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CATALYZED BY PALLADIUM COMPLEXES THE CYCLOADDITION OF HYDRAZONES TO FULLERENE C₆₀

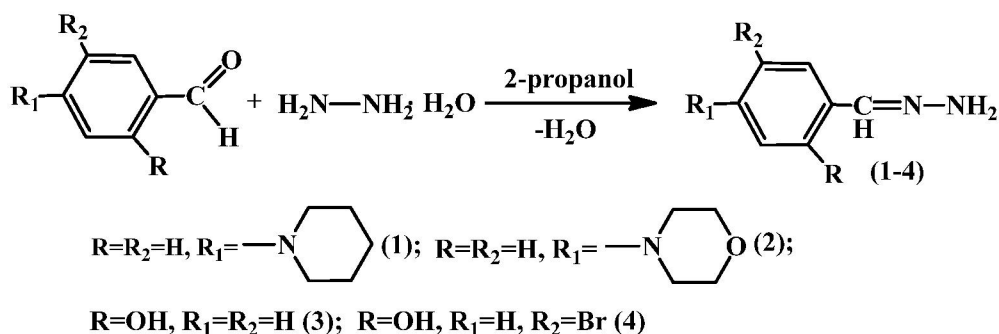
Abstract. The article is devoted to the development of a preparatively convenient method for the synthesis of new methanofullerenes by the catalytic cyclo coupling of hydrazones to fullerene C₆₀. The catalyst used was Pd(acac)₂-PPh₃-AlEt₃. The reactions were carried out under conditions of generating substituted diazomethanes *in situ* by oxidation of the hydrazones of the corresponding aldehydes with MnO₂. The use of complexes of transition metals in this reaction makes it possible to direct the cycloaddition of the diazo compounds to fullerenes towards the production of individual methanofullerenes. Initially, the synthesis of the initial arylhydrazones by the interaction of substituted benzaldehydes (salicylic aldehyde, 5-bromosalicylic aldehyde, 4-morpholino-benzaldehyde, 4-piperidine benzaldehyde) with an excess of hydrazine hydrate in isopropyl alcohol was carried out. The reaction of the reaction of diazoarylaldehydes with fullerene C₆₀ was monitored by HPLC. It is shown that the use of the catalyst Pd(acac)₂-PPh₃-AlEt₃ in a ratio of 1:4:4 leads to the formation of exclusively methanofullerenes with yields of 40-95%. The composition and purity of the methanofullerenes obtained are confirmed by MALDI-TOF and HPLC mass spectrometry, and the structure by NMR¹H spectroscopy. The mechanism of formation of methanofullerene is discussed.

Keywords: fullerene C₆₀, aromatic aldehydes, diazoarylaldehydes, cycloaddition, catalyst Pd(acac)₂-PPh₃-AlEt₃.

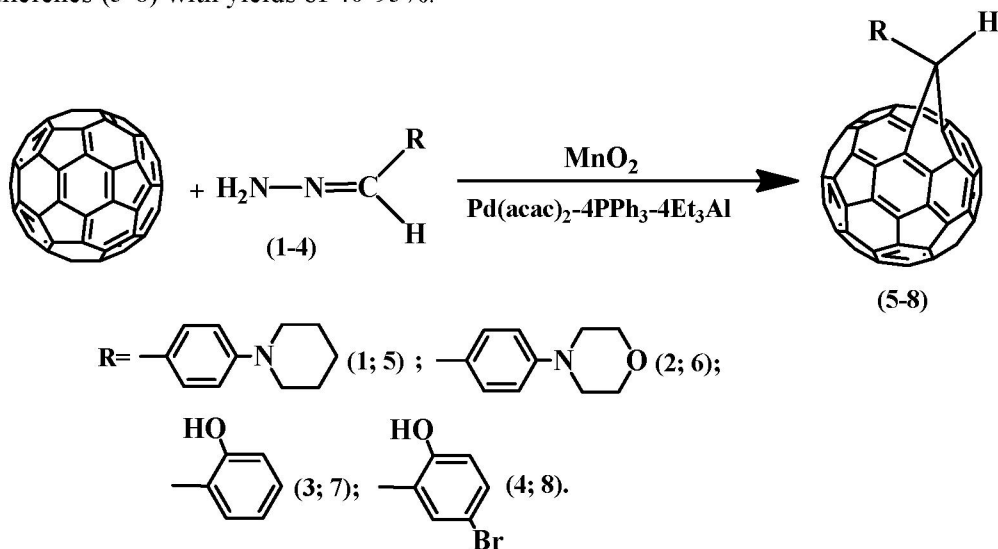
At present, the world science pays ever more attention to the prospects for the development of fundamental and applied research in the field of chemistry of carbon clusters. The organic chemistry of fullerene has acquired a special perspective and is developing [1,2]. The presence of a fullerene fragment in the structure of compounds provides a significant improvement or appearance of qualitatively new mechanical, chemical, physical, biological and other properties associated with the manifestation of nanoscale factors [3], immunomodulating [4], antioxidant [5], and other types of activity. Functionalization of fullerenes is mainly carried out using classical reagents and methods widely used in synthetic practice [6-13]. We previously studied the reactions of the [2 + 3]-cycloaddition-the three-component condensation of C₆₀ fullerene, N-methylglycine (sarcosine) and various functionally substituted aromatic aldehydes under Prato reaction conditions, leading to the formation of new fulleropyrrolidines [14-17].

One of the most commonly used methods for the synthesis of practically important functionally substituted fullerene derivatives has been and still is the reaction of carbon clusters with *in situ* generated α -halocarbanions (the Bingel-Hirsch reaction) leading to methanofullerenes [18]. Along with this method of synthesis of fullerocyclopropanes, a wide application in synthetic practice has found methods based on cycloaddition to carbon clusters of diazocompounds. However, the main disadvantage of this reaction is its low selectivity. Meanwhile, the use of transition metal complexes in this reaction makes it possible to direct the cycloaddition of diazo compounds to fullerenes towards the production of individual methanofullerenes.

In this connection, it seemed to us of interest to study the catalytic cycloaddition of diazoarylhydrazones to C₆₀-fullerene catalyzed by palladium complexes. Initially, we synthesized the initial arylhydrazones by the interaction of substituted benzaldehydes (salicylic aldehyde, 5-bromosalicylic aldehyde, 4-morpholinobenzaldehyde, 4-piperidine benzaldehyde) with excess hydrazine hydrate in isopropyl alcohol medium with heating for 6-10 hours. Theyieldsofhydrazones (1-4) 45-95%.

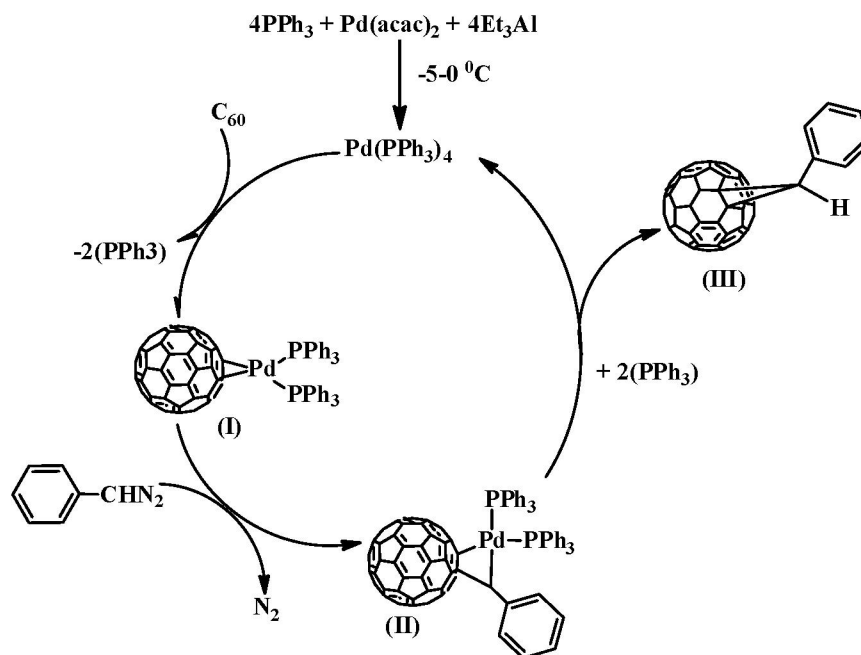


Next, we carried out for the first time the cyclic addition of diazoarylhydrazones (1-4) to fullerene C₆₀ under the action of the three-component catalyst Pd(acac)₂-PPh₃-AlEt₃ under the conditions of using the procedure for the generation of substituted diazomethanes by oxidation of the corresponding aldehydes with MnO₂. The use of the catalyst Pd(acac)₂-PPh₃-AlEt₃ in the ratio 1:4:4 leads to the formation of methanofullerenes (5-8) with yields of 40-95%.



On the basis of the literature data, we give below a scheme-the proposed mechanism of cycloaddition of diazomethane to C₆₀ involving Pd complexes. The likely mechanism of the catalytic action of the phosphine complex Pd on the cycloaddition of diazomethanes to fullerene C₆₀ is based on the results of numerous experiments [19, 20].

According to the data of the authors [19, 20], the oxidative addition of fullerene C₆₀ to the central catalyst atom (Pd(PPh₃)₄) proceeds to form the palladium of the cyclopropane complex C₆₀Pd(PPh₃) (I), which is confirmed by the presence of a single signal with a chemical shift δ_p 25.23 m. e. in the ¹H NMR spectrum of the complex (I) obtained and the color change of the fullerene solution from violet-purple to dark green. Further, diazomethane reacts with the complex (I) via a polarized Pd-C bond with the simultaneous elimination of N₂ and the formation of intermediate fulleropalladiumcyclobutane (II), which under the reaction conditions is transformed into the target methanofullerene (III) with regeneration of the initial Pd complex.



The reaction of diazoarylaldehydes (1-4) with fullerene C_{60} under the action of the $\text{Pd}(\text{acac})_2\text{-PPh}_3\text{-AlEt}_3$ catalyst was monitored by HPLC. The reaction products were analyzed on an Altex chromatograph (model 330) (USA) with a UV detector at a wavelength of 313 nm. Figure 1 shows the chromatograms of Compound (5) for the reaction time in 2 h and 4 h.

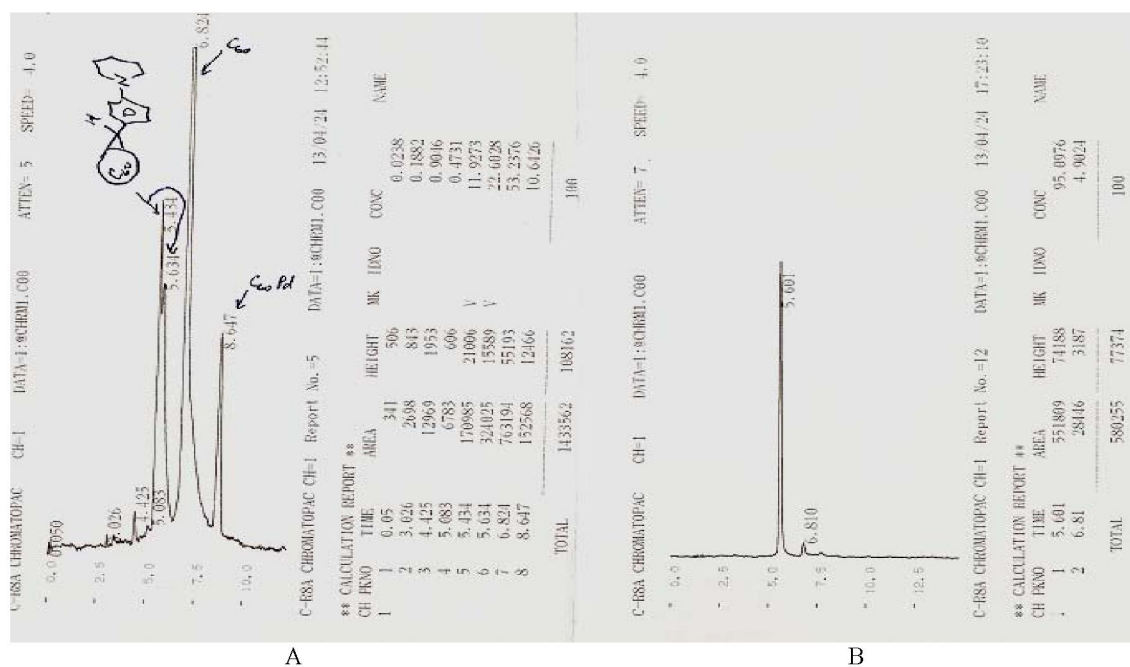
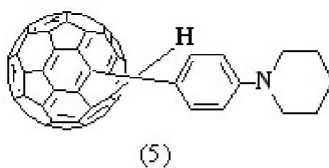


Figure 1 - Chromatograms of compound (5): A - after 2 h; (B) - after 4 h



The structure of the compounds obtained was studied using 1- (4- (piperidine) phenyl)-1aH-1(2)a-homo(C₆₀-I_h) [5,6] fullerene (5) using mass spectrometry (MALDI-TOF/TOF). Mass spectra (5) contain peaks of molecular ions with m/z 892.097 (calculated at 893.120) (Fig. 2).

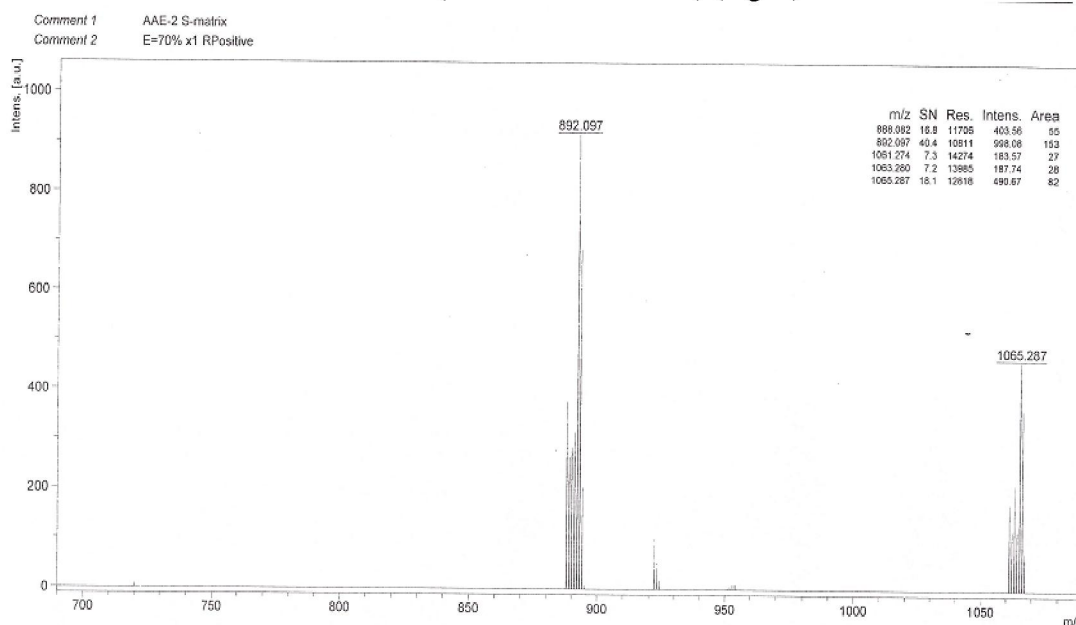


Figure 2 - Mass spectrum of 1-(4-(piperidine)phenyl)-1aH-(2)a-homo(C₆₀-I_h) [5,6] fullerene (5)

Thus, the synthesis was carried out and the catalytic cycloaddition of arylhydrazones to C₆₀ fullerene was carried out using the metal complex catalyst Pd(acac)₂-PPh₃-AlEt₃. It is shown that the use of the catalyst Pd(acac)₂-PPh₃-AlEt₃ in a ratio of 1: 4: 4 leads to the formation of exclusively methanofullerenes with yields of 40-95%. The proposed method is based on the generation of diazoalkanes in situ by oxidation of arylhydrazones with MnO₂ and using catalytic amounts of the palladium complex, the reaction is carried out at room temperature in a solution of o-dichlorobenzene.

Experimental part

The ¹H NMR spectrum of compounds (5) was taken on a JEOLFX90Q spectrometer (90 and 22 MHz). The analysis of addition products was carried out by HPLC on an Altex chromatograph (model 330) (USA) with a UV detector at a wavelength of 313 nm. The components of the mixture were separated on a metal column of 250x8 mm PLgel 100 Å with sorbent grains 5 mkm at room temperature. The mobile phase is toluene, the flow rate is 0.2 ml/min. Mass spectra were obtained on a MALDI-TOF/TOF instrument.

1-(4-(Hydrazonomethyl) phenyl) piperidine (1). To a solution of 0.2 g (0.001 mol) of 4-(piperidin-1-yl)benzaldehyde in 10 ml of 2-propanol, 0.25 g (0.005 mol) hydrazine hydrate. The reaction mixture was heated at 70 °C for 3-4 h. The precipitate which formed was filtered off, washed with 2-propanol and recrystallized from 2-propanol, 0.19 g (95%) of compound (1) was obtained, m.p. 155-156 °C. Found (%): C, 70.95; H, 8.48; N, 20.72. C₁₂H₁₇N₃. Calculated (%): C, 70.90; H, 8.43; N, 20.67.

4-(4-(Hydrazonomethyl)phenyl)morpholine (2) was prepared analogously to compound (1) from 1 g (0.005 mol) of 4-morpholybenzaldehyde and 1.3 g (0.026 mol) of hydrazine hydrate. 0.83 g (81%) of the compound (2.23) is obtained, m.p. 159-160 °C. Found (%): C, 64.42; H, 7.42; N, 20.52. C₁₁H₁₅N₃O. Calculated (%): C, 64.37; H, 4.37; N, 20.47.

2-(Hydrazonomethyl) phenol (3) was prepared analogously to compound (1) from 2 g (0.0164 mol) of salicylic aldehyde and 4.1 g (0.082 mol) of hydrazine hydrate. 1 g (45%) of the compound (3.24) was obtained, m.p. 82 °C. Found (%): C, 61.80; H, 5.97; N, 20.63. C₇H₈N₂O. Calculated (%): C, 61.75; H, 5.92; N, 20.58.

5-Bromo-2-(hydrazonomethyl) phenol (4) was prepared analogously to compound (1) from 1 g (0.005 mol) of 5-bromo-2-hydroxybenzaldehyde and 1.24g (0.025 mol) of hydrazine hydrate. 0.6 g (56%)

of the compound (3.25) is obtained, m.p. 247°C. Found (%): C, 39.15; H, 3.33; N, 13.08. $C_7H_7N_2OBr$. Calculated (%): C, 39.10; H, 3.28; N, 13.03.

1-(4-(piperidine)phenyl)-1aH-1(2)a-homo(C_{60} -I_h)[5,6]-fullerene (5). A solution containing 0.1 ml (0.00278 mmol) of $Pd(acac)_2$ in 0.4 ml of o-dichlorobenzene and 0.2 ml (0.00556 mmol) of PPh_3 in 0.42 ml of o-dichlorobenzene was charged to the glass reactor. In dry argon flow at -5°C and with stirring, 0.4 ml (0.01112 mmol) of Et_3Al in 0.1 ml of toluene was added, while the color from slightly yellow to slightly brown. 10 mg (0.0139 mmol) of C_{60} fullerene in 2 ml of chlorobenzene were added to the obtained catalyst at room temperature, and the solution acquired a dark green color. 8.46 mg (0.0417 mmol) of 1-(4-(hydrazonomethyl)phenyl) piperidine were added to the resulting fullerene complex in 9.4 ml of CH_2Cl_2 and in small portions 0.2 mmol of MnO_2 . After 1 hour, the reaction mass was treated with an aqueous solution of 5% HCl, 7 ml of toluene was added and the organic layer was passed through a column with a small amount of silica gel. The reaction products and the C_{60} fullerene were separated by preparative HPLC, eluent-toluene. The product was a brown powdered substance 11.4 mg (95%).

1-(4-(Morpholyl)-phenyl)-1aH-1(2)a-homo(C_{60} -I_h)[5,6]fullerene(6), 1-(4-(2-hydroxyphenyl)-1aH-1(2)a-homo(C_{60} -I_h)[5,6] fullerene (7) and 1-(4-(5-bromo-2-hydroxy-phenyl)-1aH-1(2)a-homo(C_{60} -I_h)[5,6] fullerene (8) were prepared analogously to compound (5) and are brown powders with yields of 95%, 45% and 51%, respectively.

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С₆₀ ФУЛЛЕРЕНГЕ ГИДРАЗОНДАРДЫҢ ПАЛЛАДИЙ КОМПЛЕКСТЕРІМЕН КАТАЛИЗДЕНЕТІН ЦИКЛОҚОСЫЛУЫ

Аннотация. Мақала С₆₀-фуллеренге гидразондарды каталитикалық циклоқосумен жаңа метанофуллерендер синтезінің препаратты тиімді әдісін әзірлеуіне арналған. Катализатор ретінде композициялық катализатор Pd(acac)₂-PPh₃-AlEt₃ қолданылды. Реакциялар MnO₂ көмегімен сәйкес альдегидтердің гидразондарының тотығуы нәтижесінде орынбасылған диазометандардың *in situ* генерациялануы әдісін қолдану жағдайында жүргізілді. Ауыспалы металдардың комплекстерінің қолданылуы диазоқосылыстардың фуллеренге циклоқосылу реакциясын жеке метанофуллерендерді алу бағытына қамтамасыз етеді. Алдымен изопропилді спирт ортасында гидразингидраттың артық мөлшері қатысында орын басылған бензальдегидтермен (салицил альдегиді, 5-бромсалицилді алдегид, 4-морфолинобензальдегид, 4-пиперидинбен-зальдегид) әрекеттесуі нәтижесінде бастапқы арилгидразондар синтезі жүргізілді. Диазоарилальдегидтердің фуллерен С₆₀-пен әрекеттестіру реакциясын ЖТСХ арқылы тексеріліп отырылды. Pd(acac)₂-PPh₃-AlEt₃ катализаторын 1:4:4 қатысында қолдану тек қана метано-фуллерендердің 40-95% шығыммен түзілуіне әкелетіні көрсетілді. Алынған метанофуллерендердің құрылымы ЯМР¹Н-спектро-скопиямен, құрамы мен тазалығы масс-спектрометрия MALDI-TOF және ЖТСХ әдістерімен расталған. Метанофуллереннің түзілуінің механизмі талқынылады.

Түйін сөздер: С₆₀-фуллерен, ароматтық альдегидтер, диазоарилальдегидтер, циклоқосылу, катализатор Pd(acac)₂-PPh₃-AlEt₃.

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КАТАЛИЗИРУЕМОЕ КОМПЛЕКСАМИ ПАЛЛАДИЯ ЦИКЛОПРИСОЕДИНЕНИЕ ГИДРАЗОНОВ К ФУЛЛЕРЕНУ С₆₀

Аннотация. Статья посвящена разработке препаративно удобного способа синтеза новых метанофуллеренов каталитическим циклоприсоединением гидразонов к фуллерену С₆₀. В качестве катализатора использовалась композиция Pd(acac)₂-PPh₃-AlEt₃. Реакции проводились в условиях генерирования замещенных диазометанов *in situ* окислением гидразонов соответствующих альдегидов с помощью MnO₂. Использование комплексов переходных металлов в этой реакции позволяет направить циклоприсоединение диазосоединений к фуллеренам в сторону получения индивидуальных метанофуллеренов. Вначале осуществлен синтез исходных арилгидразонов взаимодействием замещенных бензальдегидов (салициловый альдегид, 5-бромсалициловый альдегид, 4-морфолино-бензальдегид, 4-пиперидинбензальдегид) с избытком гидразингидрата в среде изопропилового спирта. Реакцию взаимодействия диазоарилальдегидов с фуллереном С₆₀ контролировали методом ВЭЖХ. Показано, что использование катализатора Pd(acac)₂-PPh₃-AlEt₃ в соотношении 1:4:4 приводит к образованию исключительно метано-фуллеренов с выходами 40-95%. Состав и чистота полученных метанофуллеренов подтверждены данными масс-спектрометрии MALDI-TOF и ВЭЖХ, а строение - методом ЯМР¹Н-спектроскопии. Обсуждается механизм образования метанофуллерена.

Ключевые слова: С₆₀-фуллерен, ароматические альдегиды, диазоарилальдегиды, циклоприсоединение, катализатор Pd(acac)₂-PPh₃-AlEt₃.

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