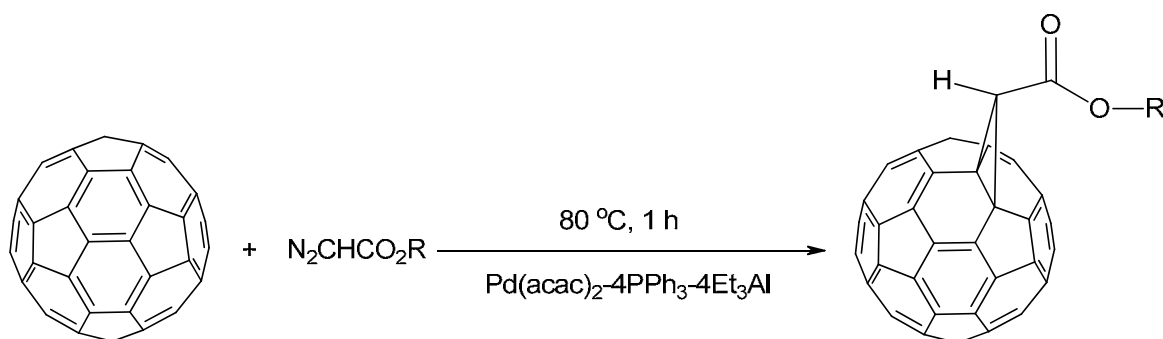
Our subsequent efforts have been focused on the possibilities to synthesize carboxy derivatives of methanofullerenes bearing various substituents in the ester group.

At the same time, we were intended to study the influence of the original diazoacetate nature upon the yield of the target cycloadducts. We believed that positive results obtained, in the future, will allow synthesizing functionally substituted methanofullerenes containing complex moieties of the steroid series being identical in all respects (composition, configuration, conformation) with the natural compound.

Taking into account the resulting data,⁶ we have implemented cycloaddition between diazoacetic esters and [60]fullerene in the presence of the catalytic system Pd(acac)₂-PPh₃-Et₃Al (1:4:4 ratio) to selectively produce the appropriate [6,6]-close adducts.

Realization of the planned study on cycloaddition between C₆₀ and diazoacetic esters bearing *iso*-propyl, cyclohexyl and *tert*-butyl substituents in the ester group under previously optimized conditions in the cycloaddition reaction for diazoacetates (80 °C, 1 h, 20 mol% Pd(acac)₂-4PPh₃-4Et₃Al) allowed to synthesize the appropriate methanofullerenes **8–10** in the yields of 70, 60 and 46% respectively (Scheme 4).

As noted, the use of diazoacetates bearing sterically hindered substituents in the ester group leads to some decrease in the yield of final products.



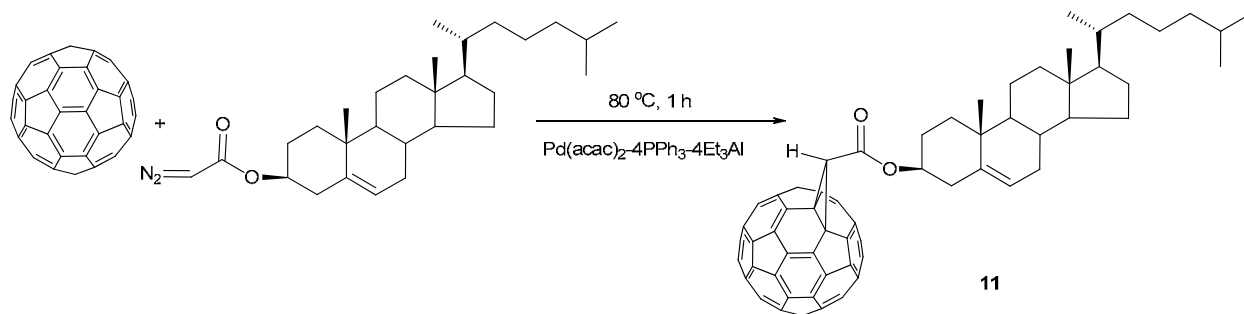
8: R = *iso*-Pr (70%); **9:** R = Cy (60%); **10:** R = *tert*-Bu (46%)

Scheme 4. Cycloaddition of diazo acetates to fullerene[60] in the presence of Pd(acac)₂-4PPh₃-4Et₃Al.

Very promising results on the synthesis of functionally substituted methanofullerenes, containing various sterically hindered substituents in the ester group, encouraged us to apply this reaction to the synthesis of methanofullerenes, which bear the carboxyl groups and complex natural moieties as well.

For the study we selected diazoacetate derived from glycine and cholesterol under previously developed conditions,⁶ and introduced it in the reaction with C₆₀. As a result, methanofullerene **11** has been first obtained in 50% yield in one preparative stage (Scheme 5).

As shown, the presence of steroid substituent in the ester group of the original diazo compound under catalytic conditions does not substantially reduce the yield of the target adduct.



Scheme 5. Synthesis of functionally substituted methanofullerenes, containing sterically hindered substituent in the ester group.

The signals of sp^3 -hybridized C atoms of the fullerene skeleton at δ_C 70.87 ppm and the methine C atom at δ (C) 39.83 ppm [δ (H) 4.74 ppm (^1H NMR)] in the ^{13}C NMR spectrum of **11** unambiguously evidenced for the formation of the cyclopropane fragment linked to the cholesterol residue via the carboxyl group [δ (C) 164.79 ppm].

The cholesterol fragment of the molecule in the ^{13}C NMR spectrum is represented by 24 signals resonated at the high field, which are characteristic of sp^3 -hybridized C atoms of cholesterol [δ (C) 12–57 ppm], a carbinol signal at δ (C) 76.40 ppm and two signals of the double bond at δ (C) 123.66 and 139.09 ppm. The spectrum of **11** also shows 17 signals attributable to the fullerene skeleton in the field of sp^2 -hybridized C atoms indicating the presence of two planes of symmetry in the molecule.

Currently, we are actively pursuing the synthesis of carboxy derivatives of methanofullerenes bearing in the ester group pharmavaluable preparations based on natural and synthetic diazo derivatives of terpenes, steroids, alkaloids and carbohydrates.

Conclusions

Thus, we have shown that the previously suggested three-component catalytic system $\text{Pd}(\text{acac})_2\text{-PPh}_3\text{-Et}_3\text{Al}$ can be successfully applied to the reaction of [60]fullerene with the simplest diazo compounds to synthesize higher homo- and methanofullerenes bearing substituents of various structure.

The interaction between C_{60} and diazoalkanes, generated *in situ* by oxidation of hydrazones derived from aldehydes, was stated to afford under catalytic conditions individual homofullerenes with the location of hydrogen atom at the bridging C atom above the plane of the fullerene six-membered ring. Replacing of mono-diazomethane in this reaction by disubstituted one resulted in the decrease in selectivity and is accompanied by the formation of a mixture of stereoisomeric [5,6]-open adducts.

For the first time, carboxy derivatives of methanofullerenes have been synthesized in one preparative stage based upon diazoacetates containing in the ester group the steroid molecule such as cholesterol.

Experimental Section

General. 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 on a HPLC chromatograph Altex (model 330) (USA) equipped with the UV detector at 340 nm. The mixtures were separated on a metal half-preparative column Cosmosil Buckyprep Waters (250×10 mm) at ~20 °C. Toluene was used as eluent, the flow rate was 2.0 mL·min⁻¹. The IR spectra were registered on a VERTEX 70V (Bruker) spectrophotometer in KBr pellets. The UV spectra were recorded on a LAMBDA 750 (Perkin Elmer) in CHCl₃. The ¹H and ¹³C NMR spectra were run on a Bruker Avance-400 spectrometer at 400.13 and 100.62 MHz, respectively. The mixture of CDCl₃ and CS₂ (1:5) was used as a solvent. The negative ion mass spectra were obtained on a MALDI TOF/TOF Autoflex-III Bruker without a matrix operating in a linear mode. For the application on a metal target, the toluene solutions of the samples were used.

Catalytic cycloaddition of diazoalkanes to [60]fullerene. General procedure

A solutions of Pd(acac)₂ (0.00278 mmol) in *o*-dichlorobenzene (0.4 mL) and PPh₃ (0.00556 mmol) in *o*-dichlorobenzene (0.4 mL) were mixed in the glass flask, then a solution of Et₃Al (0.01112 mmol) in toluene (0.1 mL) was added with stirring under stream of nitrogen at -5 °C. The color of the solution changed from light yellow to light brown. A solution of [60]fullerene (0.0139 mmol) in *o*-dichlorobenzene (0.1 mL) was added to the resulting catalyst at room temperature, the color of the solution turned dark green. A solution of the corresponding hydrazone (0.0695 mmol) in toluene (0.5 mL) and MnO₂ (1 mmol) was added. The reaction mixture was stirred for 1-1.5 h at the ambient temperature, then treated with aqueous HCl, extracted with toluene (7 mL). The organic layer was passed through short column filled with silica gel. The products **1-7** and [60]fullerene were separated by half-preparative HPLC, using toluene as eluent.

1a-Propyl-1aH-1(9)a-homo(C₆₀-I_h)[5,6]fullerene (1). IR (KBr) ν 526, 1145, 1213, 1438 cm⁻¹; UV (CHCl₃) λ_{\max} 262, 333 nm; ¹H NMR (400 MHz) δ 1.26 (t, ³J = 7.6 Hz, 3H, CH₃), 1.95 (m, 2H), 2.78 (t, ³J = 7.6 Hz, H, CH), 3.49 (q, ³J = 7.6 Hz, 2H, CH₂); ¹³C NMR (100 MHz) δ 14.68, 22.37, 36.02, 49.06, 134.03, 134.62, 136.71, 138.17, 138.61, 138.89, 140.08, 140.28, 141.63, 142.04, 142.18, 142.60, 142.74, 142.92, 143.20, 143.40, 143.56, 143.71, 143.97, 144.36, 144.92, 145.00, 147.98; MS (MALDI-TOF/TOF) m/z [M]⁺ found 776.780, calculated 776.748, C₆₄H₈.

1a-Butyl-1aH-1(9)a-homo(C₆₀-I_h)[5,6]fullerene (2). IR (KBr) ν 526, 1155, 1213, 1438 cm⁻¹; UV (CHCl₃) λ_{\max} 262, 331 nm; ¹H NMR (400 MHz) δ 1.12 (t, ³J = 7.6 Hz, 3H, CH₃), 1.66 (m,

2H), 1.89 (m, 2H), 2.75 (t, $^3J = 7.6$ Hz, H, CH), 3.50 (q, $^3J = 7.6$ Hz, 2H, CH₂); ¹³C NMR (100 MHz) δ 14.60, 23.41, 31.17, 33.76, 49.27, 134.02, 134.60, 138.14, 138.60, 138.89, 140.06, 140.34, 141.62, 141.99, 142.04, 142.17, 142.25, 142.60, 142.73, 142.91, 143.11, 143.17, 143.20, 143.47, 143.55, 143.69, 143.71, 143.75, 143.96, 144.36, 144.91, 144.99, 145.51, 147.97; MS (MALDI-TOF/TOF) m/z [M]⁺ found 790.808, calculated 790.775, C₆₅H₁₀.

1a-Amyl-1aH-1(9)a-homo(C₆₀-I_h)[5,6]fullerene (3). IR (KBr) ν 526, 1140, 1213, 1437, 1461 cm⁻¹; UV (CHCl₃) λ_{\max} 262, 333 nm; ¹H NMR (400 MHz) δ 1.04 (t, $^3J = 7.6$ Hz, 3H, CH₃), 1.51 (m, 2H), 1.63 (m, 2H), 1.91 (m, 2H), 2.75 (t, $^3J = 7.6$ Hz, H, CH), 3.50 (q, $^3J = 7.6$ Hz, 2H, CH₂); ¹³C NMR (100 MHz) δ 14.56, 23.28, 28.74, 32.31, 34.01, 49.30, 134.02, 134.60, 138.14, 138.60, 138.89, 140.06, 140.35, 141.62, 142.04, 142.18, 142.26, 142.60, 142.74, 142.92, 143.11, 143.18, 143.20, 143.47, 143.56, 143.62, 143.69, 143.72, 143.75, 143.96, 144.36, 144.91, 145.00, 147.98; MS (MALDI-TOF/TOF) m/z [M]⁺ found 804.849, calculated 804.802, C₆₆H₁₂.

Mixture of stereoisomeric 1a-methyl-1a-ethyl-1(9)a-homo(C₆₀-I_h)[5,6]fullerenes (4a and 5a). IR (KBr) ν 528, 1131, 1178, 1207, 1434, 1462 cm⁻¹; UV (CHCl₃) λ_{\max} 262, 333 nm; MS (MALDI-TOF/TOF) m/z [M]⁺ found 776.748, calculated 776.746, C₆₄H₈.

4a. ¹H NMR (400 MHz) δ 1.16 (s, 3H, CH₃), 1.54 (t, $^3J = 7.2$ Hz, 3H, CH₃), 3.72 (q, $^3J = 7.2$ Hz, 2H, CH₂); ¹³C NMR (100 MHz) δ 10.21, 19.15, 35.45, 49.49, 135.09, 136.70, 137.85, 138.78, 139.72, 140.22, 141.06, 141.50, 141.96, 142.00, 142.21, 142.33, 142.65, 142.78, 142.97, 143.04, 143.15, 143.24, 143.56, 143.69, 143.82, 143.95, 144.11, 144.84, 145.20, 147.54.

5a. ¹H NMR (400 MHz) δ 1.00 (t, $^3J = 7.2$ Hz, 3H, CH₃), 1.50 (q, $^3J = 7.2$ Hz, 2H, CH₂), 3.12 (s, 3H, CH₃); ¹³C NMR (100 MHz) δ 8.81, 26.84, 27.42, 48.93, 134.98, 135.95, 137.16, 137.83, 138.78, 139.63, 141.44, 141.91, 142.02, 142.18, 142.21, 142.59, 142.85, 143.15, 143.69, 143.75, 144.48, 145.22.

Mixture of stereoisomeric 1a-methyl-1a-hexyl-1(9)a-homo(C₆₀-I_h)[5,6]fullerenes (4b and 5b). IR (KBr) ν 526, 1027, 1102, 1186, 1261, 1428, 1461 cm⁻¹; UV (CHCl₃) λ_{\max} 260, 326 nm; MS (MALDI-TOF/TOF) m/z [M]⁺ found 832.914, calculated 832.855, C₆₈H₁₆.

4b. ¹H NMR (400 MHz) δ 0.99 (t, $^3J = 7.2$ Hz, 3H, CH₃), 1.17 (s, 3H, CH₃), 1.43-1.53 (m, 4H, 2CH₂), 1.65 (m, 2H, CH₂), 1.95 (m, 2H, CH₂), 3.66 (t, $^3J = 7.2$ Hz, 2H, CH₂); ¹³C NMR (100 MHz) δ 14.46, 19.82, 23.13, 25.93, 30.43, 32.22, 42.72, 48.99, 135.11, 137.85, 138.79, 139.73, 140.23, 141.03, 141.51, 141.99, 142.21, 142.30, 142.84, 142.92, 143.15, 143.26, 143.84, 143.96, 144.12, 144.86, 145.22, 147.56.

5b. ¹H NMR (400 MHz) δ 0.94 (t, $^3J = 7.6$ Hz, 3H, CH₃), 1.27-1.38 (m, 8H, 4CH₂), 1.42 (t, $^3J = 7.6$ Hz, 2H, CH₂), 3.13 (s, 3H, CH₃); ¹³C NMR (100 MHz) δ 14.46, 23.05, 24.31, 27.56, 30.12, 31.98, 34.74, 48.56, 135.00, 135.96, 137.13, 137.85, 138.79, 139.73, 141.44, 141.99, 142.21, 142.30, 142.59, 142.80, 142.90, 143.06, 143.16, 143.65, 143.75, 143.80, 144.48, 144.61, 145.22.

1a-Methyl-1a-(3'-thiopentylprop-2'-yl)-1(9)a-homo(C₆₀-I_h)[5,6]fullerene (6). IR (KBr) ν 527, 1384, 1437, 1462 cm⁻¹; UV (CHCl₃) λ_{\max} 262, 333 nm; ¹H NMR (400 MHz) δ 0.94 (m, 3H, CH₃), 1.04 (s, 3H, CH₃), 1.30-1.37 (m, 6H, 3CH₂), 1.59 (d, $^3J = 6.8$ Hz, 3H, CH₃), 2.58-2.66 (m, 2H, CH₂), 2.78 (dd, $^3J = 9.2$ and 12.8 Hz, H^a, CH₂), 3.16 (dd, $^3J = 4.8$ and 12.8 Hz, H^b, CH₂), 5.21 (ddd, $^3J = 4.8, 6.8$ and 9.2 Hz, H, CH); ¹³C NMR (100 MHz) δ 13.96, 14.32, 15.94, 22.71,

29.96, 31.47, 33.30, 36.51, 42.31, 52.88, 135.13, 135.45, 135.57, 135.98, 137.80, 137.83, 138.80, 138.87, 138.97, 139.85, 140.18, 140.29, 140.93, 141.31, 141.36, 141.81, 141.94, 142.04, 142.15, 142.27, 142.33, 142.70, 142.75, 142.92, 142.97, 143.03, 143.15, 143.18, 143.20, 143.61, 143.72, 143.77, 143.79, 143.98, 144.15, 144.17, 144.48, 144.86, 144.88, 145.20; MS (MALDI-TOF/TOF) m/z $[M]^+$ found 892.984, calculated 892.972, $C_{70}H_{20}S$.

1a-Methyl-1a-(3'-thiocyclohexylprop-2'-yl)-1(9)a-homo(C_{60} - I_h)[5,6]fullerene (7). IR (KBr) ν 527, 1385, 1445, 1462 cm^{-1} ; UV ($CHCl_3$) λ_{max} 262, 332 nm; 1H NMR (400 MHz) δ 1.05 (s, 3H, CH_3), 1.32 (m, 2H, CH_2), 1.36 (q, $^3J = 9.2$ Hz, 2H, CH_2), 1.59 (d, $^3J = 6.8$ Hz, 3H, CH_3), 1.65-1.68 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 2.04 (q, $^3J = 9.2$ Hz, 2H, CH_2), 2.71 (m, H, CH), 2.76 (dd, $^3J = 9.2$ and 13.2 Hz, H^a , CH_2), 3.21 (dd, $^3J = 4.8$ and 13.2 Hz, H^b , CH_2), 5.15-5.23 (m, H, CH); ^{13}C NMR (100 MHz) δ 13.96, 15.89, 26.25, 26.61, 26.73, 33.94, 34.00, 34.37, 42.59, 44.18, 52.95, 135.16, 135.44, 135.56, 136.00, 136.04, 137.83, 138.70, 138.84, 138.89, 138.99, 139.84, 140.10, 140.19, 140.30, 140.94, 141.37, 141.44, 141.88, 141.96, 142.05, 142.13, 142.17, 142.29, 142.33, 142.67, 142.75, 142.79, 142.93, 142.98, 143.04, 143.16, 143.22, 143.62, 143.73, 143.79, 143.84, 143.99, 144.18, 144.49, 144.88, 145.21, 145.24, 147.42, 147.50; MS (MALDI-TOF/TOF) m/z $[M]^+$ found 905.032, calculated 904.982, $C_{71}H_{20}S$.

Catalytic cycloaddition of diazoacetates to [60]fullerene. General procedure

A solutions of $Pd(acac)_2$ (0.00278 mmol) in *o*-dichlorobenzene (0.4 mL) and PPh_3 (0.00556 mmol) in *o*-dichlorobenzene (0.4 mL) were mixed in the glass flask, then a solution of Et_3Al (0.01112 mmol) in toluene (0.1 mL) was added with stirring under stream of nitrogen at -5 °C. The color of the solution changed from light yellow to light brown. A solution of [60]fullerene (0.0139 mmol) in *o*-dichlorobenzene (0.1 mL) was added to the resulting catalyst at room temperature, the color of the solution turned dark green. The mixture was heated to 80 °C and a solution of the corresponding diazo acetate (0.0695mmol) in CH_2Cl_2 (0.5 mL) was added dropwise over a period of 5 min. The reaction mixture was stirred for 1 h at the corresponding temperature, and then cooled to room temperature, treated with aqueous HCl, extracted with toluene (7 mL). The organic layer was passed through short column filled with silica gel. The products **8-11** and [60]fullerene were separated by half-preparative HPLC, using toluene as eluent.

iso-Propyl 3'H-cyclopropa[1,9](C_{60} - I_h)[5,6]fullerene-3'-carboxylate (8). IR (KBr) ν 540, 820, 1040, 1110, 1270, 1670 cm^{-1} ; UV ($CHCl_3$) λ_{max} 260, 327, 424 nm; 1H NMR (400 MHz) δ 1.54 (d, $^3J = 6.0$ Hz, 6H, 2 CH_3), 4.74 (s, H, CH), 5.38 (m, 1H, CH); ^{13}C NMR (100 MHz) δ 22.14, 39.61, 70.36, 70.84, 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/TOF) m/z $[M]^+$ found 820.787, calculated 820.758, $C_{65}H_8O_2$.

Cyclohexyl 3'H-cyclopropa[1,9](C_{60} - I_h)[5,6]fullerene-3'-carboxylate (9). IR (KBr) ν 570, 1040, 1060, 1220, 1480, 1660, 1750 cm^{-1} ; UV ($CHCl_3$) λ_{max} 262, 326, 427 nm; 1H NMR (400 MHz) δ 1.20-2.20 (m, 10H, 5 CH_2), 4.75 (s, H, CH), 5.05-5.16 (m, 1H, CH). ^{13}C NMR (100

MHz) δ 24.27, 25.93, 32.15, 39.79, 70.91, 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/TOF) m/z $[M]^+$ found 860.770, calculated 860.822, C₆₈H₁₂O₂.

tert-Butyl 3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerene-3'-carboxylate (10). See ref.^{3d}

Cholesteryl 3'H-cyclopropa[1,9](C₆₀-I_h)[5,6]fullerene-3'-carboxylate (11). IR (KBr) ν 527, 756, 1186, 1436, 1464, 1629, 1737, 2865, 2931 cm⁻¹; UV (CHCl₃) λ_{\max} 259, 327, 426 nm; ¹H NMR (400 MHz) δ 0.74 (s, 3H, CH₃), 0.90 (d, J = 6.8 Hz, 3H, CH₃), 0.91 (d, J = 6.8 Hz, 3H, CH₃), 0.99-2.05 (m, 27H, 6CH, 9CH₂, CH₃), 1.14 (s, 3H, CH₃), 2.06-2.11 (m, 2H, CH₂), 2.60 (d, J = 8.0 Hz, 2H, CH₂), 4.74 (s, H, CH), 4.96 (m, 1H, CH), 5.49 (m, 1H, CH); ¹³C NMR (100 MHz) 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/TOF) m/z $[M]^+$ found 1147.542, calculated 1147.316, C₈₉H₄₆O₂.

Acknowledgements

The work was financially supported by FTP "Scientific and scientific-pedagogical personnel of innovative Russia" in 2009-2013 (Contract № P1218 and № 14.740.11.0014).

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