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Sulfur-Containing Homo- and Methanofullerenes, Synthesis and Study of Tribological Properties †

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Abstract: The data obtained by the authors in the field of carbon cluster chemistry, namely, the catalytic cycloaddition of sulfur-containing diazo compounds to C_{60}-fullerene under the action of complex Pd-catalysts, are summarized. Cycloaddition reactions of diazoalkanes, diazoketones, diazothioates with C_{60}-fullerene, catalyzed by $Pd(acac)_2$-PPh_3-Et_3Al, with selective formation of new sulfur-containing methano- and homo-, and pyrazolinofullerenes, promising as modern nanosized additives to oils for highly loaded mechanisms.

Keywords: fullerenes; diazo compounds; methanofullerenes; homofullerenes; metal complex catalysis; tribology; additives

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1. Introduction

Since the discovery of fullerenes, a new form of carbon existence, the chemistry of carbon clusters has become an independent branch of the organization of chemistry. Along with the study of the chemical properties of fullerenes, much attention is paid to determining possible areas of their application.

Interest in sulfur-containing fullerenes is due to their possibility of application in medicine [1–4], electronics and nonlinear optics [5], as well as solar energy photoconverters [6,7], and supramolecular dyes [8,9]. We assumed that the spherical structure of the molecules of the simplest C_{60}- and C_{70}-fullerenes will play the role of nanobearings, which will allow them to be used as oil additives.

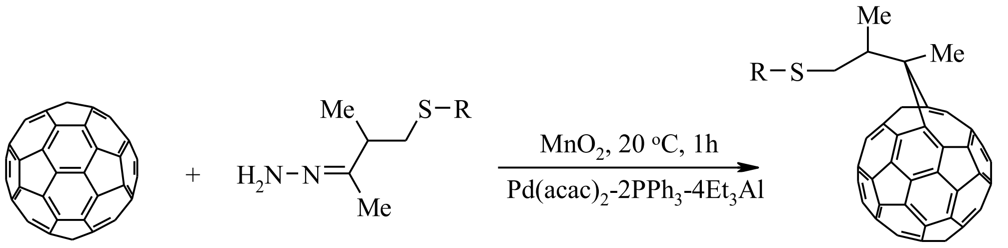
By the time we started our research in the world literature methods for the synthesis of sulfur-containing derivatives were described C_{60}-fullerene, with the most attractive synthetic point of view is a method based on thermal interaction of carbon clusters withdiazocompounds [10,11]. However, the main disadvantage the specified method is the low selectivity of the reaction. Meanwhile, it has recently been shown[12] that the introduction of methods metal complex catalysis in the reaction of fullerenes withdiazocompounds allows to achieve selective obtaining homo- or methanofullerenes.

In this regard, the use of metal complexcatalysts in the reactions of sulfur-containing diazocompounds withfullerenes, as we assumed, will allow us to develophighly selective and efficient catalytic methodssynthesis of sulfur-containing homo-, methane-, orpyrazolinofullerenes of a given structure, which will allowcreate on their basis promising nanocomponentadditives for lubricating oils and highly loadedmechanisms.

2. Results and Discussion

As a follow-up to the ongoing work in our group [13–20] related to the selective functionalization of C_{60}-fullerene with diazo compounds, we studied the catalytic cycloaddition reaction of sulfur-containing diazosoalkanes generated in situ by the oxidation of hydrazones of the corresponding ketosulfides with MnO_2 to C_{60}. Of the tested catalysts based on salts and compounds of Cu, Pd, and Rh, the three-component catalyst prepared in situ from $Pd(acac)_2$, PPh_3, and Et_3Al, taken in a ratio of 1:2:4, respectively, showed the highest activity in the reaction of diazoalkanes and C_{60}-fullerene. In this regard, all experiments on the study of the reaction of catalytic cycloaddition of sulfur-containing diazoalkanes to C_{60}-fullerene were carried out in the presence of this catalytic system.

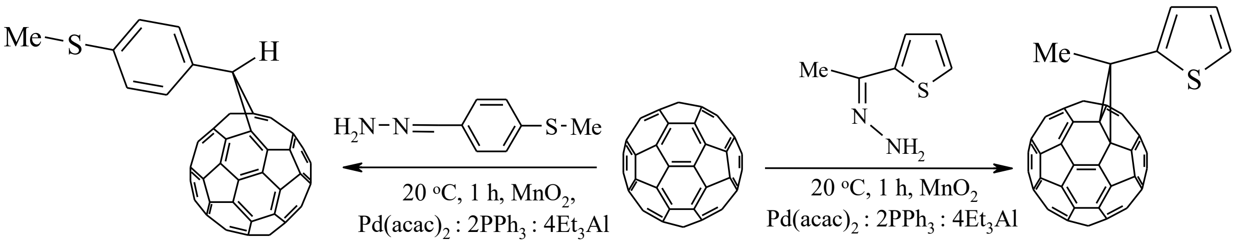
It was found that the interaction of C_{60}-fullerene with a 1.5-fold excess of 2-diazo-3-(pentylthiomethyl)- or 2-diazo-3-(cyclohexylthiomethyl)butane, generated in situ by oxidation of hydrazones of the corresponding ketones, in the presence of 20 mol .% of the three-component catalyst $Pd(acac)_2$-PPh_3-Et_3Al (1:2:4) at room temperature (18-20°C) in chlorobenzene, the corresponding homofullerenes **1** and **2** are formed in 1 h with a yield of ~50% [21].



1: R= C_5H_{11} (53 %); **2:** R= Cy (50 %)

Scheme 1. Catalytic cycloaddition of sulfur-containing diazoalkanes to C60-fullerene.

Under the developed optimal conditions (~20–22 °C, 1 h, 20 mol.% $Pd(acac)_2$-PPh_3-Et_3Al (1:2:4)) cycloaddition of sulfur-containing diazoalkanes generated in situ from hydrazones of 4-methylthiobenzaldehyde and 2- acetylthiophene to C_{60}-fullerene leads to compounds **3** and **4** in 50 and 45% yields, respectively.



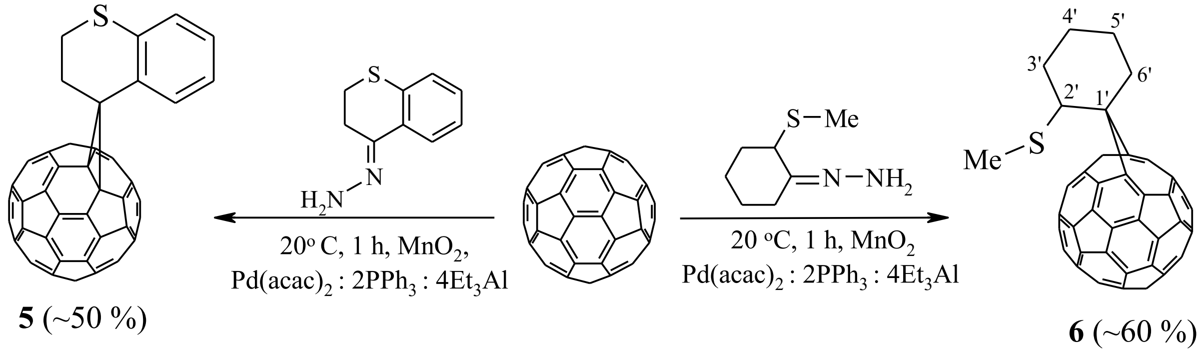
3 (~50 %)

4 (~45 %)

Scheme 2. Cycloaddition of sulfur-containing diazoalkanes to C_{60}-fullerene generated in situ.

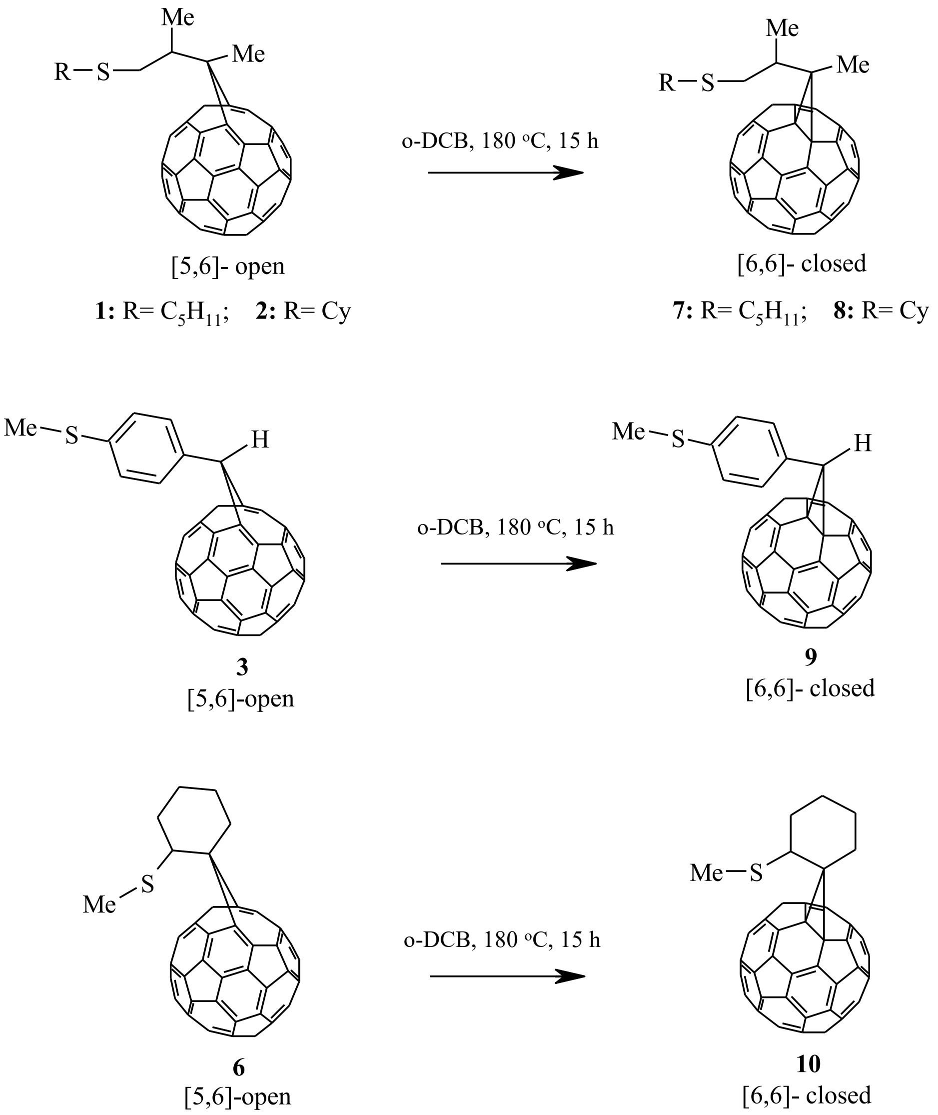
Analysis of the 1H and 13C NMR spectra, as well as the UV spectra of compound **4**, showed that the reaction of C_{60} with a diazo compound containing a thienylfragment resulted in the formation of only a [2+1]-cycloadduct of a closed structure.

Similarly, the cycloaddition of diazoalkane generated from thiochroman-4-one hydrazone [22] to C_{60} under the conditions developed above (20 °C, 1 h, 20 mol% $Pd(acac)_2$-$2PPh_3$-$4Et_3Al$) leads to the formation of spiro-methanofullerene **5**~50% yield. When using a cyclic ketone hydrazone that does not contain a heteroatom in the cyclic fragment, for example, o-methylsulfanylcyclohexanonehydrazone, individual spiro-homofullerene **6** is formed in the reaction under discussion. We assume that the formation of methanofullerenes, in the case of heterocyclic diazo compounds, is due to the stabilization of the corresponding carbenes formed during the reaction due to delocalization of unpaired electrons with an aromatic nucleus [22].



Scheme 3. Formation of spiro-methane and spiro-homofullerenes.

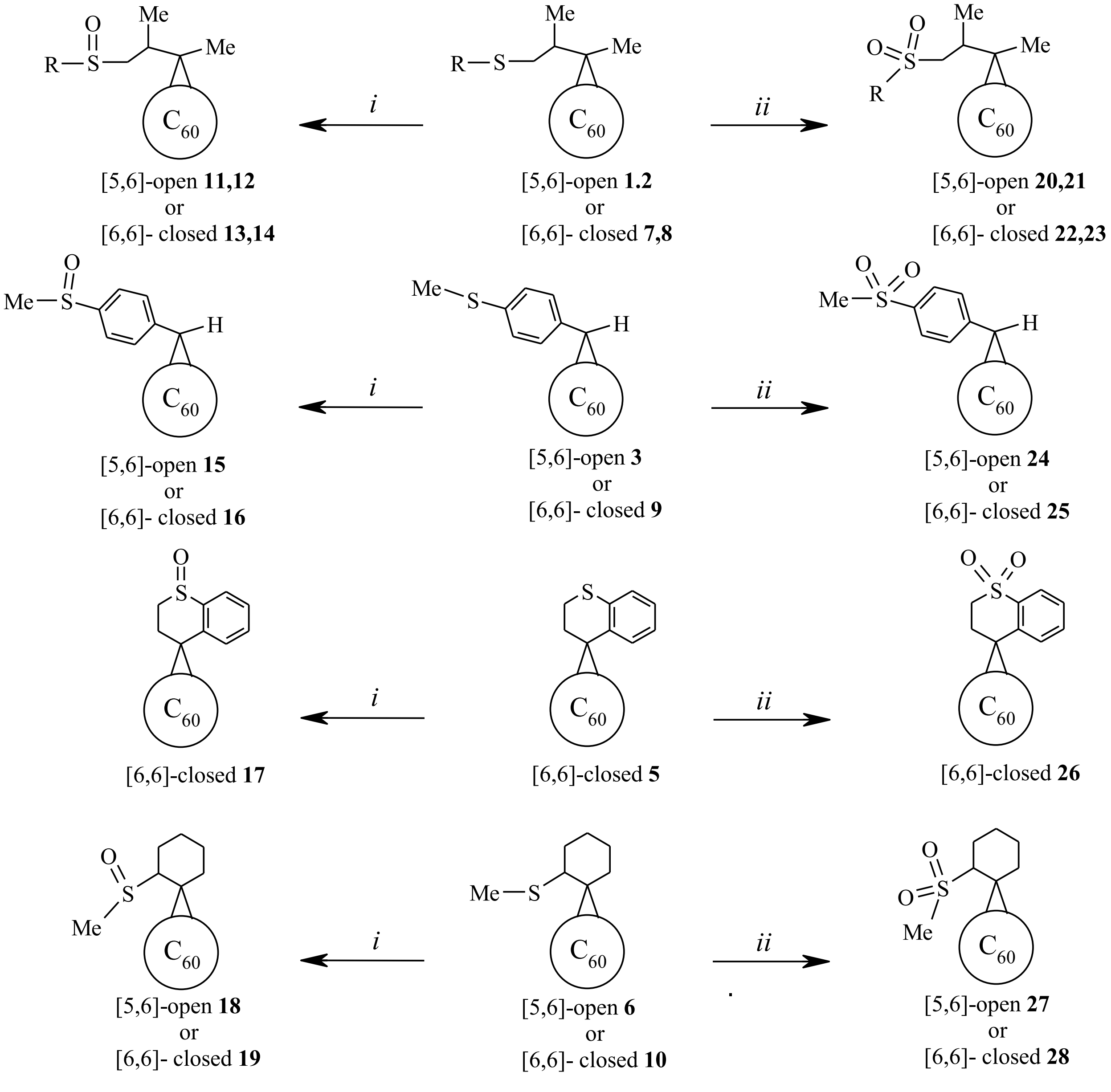
According to the literature, [23] substituted homofullerenes can be quite easily isomerized into the corresponding methanofullerenes. In this regard, and also in order to obtain previously undescribed sulfur-containing methanofullerenes, we carried out thermal isomerization of the synthesized [5,6]-open cycloadducts **1**-**3**,**6**. As a result of refluxing the indicated homofullerenes in 1,2-dichlorobenzene (o-DCB) for 15 h, individual [6,6]-closed isomers **7–10** were obtained in high yields of ~100%.



Scheme 4. Thermal isomerization of [5,6]-open cycloadducts.

In the UV spectrum of individual methanofullerenes **7-10**, a narrow low-intensity absorption band is observed in the region of 427-430 nm, which is a fairly simple and reliable characteristic of the formation of [6,6]-closed cycloadducts.

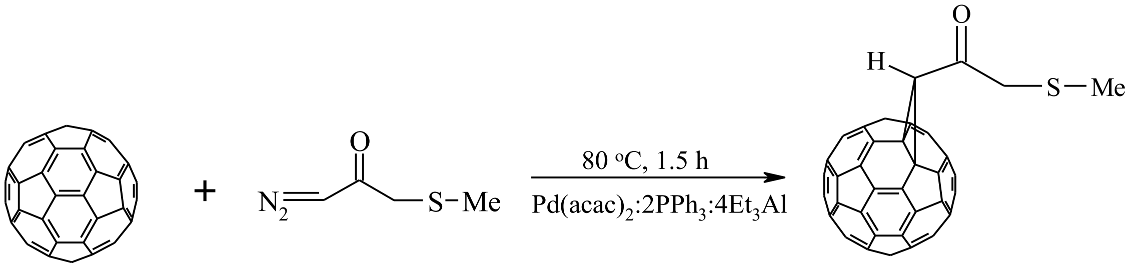
In order to obtain C_{60} adducts containing sulfoxide or sulfonegroups, we oxidized the cycloadducts **1-3**, **5-10** synthesized by us, which contain sulfide sulfur. It has been shown that treatment of sulfides with **1-3**, **5-10** equimolar amounts of m-CPBA leads to the formation of the corresponding individual sulfoxides **11-19** in quantitative yield (control by HPLC and 1H NMR). An increase in the amount of m-CPBA relative to the initial sulfide **1-3**, **5-10** to 3:1 leads to the formation of individual sulfones **20-28**, which are characterized by an even longer retention time.



The reaction conditions: *i* - m-CPBA (1 equiv.), toluene, 20 °C, 1 h
ii - m-CPBA (3 equiv.), toluene, 20 °C, 1 h

Scheme 5. Oxidation of C_{60} adducts containing sulfide sulfur to sulfoxide or sulfonic.

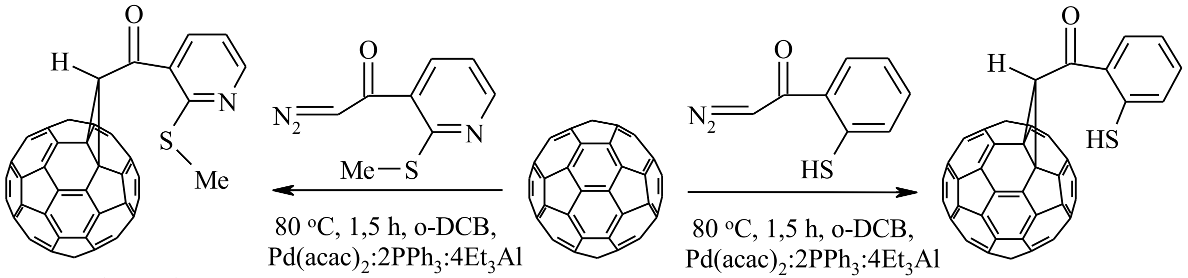
In order to develop our research, we carried out the catalytic cycloaddition of sulfur-containing diazoketones to C_{60} under conditions (~80 °C, 1.5 h, chlorobenzene or 1,2 dichlorobenzene) only methanofullerene **29** is formed with a yield of ~70%. An increase in the reaction time to 2 h leads to the formation of dicycloadducts. Homofullerene and fullerodihydrofuran, which are usually formed under the conditions of the thermal reaction of C_{60} with diazoketones, were not found in our experiments.



29 (~70%)

Scheme 6. Catalytic cycloaddition of sulfur-containing diazoketones to C_{60}-fullerene.

In order to study the effect of the structure of the starting diazoketone on the course and direction of the reaction under discussion, we studied the cycloaddition of diazoketones containing methylthiopyridyl and mercaptoaryl substituents to C_{60}. It has been shown that under the previously developed conditions (80 °C, 1.5 h, o-dichlorobenzene), these aromatic diazoketones react with C_{60}-fullerene in the presence of a three-component catalyst $Pd(acac)_2$-PPh_3-Et_3Al (1:2:4) to give the corresponding methanofullerenes **30** and **31** with a yield of ~55 and 60%, respectively.



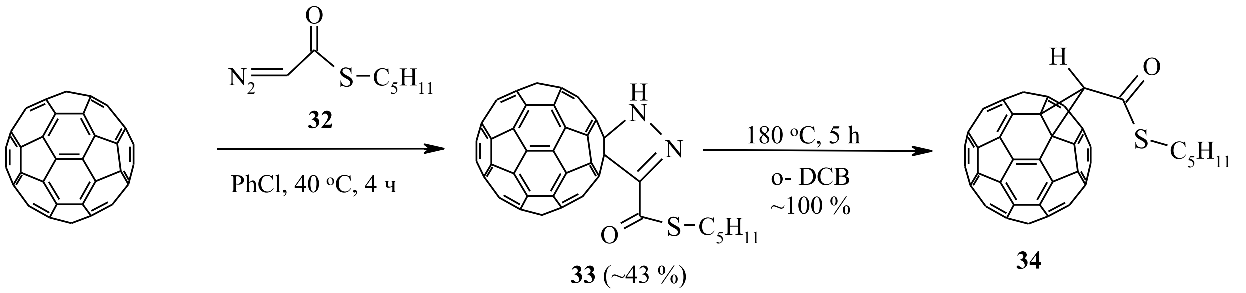
30 (~55 %)

31 (~60 %)

Scheme 7. Catalytic cycloaddition of sulfur-containing diazoketones to C_{60}-fullerene.

In order to develop effective methods for the synthesis of functionally substituted sulfur-containing C_{60}-carbon clusters, we for the first time carried out the interaction of C_{60} with diazothioates under conditions of thermal and catalytic reactions [24]. Diazo compounds synthesized on the basis of α amino acids (glycine, alanine, leucine, and methionine) and alkyl mercaptans were chosen as initial diazothioates.

It was found that diazothioate **32** quite easily reacted with C_{60} (20 °C, 7 h, solvent chlorobenzene) to form pyrazolinofullerene **33** in ~28% yield. An increase in the reaction temperature to 40 °C leads to the target [3+2]-cycloadduct **33** in the same yield in 2 h. An increase in the reaction time at 40 °C to 4 h makes it possible to synthesize pyrazolinofullerene **33** in ~43% yield.

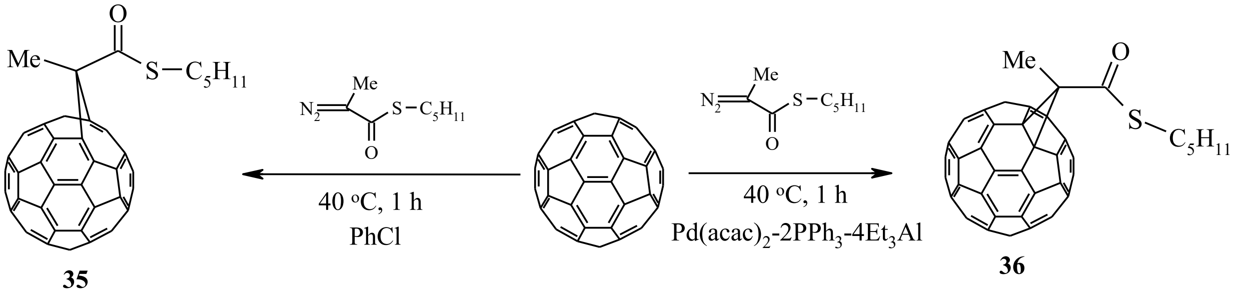


Scheme 8. Cycloaddition of diazothioates to C_{60}-fullerene.

Boiling pyrazolinofullerene **33** in 1,2-dichlorobenzene led to the extrusion of the N_2 molecule from the pyrazoline fragment and the quantitative formation of the corresponding methanofullerene **34**.

In order to study the influence of the structure of the initial diazothioate on the course and direction of the reaction, cycloaddition of α-substituted diazothioates to C_{60}-fullerene was carried out.

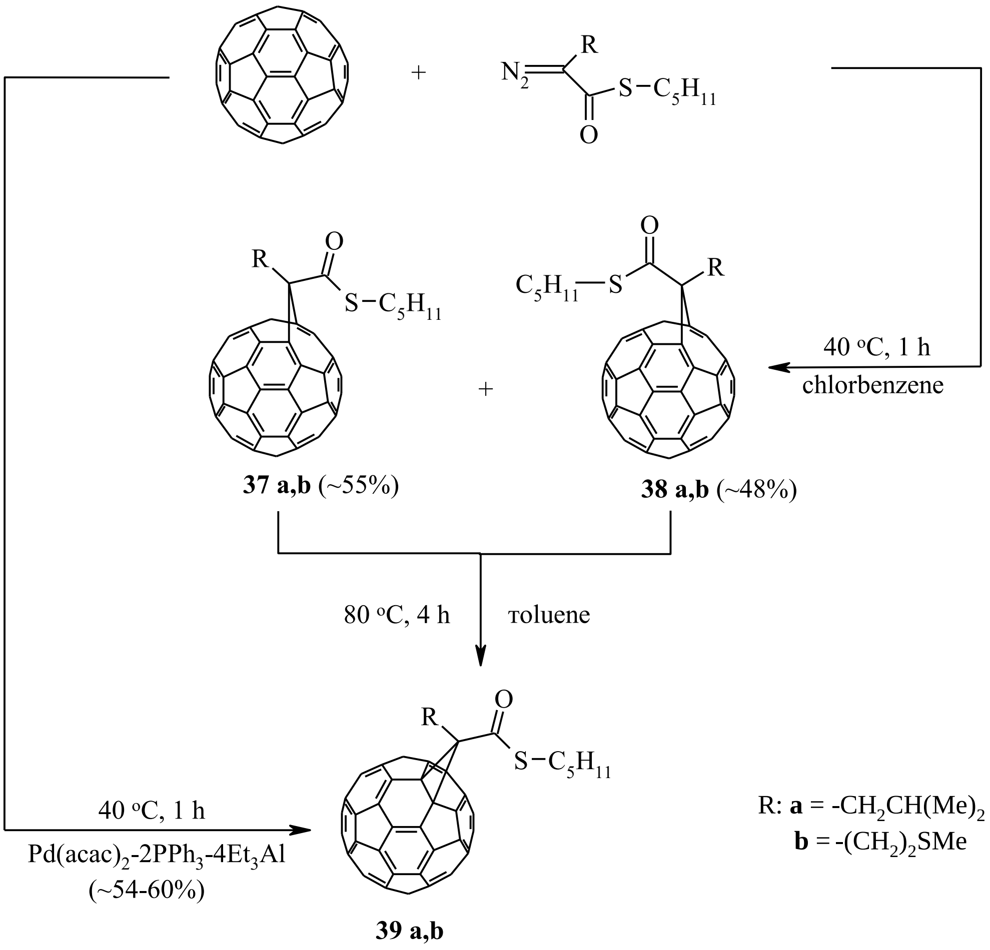
Thus, we found that, in contrast to the reaction of C_{60}-fullerene with unsubstituteddiazothioates, the interaction of C_{60} with thiopentyl-2-methyl-2-diazothioate in chlorobenzene takes place at 40 °C for 1 h with the formation of an individual [5,6]-open fullerene adduct **35** with the arrangement methyl group at the bridging carbon atom above the plane of the five-membered fragment of the fullerene core.



Scheme 9. Cycloaddition of α-substituted diazothioates to C_{60}-fullerene.

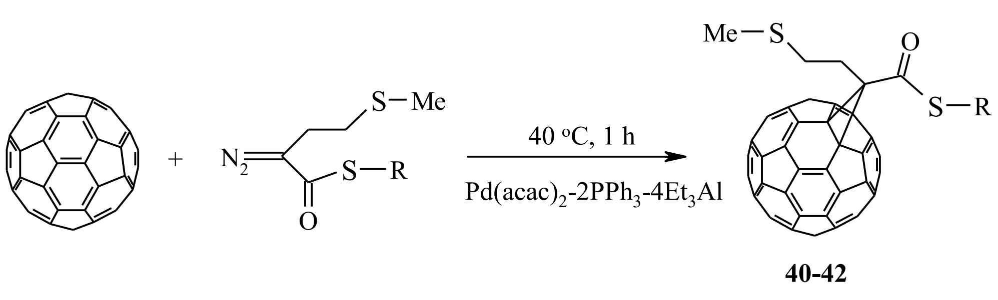
Subsequent experiments showed that the use of a 20 mol.% three-component catalyst based on the Pd phosphine complex ($Pd(acac)_2$-PPh_3-Et_3Al) with a component ratio of 1:2:4 in the reaction of C_{60}-fullerene with thiopentyl-2-methyl-2 -diazothioat makes it possible to direct it towards the formation of an individual [6,6]-closed cycloadduct **36** with a yield of ~47%.

Later, we studied the effect of the size of the alkyl substituent in the α-position of the diazo compound on the yield and selectivity of the formation of C_{60}-fullerene cycloadducts using the example of diazothioates synthesized from amyl mercaptan, leucine, and methionine. It was established that under the developed conditions (40 °C, 1 h) C_{60} reacts with the indicated diazo compounds (molar ratio 1:5) in the absence of a catalyst, forming a mixture of the corresponding stereoisomerichomofullerenes **37a,b** (55%) and **38a,b** (48%). Heating a mixture of homofullerenes **37a,b** and **38a,b** in toluene (80 °C) for 4 h leads to isomerization of [5,6]-open cycloadducts into [6,6]-closed **39a,b**, respectively.



Scheme 10. Catalytic cycloaddition of α-substituted diazothioates to C_{60}-fullerene.

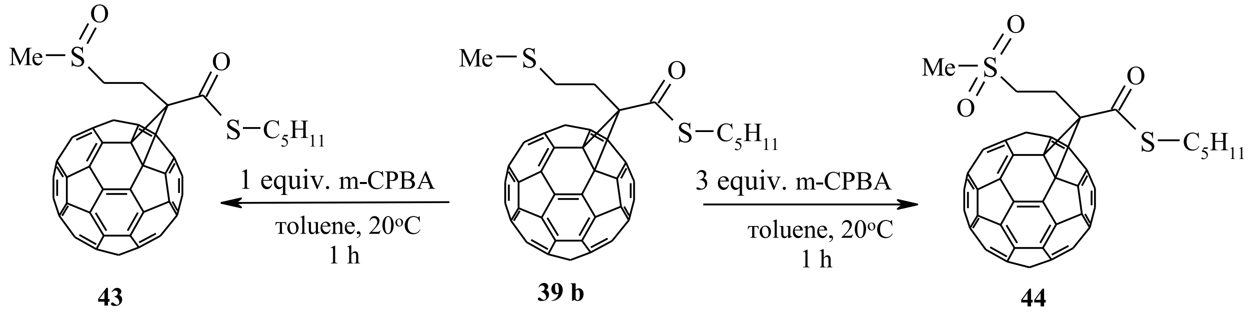
Carrying out the above reaction under catalytic conditions (40 °C, 1 h, 20 mol% $Pd(acac)_2$–$2PPh_3$–$4Et_3Al$) leads to the production of exclusively methanofullerenes **39a,b** in 54–60% yield. Similar results were obtained using isopropyl, cyclohexyl, and benzyl diazothioates. In all experiments using the $Pd(acac)_2$–$2PPh_3$ - $4Et_3Al$ catalytic system, the corresponding methanofullerenes **40-42** are formed.



40: R= *i*-Pr (~ 35%); **41:** R= Cy (~ 52%); **42:** R= Bn (~35%)

Scheme 11. Catalytic cycloaddition of isopropyl, cyclohexyl, benzyl diazothioates to C_{60}-fullerene.

Using the example of methanofullerene **39b**, the possibility of selective oxidation of sulfide sulfur to sulfoxide and sulfone treatment of the starting compound with an equimolar amount or a 3-fold excess of m-CPBA.

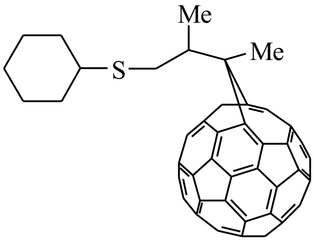


Scheme 12. Selective oxidation of sulfide sulfur compound **39b** to sulfoxide and sulfonic.

Thus, for the first time, we cycloaddition of diazothioates to C_{60} fullerene under conditions thermal and catalytic reactions. Determined that interaction of C_{60} with α-substituted diazothioates in presence of a three-component catalyst based on Pdleads to the selective formation of the corresponding methanefullerenes, while in the absence of a catalyst only homofullerenes are formed.

Considering that the majority of additives currently used in industry are sulfur-containing compounds, it can be assumed that oil-soluble sulfur-containing fullerenes are promising as new functional nanomaterials for improving the lubricating and antifriction properties of additives, as well as materials that significantly improve extreme pressure and antiwear properties.

In this regard, within the framework of this work, we studied the antiwear and extreme pressure properties of oils containing synthesized C_{60} derivatives, the structure of which contains sulfur atoms of various nature, as well as various functional groups [25]. The following compounds were chosen as model sulfur-containing C_{60} adducts:



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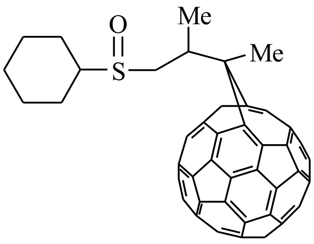

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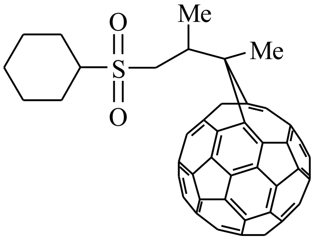

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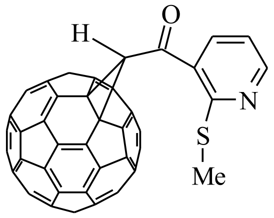

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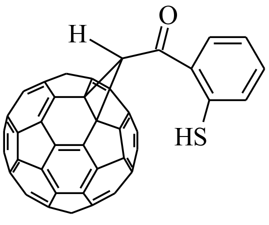

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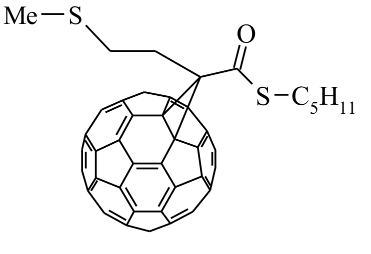
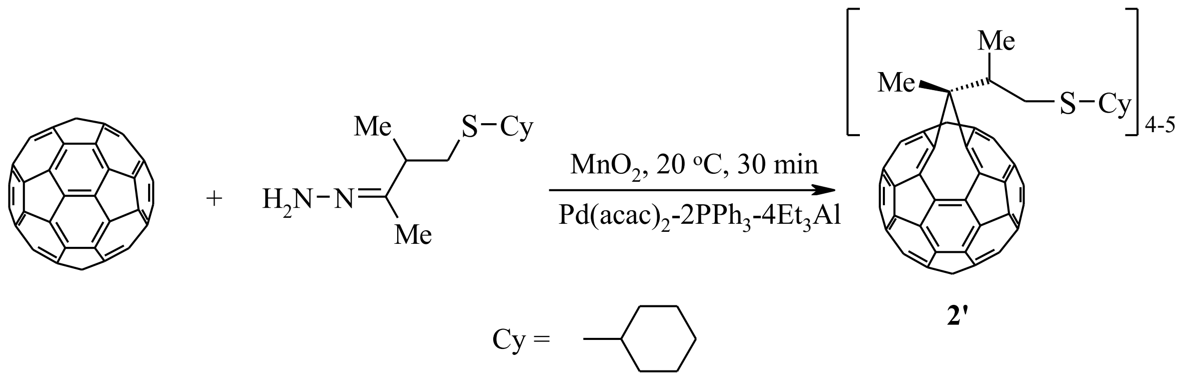


39 b

Table 2. is practically insoluble in industrial oils, as well as in known sulfur-containing additives, as a result of which we attempted to carry out the polyaddition of the corresponding diazoalkane generated in situ by the oxidation of hydrazone 3 (cyclohexylthiomethyl)-2-butanone with MnO_2, to C_{60}, taken in a ratio of 50:1, respectively, in the presence of 20 mol% $Pd(acac)_2$-$2PPh_3$-$4Et_3Al$ catalyst, hoping to obtain polycycloadducts with good solubility. Under these conditions, a mixture of regioisomeric cycloadducts **2′** is formed, which are built from one C_{60} fullerene molecule and five molecules of residues of the initial sulfur-containing diazoalkane. The fullerene C_{60} conversion in this experiment is ~100%.



Scheme 13. Obtaining a sulfur-containing polycycloadduct of fullerene C_{60}.

The regioisomeric mixture of cycloadducts **2′** synthesized by us, as well as monoadducts **12**, **21** and **30**, did not dissolve in I-20A industrial oil, so we tried them dissolved in a well-known PRP additive, which is a sulfided propylene tetramer. The additive compositions obtained in this way were easily dissolved in industrial oil I-20A in an amount of 5 wt.% with vigorous stirring under conditions (4 h, 60 °C), which made it possible to compare the effectiveness of the prepared additives with known samples.

The study of the obtained additives for extreme pressure properties was carried out on a four-ball friction machine ChMT-1 (State Standard 9490-75).When testing on the ChMT, balls were used according to State Standard 3722-81 made of steel with a diameter of 12.7 mm, degree of accuracy 20. Welding load (P_{w}), which characterizes the maximum performance of the lubricant under test conditions, critical load (P_{cr}), as well as the wear diameter (d_{ws}), which determine the ability of the lubricant to prevent the occurrence of scuffing of rubbing surfaces and anti-wear properties. The results of the tests carried out are presented in Table 1.

Table 1. Testing oils containing C_{60} fullerene cycloadducts **2′, 12, 21, 30.**

№	Testsamples	P_{cr}, kgf	P_{w}, kgf	d_{ws}, mm
1	Industrial oil+ **5wt% STP** * + **0.005wt% of compound 2′**	71	596	0.73
2	Industrial oil+ **5wt% STP** + **0,005 мас.%of compound 12**	75	>1000	0.76
3	Industrial oil+ **5wt% STP** + **0,005 мас.%of compound 21**	71	>1000	0.74
4	Industrial oil + **5wt% STP** + **0,005 мас.%of compound 30**	71	>1000	0.51
5	Industrial oil + **5wt% of sulfidized tetramers of propylene (STP)** (Control sample)	79	398	0.93
6	Industrial oil + **40wt% of sulfidized tetramers of propylene (STP)** (Control sample)	100	596	0.75

* STP—sulfidized tetramers of propylene.

As can be seen from the data in Table 2, the obtained new compositions of additives, in comparison with the original (STP), have better antiwear and extreme pressure properties, good compatibility with industrial oils, which makes it possible to reduce the consumption of sulfur-containing extreme pressure and antiwear additives currently used and produced by the industry by 8 times. Additives for highly loaded machines and mechanisms, while maintaining their efficiency, as well as to expand the range of new domestic multifunctional additives. It should be noted that C_{60} adducts containing sulfoxide, sulfone, or sulfide and carbonyl groups have better solubility in the STP additive, in contrast to monocycloadducts containing only a sulfide group. Methanofullerene **31** does not dissolve in oil and STP additive, as a result of which the tribological properties of this compound could not be studied.

When preparing composite oils for the study of tribological properties, we found that monoadduct **39b**, in contrast to the compounds **2′,12,21,30** used above, dissolves well directly in industrial oil I-20A, as a result of which the addition of STP in this case, we was not carried out.

As a result of the research, it was shown that the industrial oil I-20 A, containing 0.005 wt.% adduct C_{60} with a thioate group, significantly exceeds the weldability load of oils containing 40 wt.%STP ($P_w > 1000$ kgf), however, it has a low P_{cr} index (45 kgf).

The low critical load is likely due to the low sulfur content of the test samples, as we have abandoned the use of 5 wt% STP. In this regard, we assumed that an increase in the number of fragments attached to the fullerene molecule will lead to an increase in the critical load index. To confirm our idea, we synthesized a model polyadduct **39b′**, which is an analogue of monoadduct **39b** and contains from 3 to 5 attached cyclopropane fragments.

The test of the prepared composition consisting of industrial oil I-20 A and 0.005 wt.% compound **39b′** showed that, indeed, an increase in the number of attached fragments contributes to an increase in the critical load (P_{cr}) from 45 kgf to 63, while the welding load (P_w) slightly decreases to 942 kgf.

Using an electron microscope, as well as using atomic force microscopy (AFM), it was established that the introduction of sulfur-containing C_{60}-fullerene derivatives into industrial oil I-20A leads to a smoothing of the steel ball surface at the wear spot after tribocontact.

3. Conclusions

Thus, for the first time, we have developed effective methods for the synthesis of fullerene derivatives containing sulfur atoms of various natures by cycloaddition of sulfur-containing diazo compounds to C_{60} fullerene in the presence of the $Pd(acac)_2$-PPh_3-Et_3Al three-component catalytic system, which opens up a fairly simple and effective way to the synthesis of homo- and methanofullerenes—effective additives to oils for highly loaded machines and mechanisms.

Author Contributions: Conceptualization, U.M.D., A.R.T. and A.A.K.; methodology, validation, and execution of chemistry experiments, A.A.K.; manuscript preparation, A.A.K. and A.R.T. All authors have read and agreed to the published version of the manuscript.

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