Russian Chemical Reviews **79** (7) 585 – 610 (2010) © 2010 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2010v079n07ABEH004111

Diazo compounds in the chemistry of fullerenes

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Abstract. Experimental and theoretical data on the reactions of different diazo compounds (diazomethane, its derivatives, cyclic diazo compounds and diazocarbonyl compounds) with fullerenes are summarized. The structures and stereochemistry of cycloadducts formed in these reactions are considered. The bibliography includes 142 references.

I. Introduction

Although 25 years have passed since the discovery of fullerenes, the numbers of publications devoted to them and of the scientists dealing with different aspects of fullerene chemistry continue to rapidly grow. This is not by accident, because the most fantastic properties are assigned to fullerenes, and the prospects of their use in different industrial fields are very attractive.

Functionally substituted fullerenes are of special interest and practical value, and a record-breaking number of publications are devoted to their synthesis and properties. A considerable part of these studies dealt with the synthesis and properties of methanofullerenes obtained by the Bingel[1] reaction or the Bingel – Hirsch cycloaddition to fullerene C_{60} (**1**) of carbanions derived from esters of haloacetic or halomalonic acids and by the [2 + 3] or [2 + 1] cycloaddition of diazo compounds or carbenes to fullerene C_{60}.

In 1993, the first publication by Bingel appeared[1] on the addition of diethyl bromomalonate to C_{60} in the presence of NaH to afford methanofullerene.

Virtually simultaneously, the [2 + 3] cycloadition of diazomethane to C_{60} at 0 °C to afford a pyrazoline derivative of fullerene was carried out.[2] The subsequent thermal elimination of N_2 at 100 °C yielded the simplest unsubstituted homofullerene.

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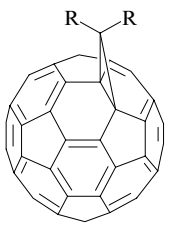
Received 8 October 2009
Uspekhi Khimii **79** (7) 645 – 671 (2010); translated by T Ya Safonova

Since the appearance of these studies, numerous papers and reviews[3 – 11] devoted to the synthesis of miscellaneous methanofullerenes by the Bingel and Bingel – Hirsch reactions have been published. At the same time, only discrete publications on the synthesis of homo- and methanofullerenes involved the use of diazo compounds or carbenes, although this method provides to date wider synthetic potential and, in contrast to the Bingel reaction, both [5,6]-open (homofullerenes) and [6,6]-closed adducts (methanofullerenes) can be synthesized.

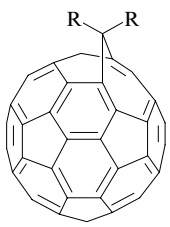
In the present review, an attempt was undertaken to summarize the known data on the synthesis of homo- and methanofullerenes that involve the use of diazo compounds; moreover, attention was focused on the catalytic cycloaddition of the latter to fullerenes.

II. Reactions of fullerenes with diazomethane

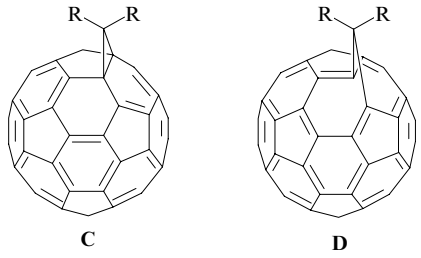
Thermal cycloaddition of diazo compounds to carbon clusters is known[9] to follow two routes, namely, synchronous [2 + 1] cycloaddition of carbenes, generated *in situ* by thermolysis of the corresponding diazo compounds, to the [6,6]-bond of fullerene C_{60} to form metanofullerenes **A** and 1,3-dipolar cycloaddition of diazo compounds to fullerene followed by extrusion of the dinitrogen molecule from the pyrazolinofullerene to afford a mixture of [5,6]-open (**B**) and [6,6]-closed (**A**) isomers. The reactions of fullerenes with diazo compounds remain so far the main method for the synthesis of [5,6]-open adducts, *i.e.*, homofullerenes.



A
[6,6]-closed
0 kcal mol^{-1}



B
[5,6]-open
+6 kcal mol^{-1}



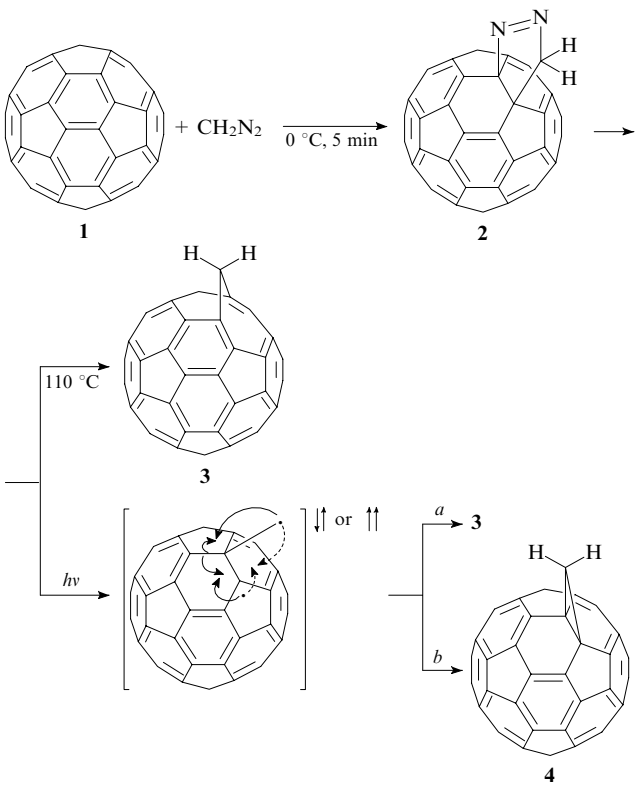
C [5,6]-closed
+21 kcal mol^{-1}

D [6,6]-open
does not correspond to any energy minimum

It should be noted that information on the synthesis of [5,6]-closed (**C**) and [6,6]-open (**D**) isomers by the reaction of fullerene C_{60} with diazo compounds is lacking. It was shown [3, 12, 13] that isomers **C** and **D** are energetically unfavourable structures because they contain two and three double bonds in the five-membered rings of the original molecule for [5,6]-closed (**C**) and [6,6]-open (**D**) isomers, respectively.

As was reported in one of the first publications on fullerene chemistry,[2] the reaction of fullerene C_{60} with diazomethane on cooling afforded pyrazolinofullerene **2** in the yield of ~44% in 5 min. On refluxing in toluene, it quantitatively converted to [5,6]-open adduct **3**. Its irradiation produced open (**3**) and closed (**4**) adducts in the 3 : 4 ratio in the overall yield of 21%.[14, 15] They are probably formed *via* a biradical intermediate in the singlet (pathway *a*) or triplet (pathway *b*) states (solid and dashed arrows, respectively, Scheme 1).

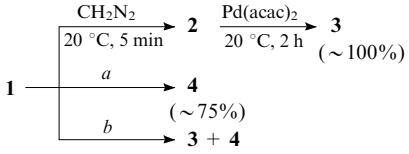
Scheme 1



The authors of the above study [15] were the first to carry out the catalytic breaking of pyrazolinofullerene **2**. Compound **2** was synthesized by a method described elsewhere [2] and then, in the presence of 20 mol.% $Pd(OAc)_2$ (toluene, 8 h), converted to individual homofullerene **3**; at longer reaction time, methanofullerene **4** was found in the reaction mixture. It was selectively formed (in the yield of ~15%) in the reaction of fullerene C_{60} with a 3–4-fold molar excess of diazomethane in the presence of stoichiometric amounts of $Pd(OAc)_2$.

The presence of catalytic amounts of $Pd(acac)_2$ (20 mol.%) was found [16] to substantially accelerate the nitrogen extrusion from pyrazolinofullerene **2**, which allowed adduct **3** to be selectively synthesized in 2 h in a virtually quantitative yield.

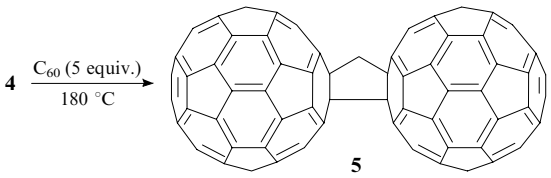
At the same time, when diazomethane was generated *in situ* from *N*-methyl-*N*-nitrosourea in chlorobenzene in the presence of fullerene C_{60} and 20 mol.% $Pd(acac)_2$, the selective formation of methanofullerene **4** in the yield of 75% was observed [16] (Table 1). With the substitution of toluene or *o*-dichlorobenzene (*o*-DCB) for chlorobenzene, a mixture of [2 + 1]-cycloadducts **3** and **4** was obtained, as under conditions of the photochemical reaction,[14] but in higher yield.



(*a*) MeN(NO)C(O)NH_2, $Pd(acac)_2$, KOH, PhCl, 40 °C, 1 h;
(*b*) MeN(NO)C(O)NH_2, $Pd(acac)_2$, KOH, PhMe or *o*-DCB, 40 °C, 1 h

In was shown [12] that, in contrast to [5,6]-open cycloadducts synthesized by cycloaddition of substituted diazomethanes or diazoacetates to fullerene C_{60} (see Sections III–V), homofullerene **3** did not undergo isomerization to methanofullerene **4** upon photolysis or thermolysis, even on prolonged reflux.

Heating of metanofullerene **4** with an excess of fullerene C_{60} at 180 °C in *o*-DCB for 1 weak afforded cycloadduct **5**.[17]



In contrast to highly symmetrical (I_h group) fullerene C_{60}, which contains 30 equivalent double bonds, the C_{70} molecule (the symmetry group D_{5h}) where some of six-membered rings are surrounded only by identical hexahedra, has bonds of eight different types (Fig. 1),[18] which theoretically can lead to a larger number of isomeric cyclo-

Table 1. The effect of the nature of solvent on the yield and ratio of adducts **3** and **4**.[a]

Solvent	Time /h	Total yield (%)	Ratio of adducts **3** and **4**
Chlorobenzene	1	75	0 : 1
o-Dichlorobenzene	1	80	8 : 5
1,2,4-Trichlorobenzene	1	65	2 : 3
Toluene	2	60	1 : 1

[a] Reaction conditions: 20 mol.% $Pd(acac)_2$, 40 °C.

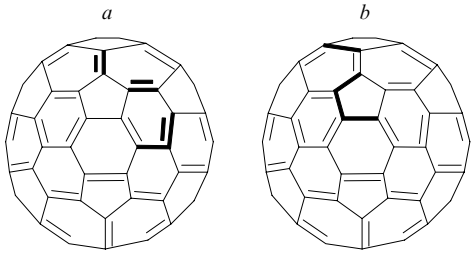


Figure 1. Possible channels of diazomethane addition to fullerene C_{70}.
(*a*) [6,6]-bonds, (*b*) [5,6]-bonds.

adducts. However, C_{70} and the other higher fullerenes demonstrated amazing selectivity in the formation of mono- and bisadducts,[7,19–21] as followed from calculations[22–24] and experimental data.[25,26]

Thus the reaction of fullerene C_{70} with diazomethane at 0 °C afforded in 1 min three regioisomeric pyrazolinofullerene[70] **6**–**8** in the 12 : 1 : 2 ratio in a total yield of ~34% (Scheme 2).[15] Compounds **6** and **7** are isomeric [2 + 3]-cycloadducts formed as the result of cycloaddition of diazomethane to the C(26)–C(27) bond, because of two different orientations of diazomethane with respect to the double bonds of C_{70} that are not located at the equator of the fullerene molecule. {The numbering of fullerene C_{70} follows the IUPAC recommendations [see *Pure Appl. Chem.* **74** 629 (2002)].} Pyrazolinofullerene **8**, in turn, formed as the result of 1,3-dipolar cycloaddition of diazomethane to the C(9)–C(10) bond. Refluxing of synthesized pyrazolinofullerene **6**–**8** in a hexane–toluene mixture led to [5,6]-open adducts **9** and **10** in the 4 : 1 ratio. In contrast to thermal decomposition of pyrazolines, the photochemical extrusion of the nitrogen molecule led to methanofullerenes **11** and **12** in the 7 : 1 ratio and traces of homofullerene **9**.

The structure of synthesized compounds was reliably established by spectral methods (IR, UV and ^1H and ^{13}C NMR spectroscopy).

Similar results were obtained in studies of the reaction of diazomethane with endofullerenes, particularly, $^3He@C_{60}$ and $^3He@C_{70}$.[27]

In contrast to properties of fullerenes C_{60} and C_{70} that were extensively studied, the reactivities of less accessible fullerenes (C_{20}, C_{36}, C_{76}, C_{80}, *etc.*) remain virtually unexplored. To date, in addition to experimental estimates of the reactivity, quantum chemical calculations have been used, which opens up wide prospects for predicting the chemical properties of different fullerenes.[28]

Thus using the DFT method in the PBE/3*z* approximation (the PRIRODA 2.02 + programme), structural features of fullerenes C_{20}, C_{36}, C_{76} and hypothetical molecules C_{24}, C_{30} and C_{40} as well as of their adducts with diazomethane

Scheme 2

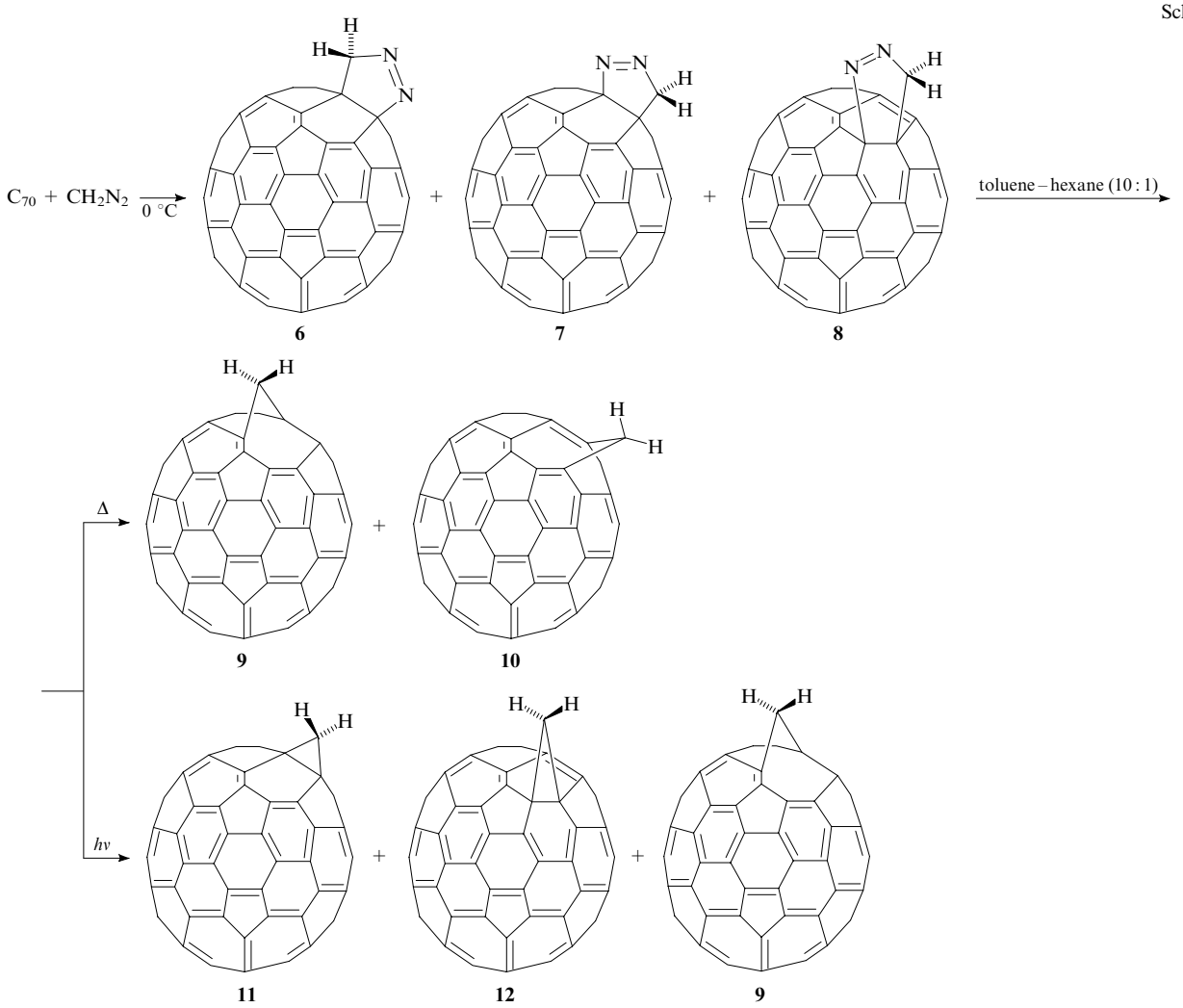


Table 2. Curvature k, bond orders and bond lengths (possible channels of 1,3-cycloaddition) in fullerenes C_{20}, C_{24}, C_{30}, C_{36}, C_{40} and C_{76}.[28]

Fullerene [a]	Bond type	Bond order		k /Å^{-1}	Bond length /Å
		p_M	p_{NBO}		
C_{20} (C_i)	5,5	1.45	1.65	0.5102	1.410
C_{24} (D_6)	5,5 [b]	1.56	1.59	0.4769	1.373
C_{30} (C_{2v})	5,5	1.51	1.69	0.4792	1.369
	5,6	1.40	1.62	0.4116	1.396
	5,6	1.40	1.61	0.3986	1.401
C_{36} (D_{6h})	5,6	1.35	1.56	0.4079	1.414
	5,6	1.30	1.52	0.3464	1.434
C_{40} (D_2)	6,6	1.46	1.68	0.3142	1.400
	5,6	1.47	1.65	0.3811	1.384
	5,6	1.49	1.63	0.3765	1.377
C_{76} (D_2)	6,6	1.43	1.60	0.2935	—
	6,6	1.45	1.56	0.2978	—

[a] Isomers shown in Fig. 2 are meant; [b] equatorial.

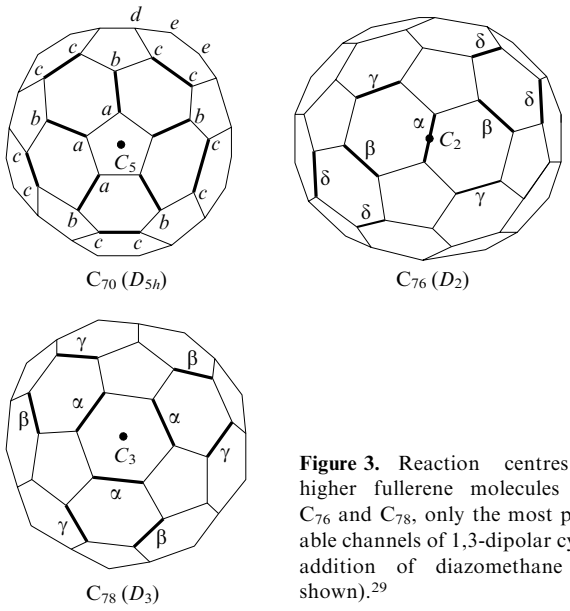


Figure 3. Reaction centres in higher fullerene molecules (for C_{76} and C_{78}, only the most probable channels of 1,3-dipolar cycloaddition of diazomethane are shown).[29]

were studied.[28] The probable channels of 1,3-cycloaddition of diazomethane include the bonds characterized by the maximum values of p_M, p_{NBO} and k [p_M and p_{NBO} are the bond orders according to Mulliken and to the NBO (Natural Bond Orbital) analysis, respectively, k is the local surface curvature] (Table 2, Fig. 2). The addition of diazomethane to a C—C bond that was not crossed by any symmetry elements (for example, b-bonds of fullerenes C_{36} and C_{76}, Fig. 3) could afford two isomeric pyrazolinofullerenes. It was assumed [28] that the linear dependence of the thermal effect of 1,3-dipolar cycloaddition of diazomethane to fullerenes on the carbon surface curvature can be used for the reliable prediction of the reactivities of higher fullerenes in similar reactions without carrying out laborious quantum chemical calculations.

The same research group [29] proposed a new alternative approach to the assessment of the reactivities of poorly accessible fullerenes by the example of 1,3-dipolar cycloaddition of diazomethane. This approach is based on the analysis of polarizability ellipsoids. Thus cycloaddition of diazomethane should proceed to the *ab* and *cc* bonds for fullerene C_{70}, to the α, β, γ and δ bonds for C_{76} and to the α, β and γ bonds for C_{78} (see Fig. 3), *i.e.*, to the bonds characterized by polarizability indices exceeding the average polarizability of these molecules. Such reactions should be

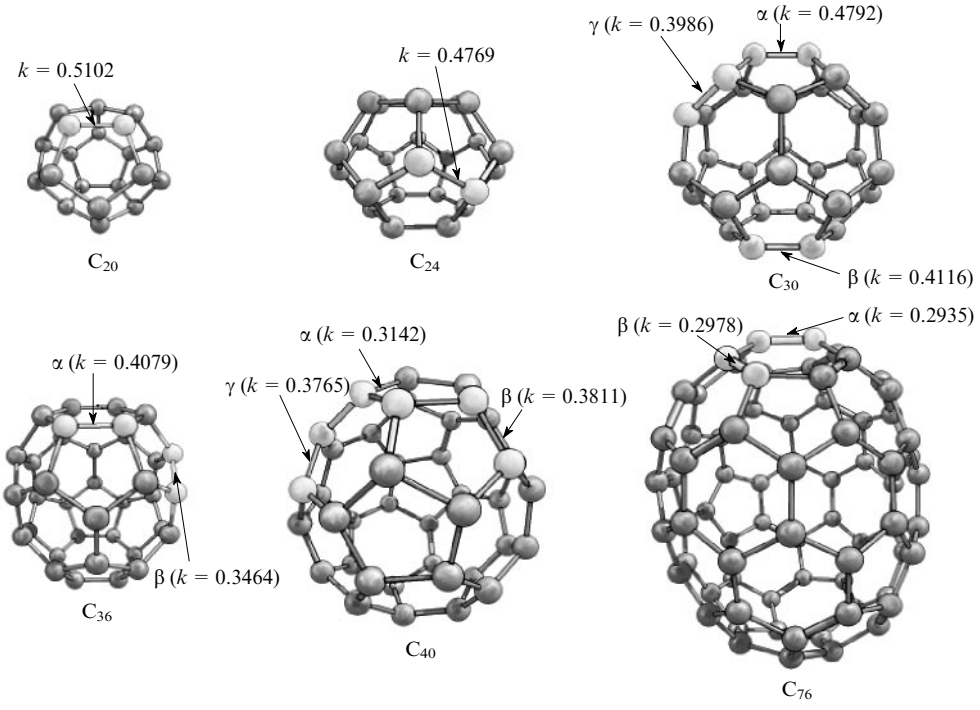


Figure 2. Reaction centres of 1,3-dipolar cycloaddition of diazomethane to fullerenes C_{20}, C_{24}, C_{30}, C_{36}, C_{40} and C_{76}.[28] Arrows point to bonds to which the addition occurs with the highest probability (k is the surface curvature).

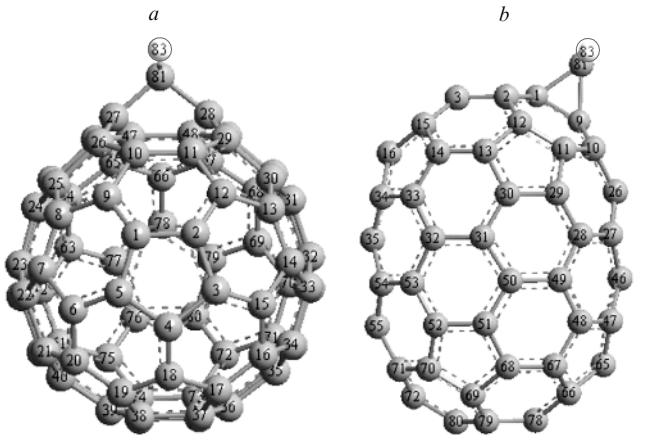


Figure 4. The most probable [5,6]-open (*a*) and [6,6]-closed (*b*) methano derivatives of fullerene C_{80} (D_{5d}) with the geometry optimized by the B3LYP/6-31G method.[30]

accompanied by the highest thermal effects. The results of calculations agreed well with the experimental data on the structures of cycloadducts to fullerenes C_{76} (D_2) and C_{78} (D_3).[8]

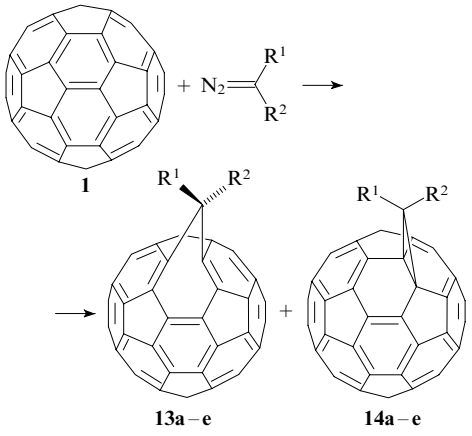
Similar results were obtained [30] in the theoretical analysis of the stability of nine possible isomers of methanofullerene derivatives C_{80} (D_{5d}). Calculations by the PM3 and DFT methods (B3LYP/STO-3G, B3LYP/3-21G and B3LYP/6-31G) with the Gaussian 03 software [31] have shown that the most energetically favourable adduct was the [5,6]-open adduct (Fig. 4 *a*), which is more stable than the cyclopropane adduct (Fig. 4 *b*).

It deserves mention that in addition to carbon clusters ($C_{20}-C_{80}$), the theoretical studies also considered carbon nanotubes.[32]

III. Cycloaddition of substituted diazomethanes to fullerenes

In contrast to diazomethane, substituted diazo compounds reacted with fullerene C_{60} to form mixtures of homo- and methanofullerenes; moreover, no pyrazolinofullerenes were detected due to their low stability.

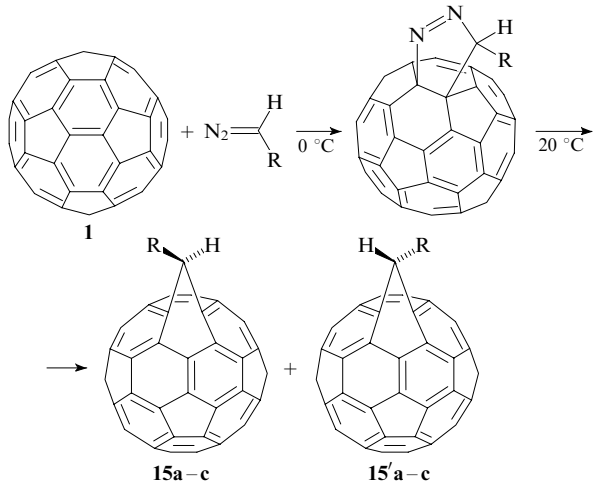
Thus aryl-substituted diazomethanes $R^1R^2CN_2$ react with fullerene C_{60} at ~20 °C to afford a mixture of [5,6]-open structures **13a**–**e** and [6,6]-closed forms of methanofullerenes **14a**–**e**.[33] For $R^1 \neq R^2$, the [5,6]-open structure existed as two stereoisomers (**13b** and **13′b**).



1 **13a**–**e** **14a**–**e**

$R^1 = R^2$ = Ph (**a**); R^1 = H, R^2 = Ph (**b**);
$R^1 = R^2$ = 4-MeC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 4-BrC_6H_4 (**e**).

Despite the fact that monosubstituted pyrazolinofullerenes are unstable, not only their formation could be observed, but they were also isolated and reliably characterized.[34] As the temperature increased from 0 to 20 °C, the extrusion of the nitrogen molecule from the pyrazoline ring occurred to afford the corresponding fulleroid isomers **15** and **15′**.



1 **15a**–**c** **15′a**–**c**

R = $CH(OEt)_2$ (**a**), $CH_2C_6H_4OMe$-4 (**b**), $(CH_2)_5OH$ (**c**).

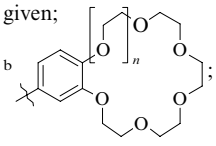
Table 3 lists aryldiazomethanes used in the reactions with fullerene C_{60} and the total yields of the target [2 + 1] cycloadducts. As is seen from the Table, the structure of the starting diazoalkane had virtually no effect on the yields of homo- and methanofullerenes.

Certain homo- and methanofullerenes are considered in detail below.

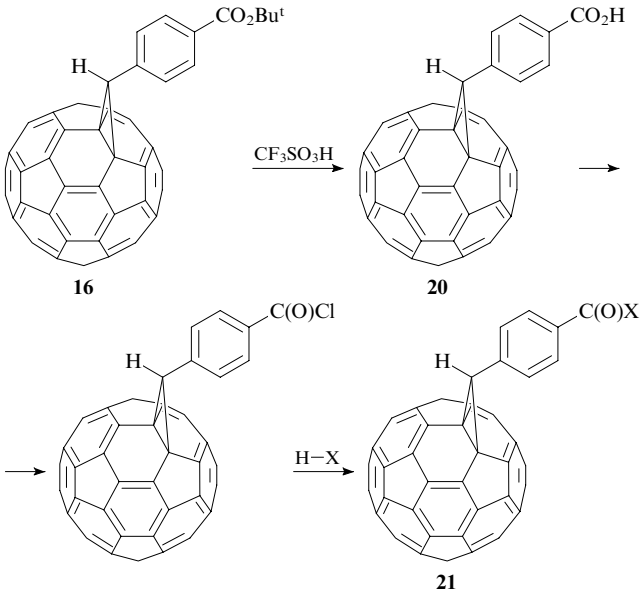
Table 3. Reaction of aryldiazoethanes with fullerene C_{60}.

Aryldiazomethane		Overall yield of products (%) [a]	Ref.
R^1	R^2		
H	4-$MeOC_6H_4$	–	33
	4-$MeO_2CC_6H_4$	–	35
	4-$Bu^tO_2CC_6H_4$	– (**16**)	36
Me	4-$MeOC_6H_4$	–	33
cyclo-C_3H_5	4-$MeOC_6H_4$	45	37
Ph	4-$MeOC_6H_4$	49	37
$MeO_2C(CH_2)_3$	Ph	– (**17**)	38
3,4-$(MeO)_2C_6H_3$	Ph	30	39
See [b], n = 0	Ph	43	39
See [b], n = 1	Ph	42	40
4-HOC_6H_4	4-HOC_6H_4	– (**18**)	41
4-$Pr^iOC_6H_4$	4-$Pr^iOC_6H_4$	–	33
4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	–	42
4-$PhO_2CC_6H_4$	4-$PhO_2CC_6H_4$	–	42
See [c]	see [c]	38 (**19**)	43

[a] In parentheses, the numbers of compounds mentioned in the text are given;

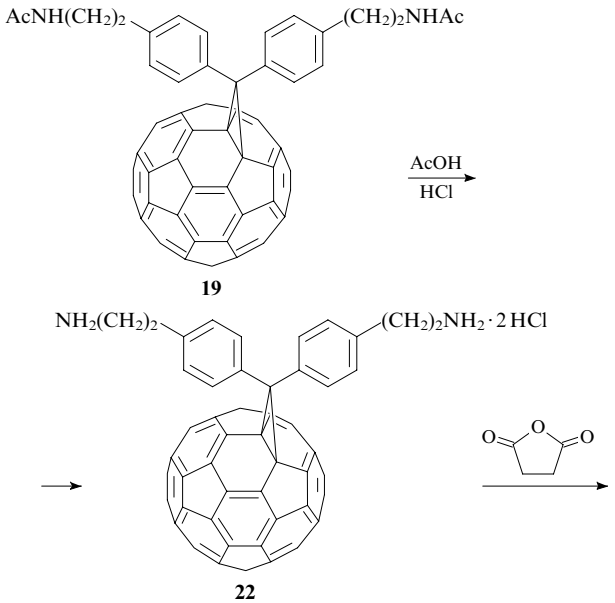
[b]  ; [c] 4-$AcNH(CH_2)_2C_6H_4$.

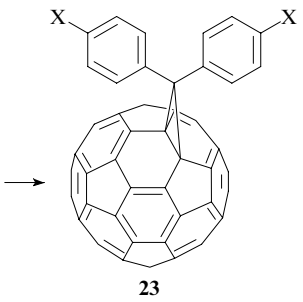
Hydrolysis of [6,6]-closed isomer **16** prepared by refluxing the reactants for 3 days afforded acid **20**. The respective chloride was introduced into peptide synthesis to afford the first optically pure fullerene-containing peptide **21**.[36]



X = (L-Ala-Aib)$_2$-L-Ala-OMe (Aib is α-aminoisobutyric acid).

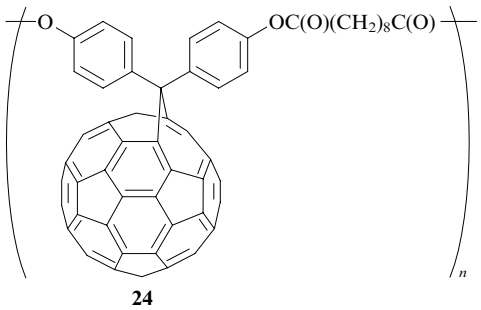
Treatment of [6,6]-closed isomer **19** with a mixture of acetic and hydrochloric acids afforded diamino derivative **22**.[43] The reaction of the latter with succinic anhydride yielded adduct **23**; its disodium salt is water-soluble (1 mg ml^{-1}) and possesses the inhibitory activity with respect to HIV enzymes [the HIV-1 protease (HIVP) and reverse transcriptase (HIVRT)].[43,44]

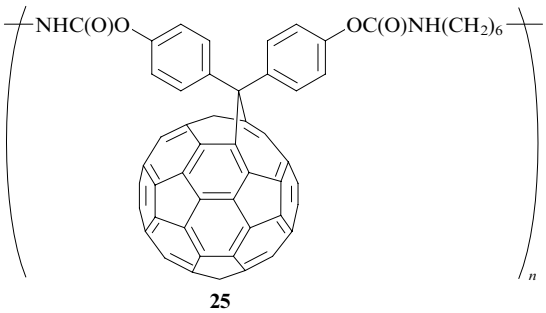




X = $(CH_2)_2NHC(O)(CH_2)_2CO_2H$.

Functionalization of [5,6]-open adduct **18** with decanoyl chloride and hexamethylene diisocyanate affords products **24** and **25** with dangling fulleroid fragments.[41]

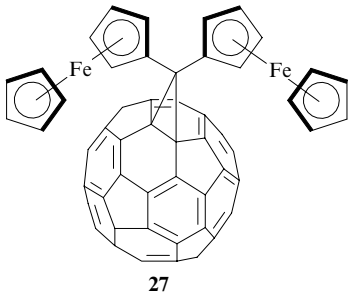


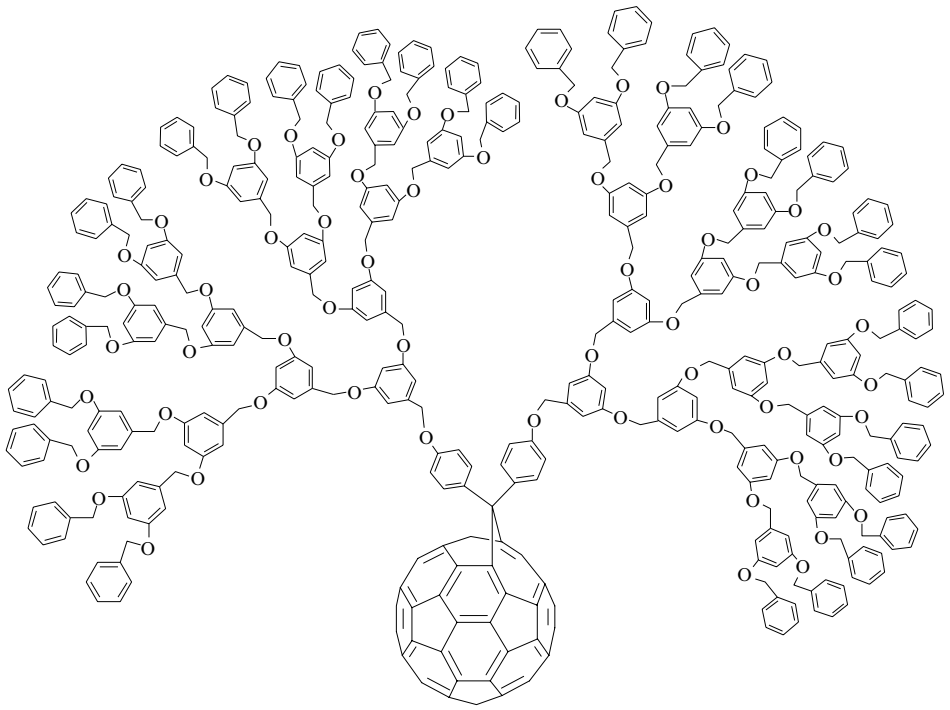


Based on adduct **18**, dendrimeric water-soluble methanofullerene **26** was also synthesized.[45]

Comparative studies of the reactivities of fullerenes C_{60} and C_{70} with respect to *meta*- and *para*-substituted diphenyldiazomethanes have shown that C_{60} is 1.5-times more reactive than C_{70} as followed from the rate constants for these reactions.[46]

Starting from bis(ferrocenyl)diazomethane, the first methanofullerene (**27**) containing two ferrocenyl substituents was synthesized, this was used in studies of the intramolecular electron transfer between the electron-donating ferrocenyl group and fullerene.[47]



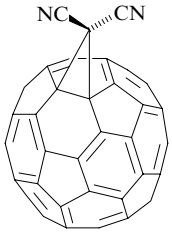


26

Phosphorylated derivatives of C_{60} are of special interest and practical value. One of the first syntheses of phosphorus-containing fullerene derivatives involved the thermal addition of dimethyl diazomethylphosphonate to fullerene C_{60}.[48]

The analogous reaction of diethyl (α-diazoethyl)phosphonate produced isomeric homo- (**28**, **28′**) and methanofullerenes (**29**). Adducts **28**, **28′** were the first open phosphorylated derivatives of fullerene C_{60}, because all the other methods (without recourse to diazo compounds) afforded [6,6]-closed adducts. It should be noted that the reaction of fullerene C_{60} with diethyl (α-diazobenzyl)-phosphonate afforded methanofullerene **30** exclusively (Scheme 3).[49]

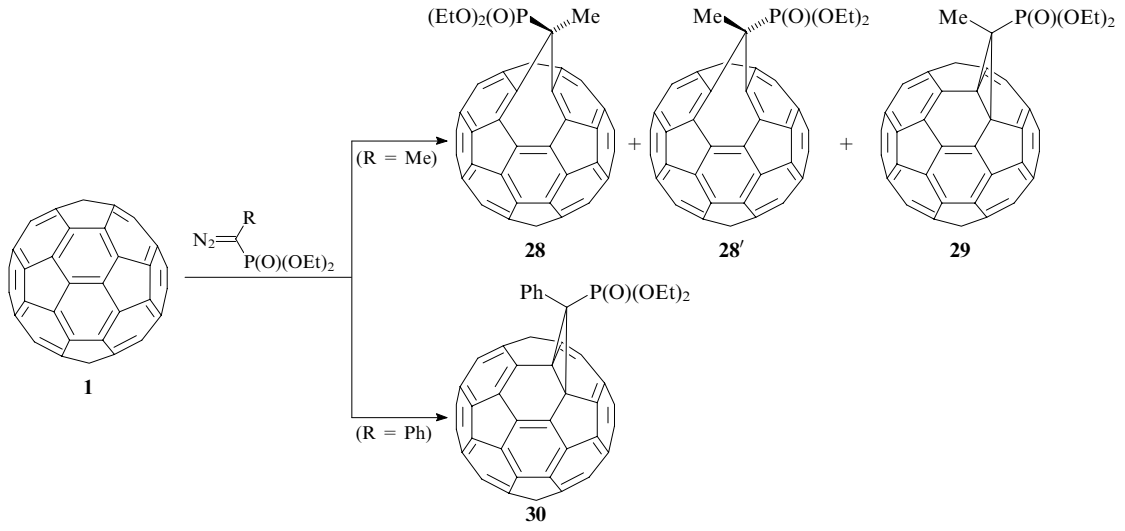
In contrast to the reactivities of diazoalkanes or diazophosphonates, that of dicyanodiazomethane as a 1,3-dipole is low.[50–52] Thus it does not add to fullerene C_{60} under thermal reaction conditions. However, under conditions of a photochemical reaction (9 h), dicyanodiazomethane reacted with C_{60} to form [6,6]-closed structure **31** in a yield of ~26%.[53]



31

Compound **31** was characterized by spectral methods (IR, UV and ^{1}H and ^{13}C NMR spectroscopy). Thus the ^{13}C NMR spectrum of methanofullerene **31** contained 19 signals of which 16 resonated in the region of sp^2-hybridized

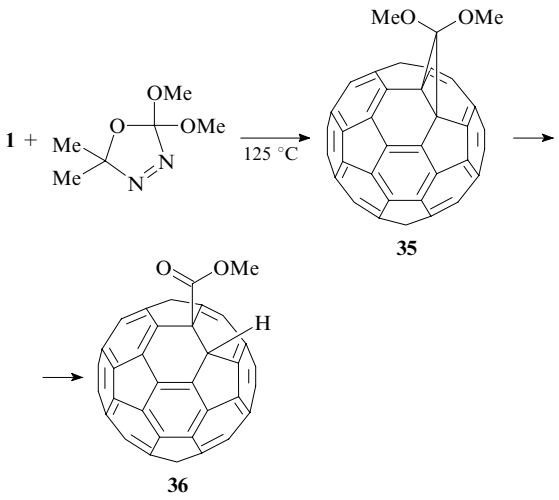
Scheme 3



carbon atoms of the fullerene sphere (δ 139–146). The signals for the sp^3-hybridized bridgehead and bridging carbon atoms were found at δ 67.9 and 20.3, respectively, whereas the signal for the sp-hybridized carbon atom of the cyano group was observed at δ 110. Unfortunately, no X-ray diffraction analysis was carried out, although the crystals of compound **31** have been grown.

Diazirines behaved in the similar way in their reactions with fullerene C_{60}. Thus under conditions described above, the photolysis of 3-isopropyl-3-chlorodiazirine in the presence of fullerene C_{60} afforded a mixture of [5,6]-open (**32**, **32′**) and [6,6]-closed (**33a**) adducts in the total yield of ~18%. 3-Chloro-3-(chloromethyl)diazirine gave exclusively methanofullere **33b**. Different outcome of these reactions is due to the ability of diazirine to form either a free carbene or a diazo compound upon photolysis. It is the reactions of fullerenes with carbenes that usually afford methanofullerenes, whereas the reactions with diazo compounds result in mixtures of homo- and methanofullerenes. At −40 °C, 3-chloro-3-isopropyldiazirine yields pyrazolinofullerene **34**,[54] which transformed at room temperature to a mixture of homofullerenes **32** and **32′** with the isomer **32** predominating (Scheme 4).

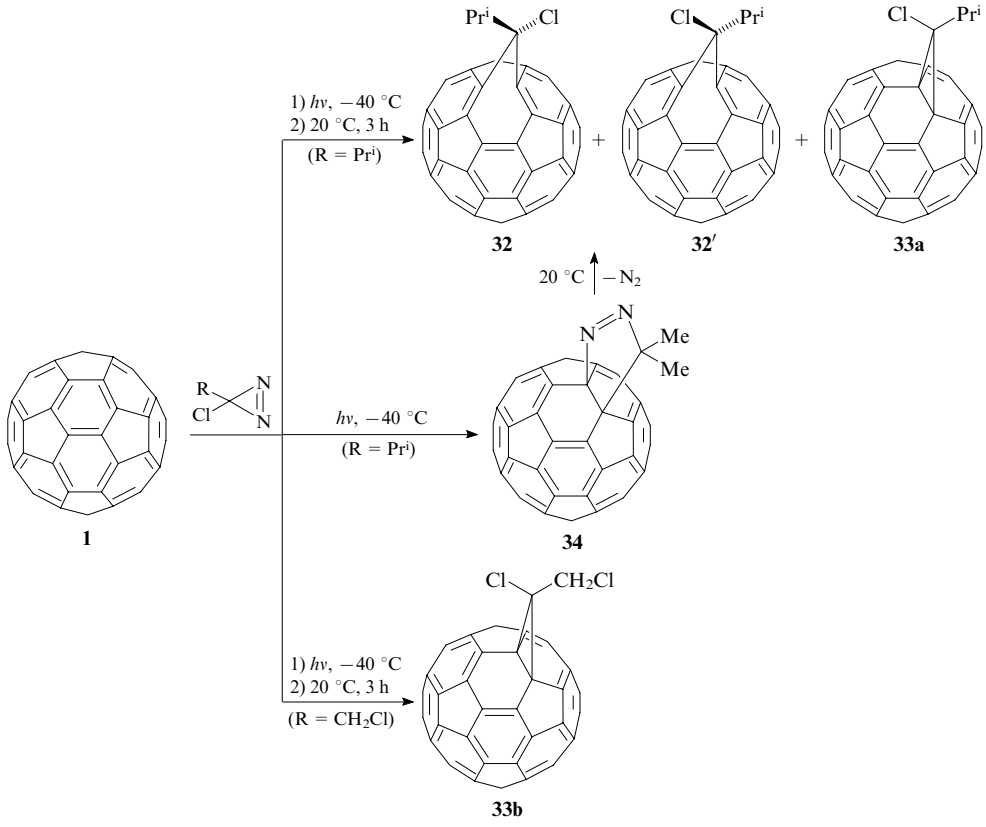
With the aim of preparing dimethoxymethanofullerene **35**, which is of interest as a precursor for various water-soluble derivatives of fullerene C_{60}, the reaction of the latter with 2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazolines was studied.[55] However, adduct **35** gave only methyl fullerenecarboxylate **36**, which could not be hydrolyzed under standard conditions.



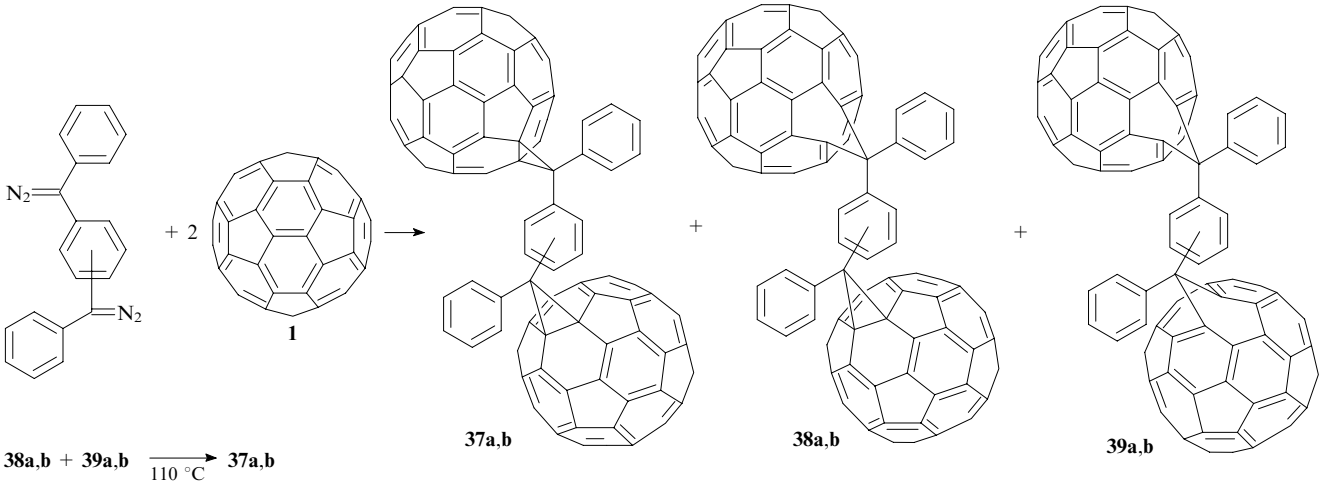
Of indubitable interest was the reaction of aromatic bisdiazo compounds with fullerene C_{60} to afford a mixture of isomeric *p*- or *m*-phenylenebis(phenylhomofullerenes) and -methanofullerenes **37**–**39**. The isomers could not be separated; this is why the thermal isomerization of [5,6]-open isomers **38a**,**b** and **39a**,**b** was carried out to afford **37a**,**b** ([6,6]-closed) (Scheme 5).[56]

Analogous *m*-phenylenedimethane **40** with two [6,6]-closed fullerene fragments underwent intramolecular [2p + 2p]-photodimerization to yield cycloadduct **41** with an unusual structure.[57]

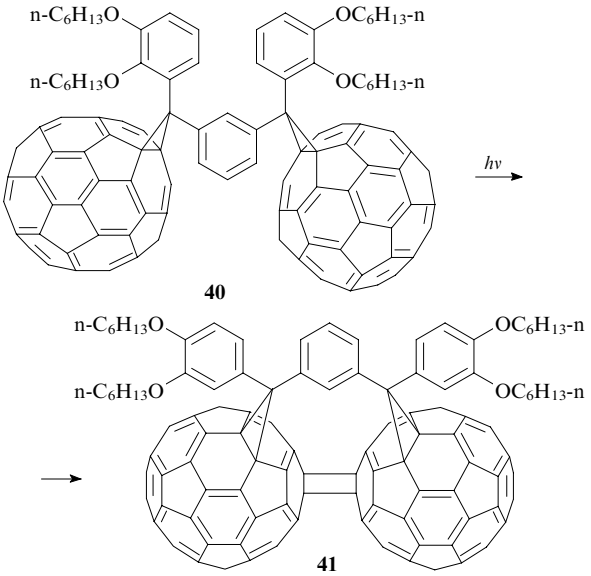
Scheme 4



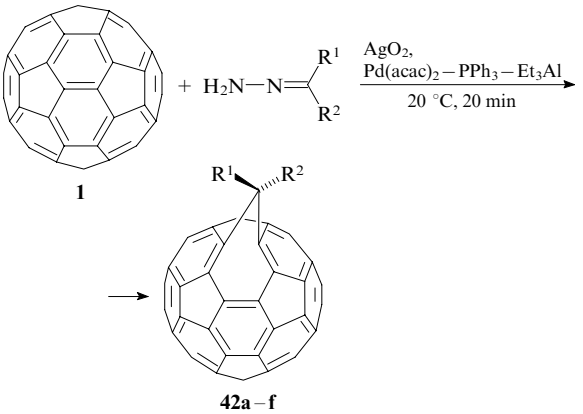
Scheme 5



Isomers: *para* (**a**), *meta* (**b**).



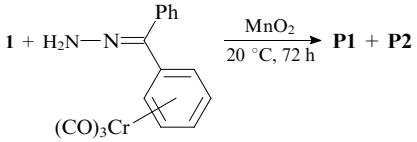
In addition to the direct reaction of fullerenes with diazo compounds, the *in situ* generation of the latter is widely used. Thus in contrast to aforementioned procedures, an efficient method was developed [58] for the selective synthesis of [5,6]-open adducts **42a**–**f** by the reaction of mono- and disubstituted diazomethanes (generated *in situ* from the corresponding aldehyde or ketone hydrazones under the action of silver oxide) with C_{60} in the presence of a Pd-based three-component catalyst. The yields of the target products reached 80%. In the absence of the palladium catalyst, the reaction was non-selective to yield a mixture of [5,6]-open and [6,6]-closed isomers.



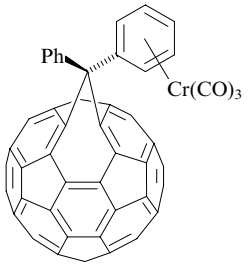
R^1 = H: R^2 = Me (**a**), Ph (**b**); R^1 = Me: R^2 = Ph (**c**), Me (**d**), cyclo-C_3H_5 (**e**), cyclo-C_6H_{11} (**f**).

In the same way homo- and methanofullerenes comprising benzocrown residues [59] (**43**, **44**) or 'tweezer' ligands [60, 61] (**45**–**47**), which are of interest for complexation studies, were prepared (Scheme 6).

Likewise, C_{60} reacted with the *in situ* generated chromium-containing diphenyldiazomethane to afford a mixture of two (**P1**, **P2**) of three possible isomers in the 1 : 1 ratio and the overall yield of ~25%.

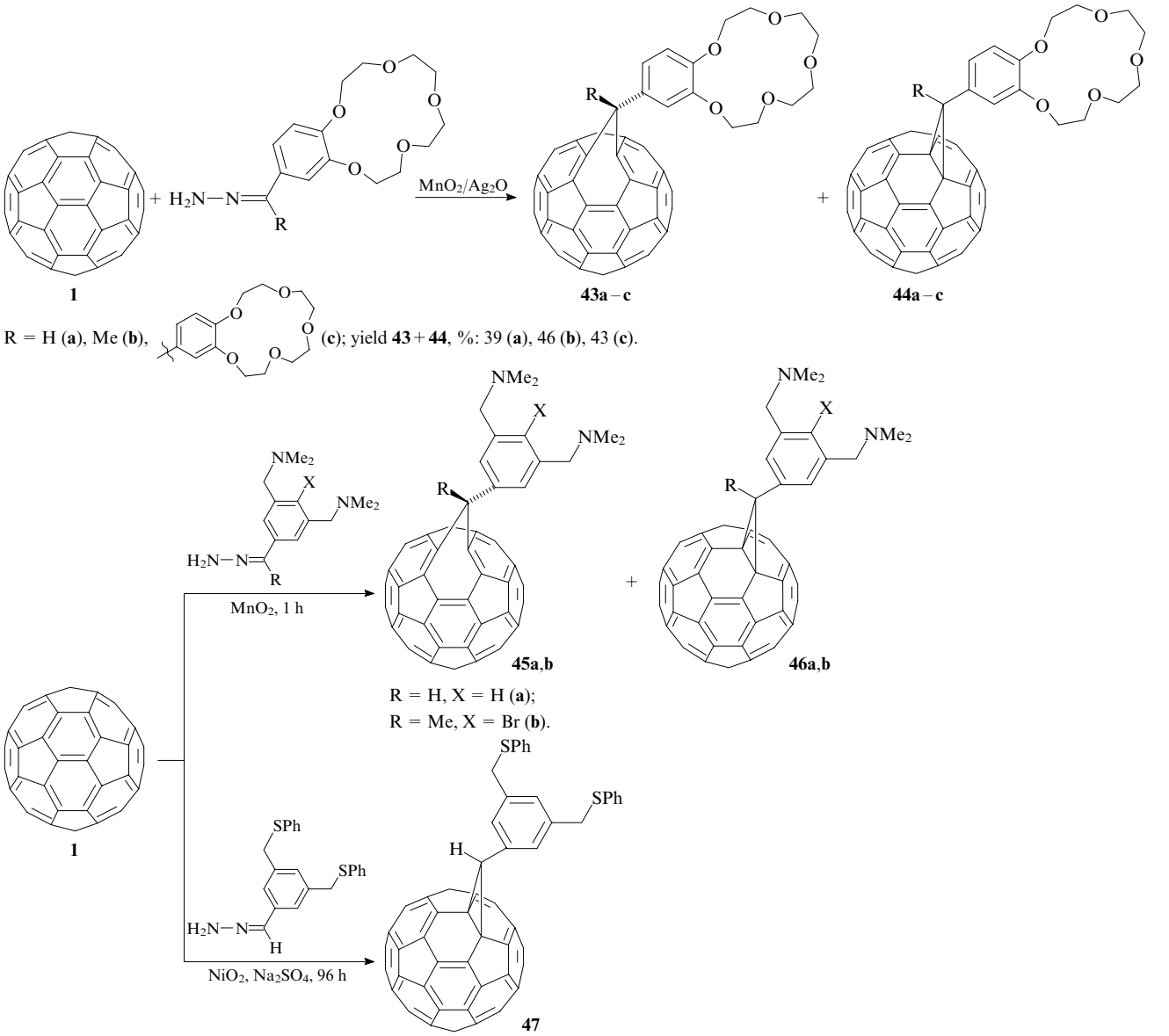


Unfortunately, the obtained isomers [62] have not been identified. Presumably, one of the products represented [5,6]-open fulleroid **48** with the bulkier tricarbonylchromiumphenyl substituent above the plane of a five-membered ring of the fullerene molecule.



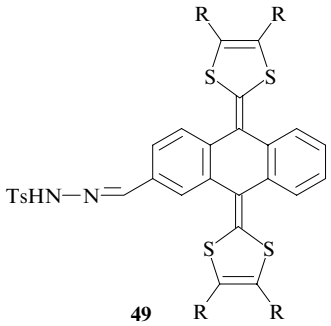
An alternative method of the *in situ* generation of diazo compounds consisted of the thermolysis of the tosylhydrazone anions. These reactions produced also mixtures of homo- and methanofullerenes; however, by shortening the reaction time, it was possible to synthesize exclusively a

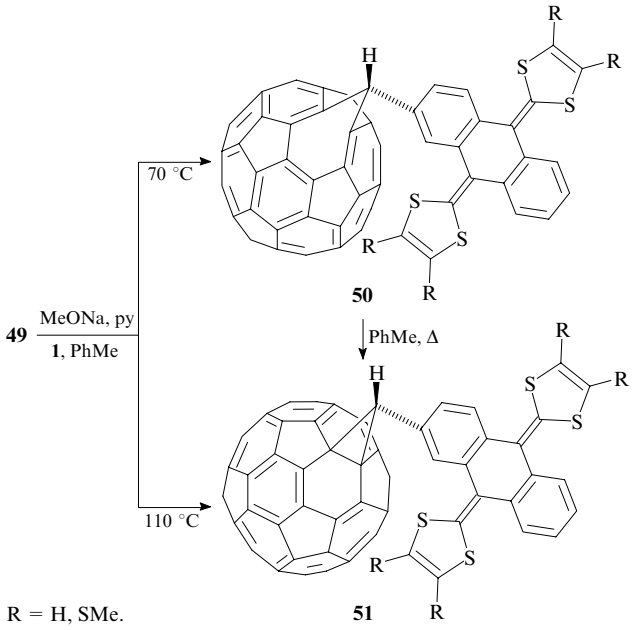
Scheme 6



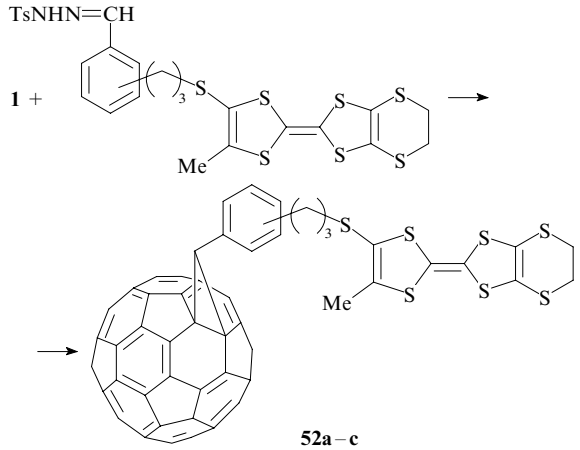
[5,6]-open isomer containing the bulkier substituent located above a five-membered ring of the fullerene cage. A sufficiently broad series of tosylhydrazones was studied,[37] which illustrates the applicability of the method.

Depending on conditions, tosylhydrazone **49** reacted with fullerene C_{60} to yield selectively [5,6]-open (**50**) or [6,6]-closed (**51**) isomers containing a tetrathiafulvalene substituent.[63]





Somewhat later, analogous fullerenethiafulvalene derivatives **52a–c** were synthesized from the corresponding tosylhydrazones and their properties were studied.[64]

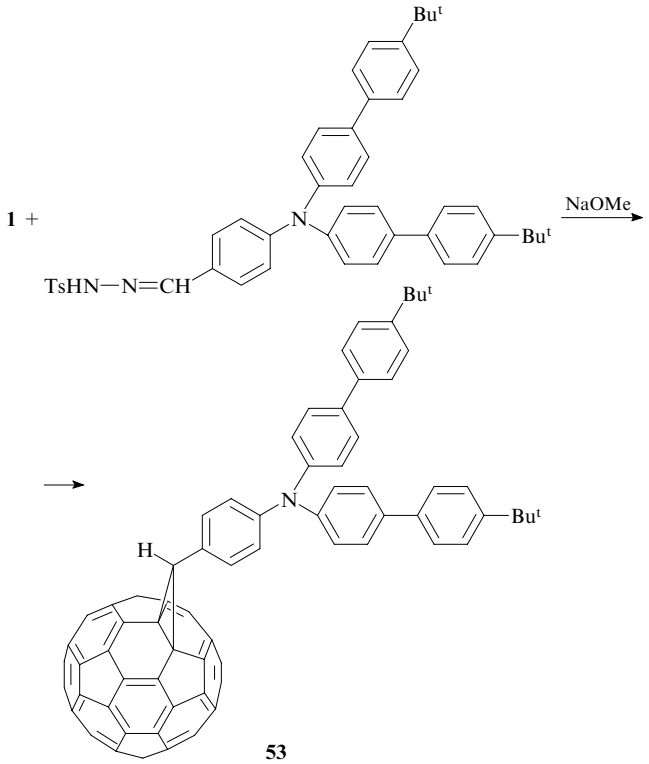


52a–c

Isomers: *ortho* (**a**, 6.5%), *meta* (**b**, 1.2%), *para* (**c**, 2.8%).

Methanofullerene **53** was obtained selectively from the corresponding 4-(diarylamino)benzaldehyde tosylhydrazone.[65]

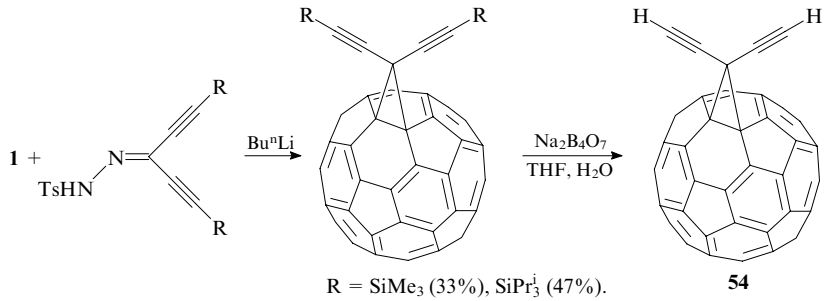
Compound **54**, which is a 'building block' for the preparation of macrocyclic (**55**) and polymeric (**56**) allotropic carbon forms, was synthesized by the reaction of fullerene with di(silylethynyl) ketone tosylhydrazones (Scheme 7).[66]



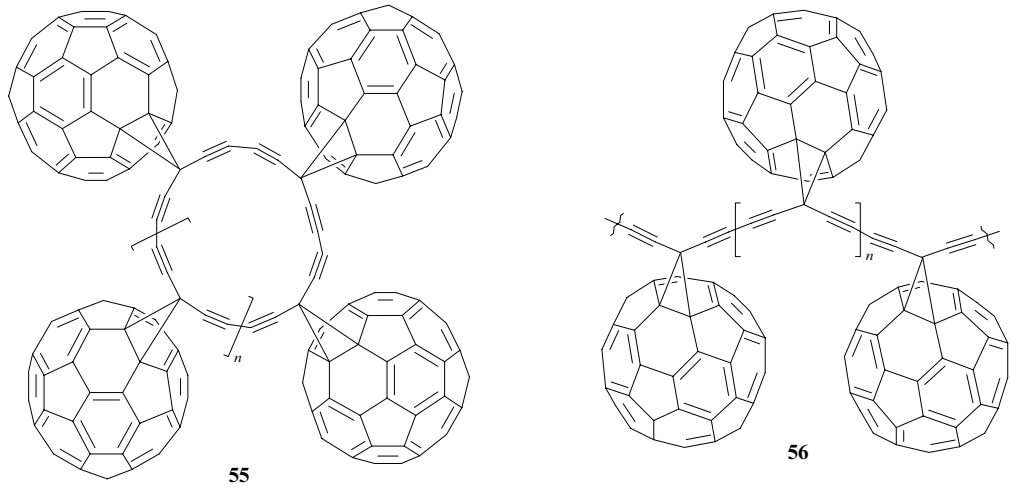
53

Yet another building block for the synthesis of fullerene-containing macromolecules is platinum methanofullerene complex **57**, a precursor of the binuclear fullerene complex **58** (Scheme 8).[67]

Scheme 7



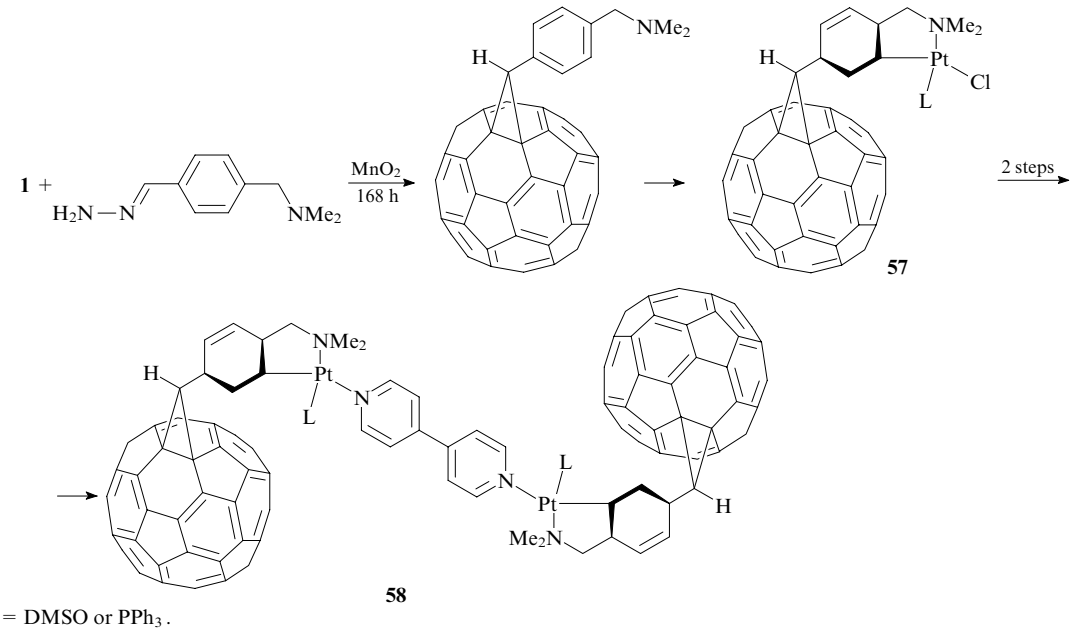
R = $SiMe_3$ (33%), $SiPr^i_3$ (47%).



55 **56**

n = 1–3.

Scheme 8

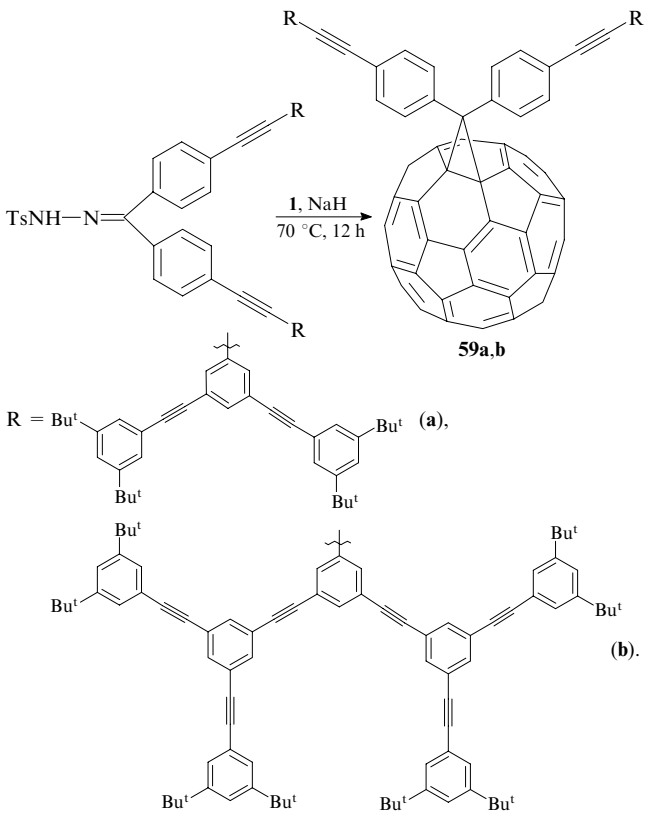


L = DMSO or PPh_3.

Similarly, the *in situ* generation of diaryldiazomethanes from the corresponding dendrimeric benzophenone-based tosylhydrazones [68] described earlier [69, 70] as molecular 'antennas' was used to synthesize poly(aryl)acetylene dendrimers **59a**,**b** with a methanofullerene core; their electrochemical behaviour was studied (Scheme 9).

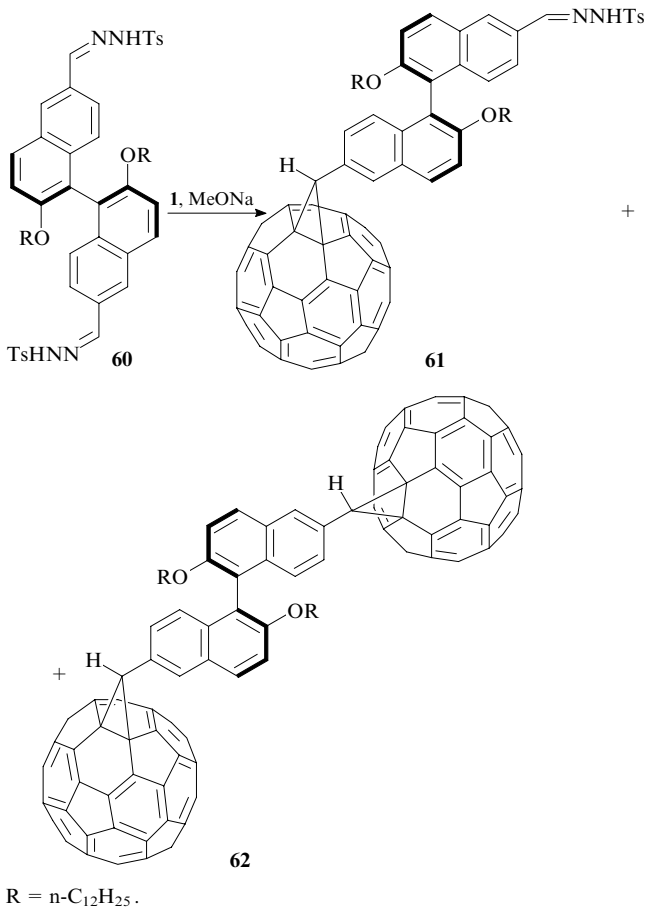
The reaction of symmetrically substituted 1,1′-binaphthyl **60** with fullerene C_{60} mainly produced monomethanofullerene derivative **61** (the ratio **61** : **62** = 2 : 1) (Scheme 10).[71]

Scheme 9



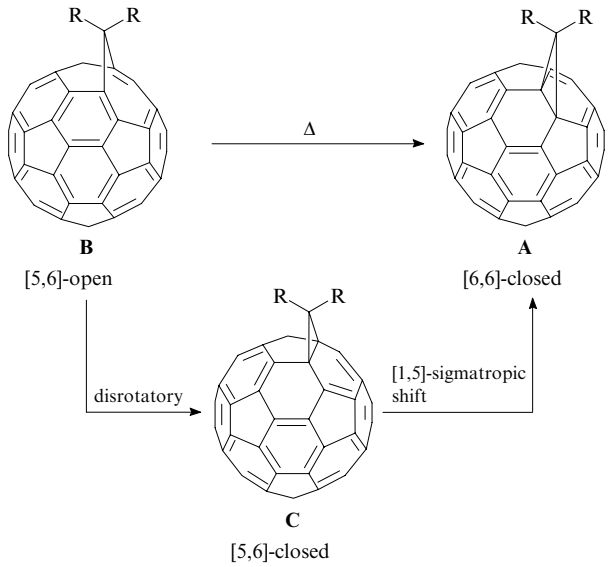
It is known that, in contrast to reaction products of fullerene C_{60} with diazomethane, substituted fulleroids formed under kinetic control, by thermal,[15] photochemical [38, 72] and electrochemical [35] methods and also in acid-catalyzed reactions [73, 74] isomerize into thermodynamically more stable [6,6]-closed adducts **A** (see the beginning of Section II). Thus, it was shown [37, 75] that [5,6]-open adducts **B** could be

Scheme 10

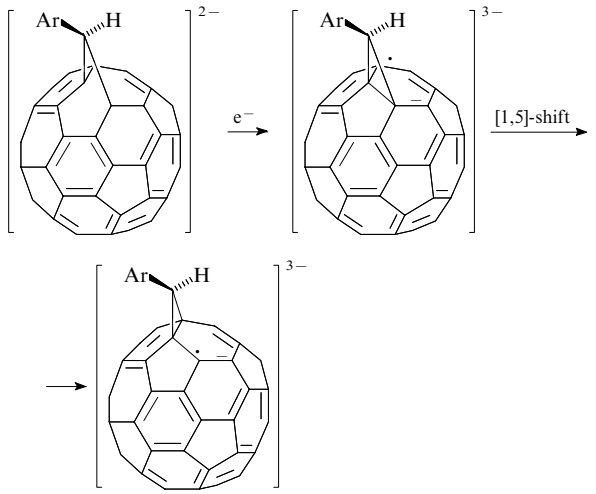


R = n-$C_{12}H_{25}$.

rearranged into the corresponding methanofullerenes both by a zero-order photochemical process and a high-energy monomolecular route. The first step involved the disrotatory closure into [5,6]-closed fullerene **C**, which later rearranged to methanofullerene *via* a biradical intermediate.

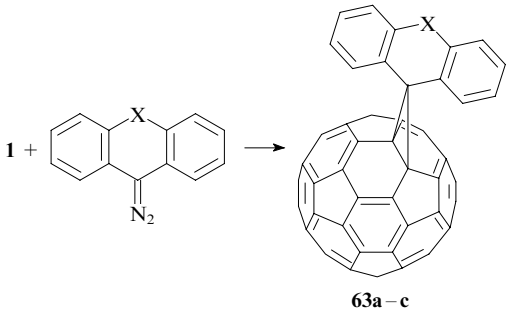


Presumably,[35] the electrochemical isomerization of [5,6]-homofullerenes into [6,6]-closed isomers occurred by the radical anion mechanism.

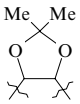


IV. Reactions of cyclic diazo compounds with fullerenes

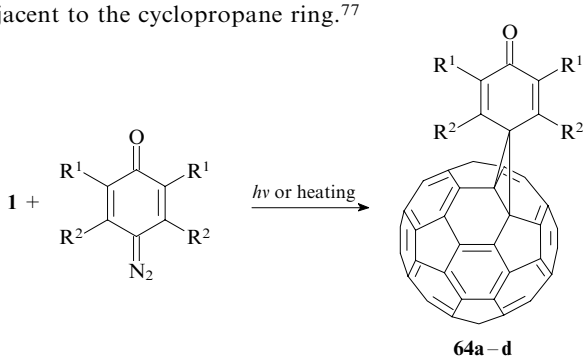
The first example of the cycloaddition of a cyclic diazo compound to fullerene C_{60} leading selectively to spirocyclopropafullerenes **63a–c** dates back to 1993.[76] The physicochemical characteristics of the identified compounds agree well with the computer-assisted optimization of hypothetic structures performed by semi-empirical methods that confirmed the formation of spirocyclopropafullerenes with C_s symmetry.



63a–c

X = CH=CH (**a**), CH_2CH_2 (**b**),  (**c**).

Under the conditions of photochemical and thermal reactions, the reaction of C_{60} with quinonoid-type diazo compounds also led to the corresponding [6,6]-closed fullerene spiroadducts **64a–d** in 13%–47% yields. Electrochemical studies showed that spirocyclopropafullerenes are stronger acceptors than the original C_{60}. This was explained by periconjugation of the $p_z-\pi$-orbitals of the cyclohexadiene fragment and p-orbitals of the fullerene carbon atoms adjacent to the cyclopropane ring.[77]

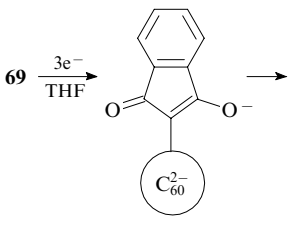


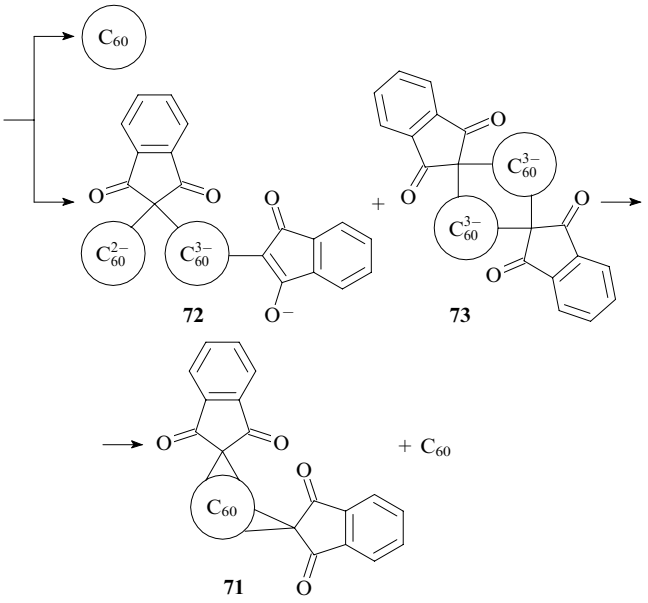
64a–d

R^2 = H: R^1 = H (**a**, 16%), Me (**b**, 13%), Bu^t (**c**, 26%);
R^1-R^2 = $(CH=CH)_2$ (**d**, 47%).

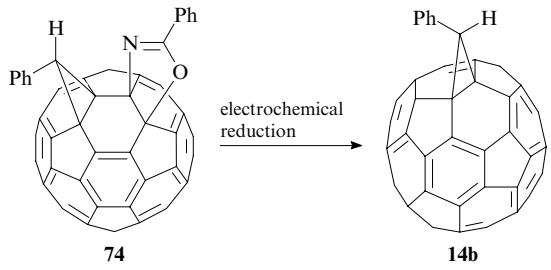
Several spiromethanofullerenes, for example, compounds **65–70**, were synthesized similarly and their electrochemical reduction was carried out[78–82] to afford the original fullerene C_{60} (Scheme 11).

The electrochemical reduction of spirocyclopropafullerene **69** produced, in addition to C_{60}, a mixture of regioisomeric bisadducts **71**.[82] It was assumed that heterolytic opening of the cyclopropane ring leads to charge formation on the fullerene core and the addend. Further, two processes are feasible, *viz.*, the elimination of the addend to form fullerene C_{60} or the addition of the second indanedione fragment to another fullerene to yield the corresponding bisadduct (**71**) *via* intermediates **72** and **73**.

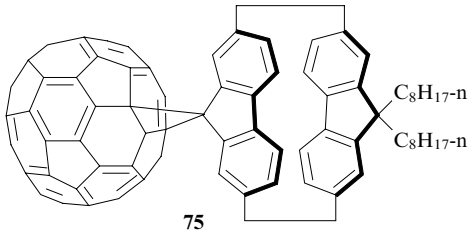




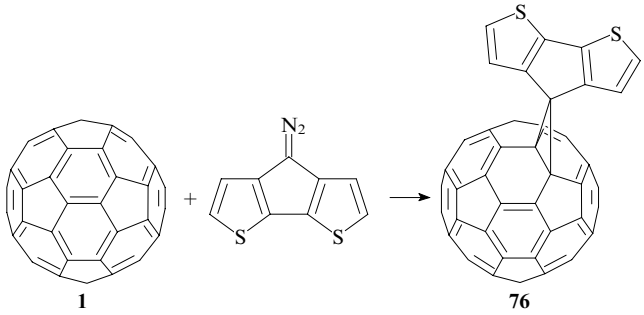
The electrochemical reduction of adduct **74** with a cyclopropane and an oxazole fragments included first the oxazole ring opening to form the corresponding methanofullerene **14b**.[83]



The reaction of fullerene with diazofluorenophane afforded [6,6]-closed adduct **75**.[84]



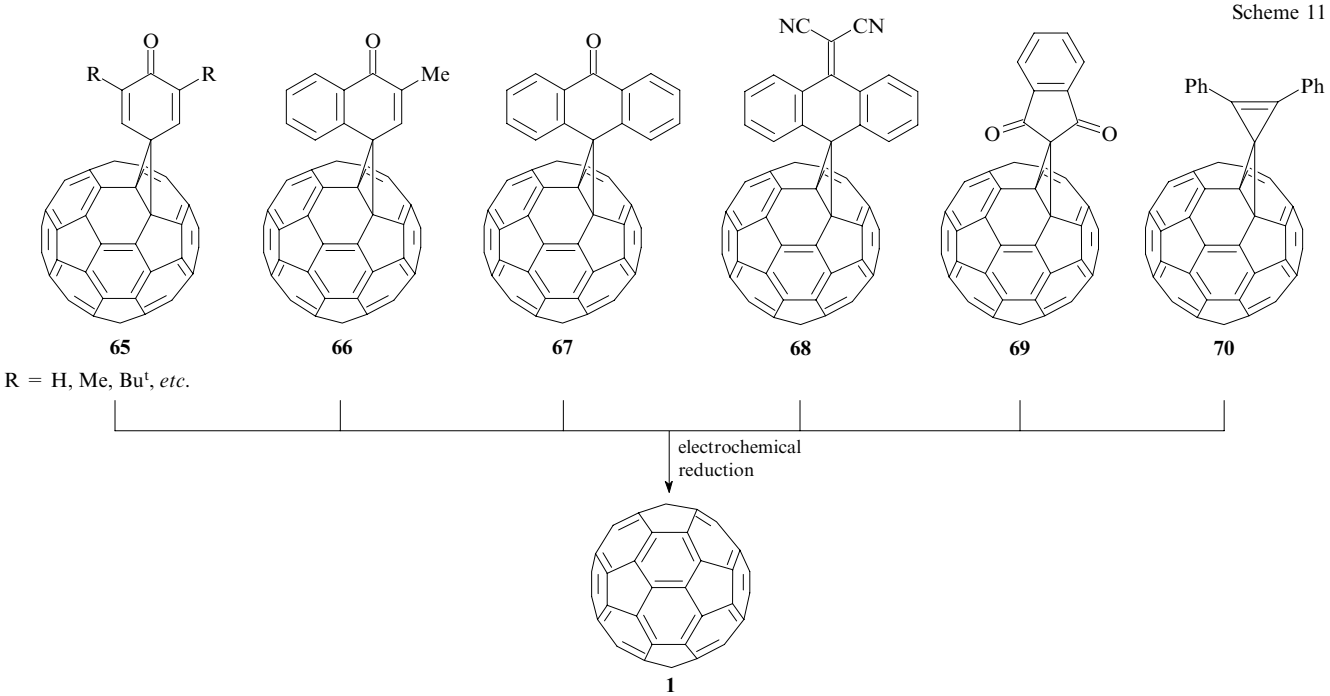
The reaction of fullerene with diazodithiophenocyclopentadiene produced compound **76**, which was subjected to electropolymerization.[85] The resulting oligomer was tested as a new material for optoelectronics.[86]

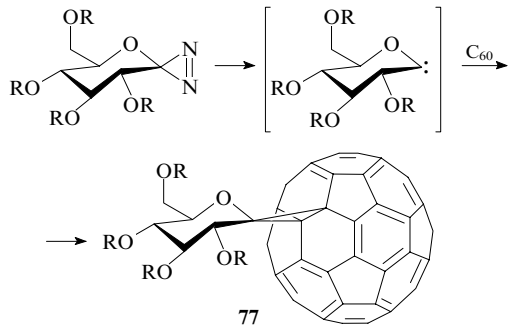


The above examples show the feasibility of the cycloaddition reactions of complex diazo compounds, including those containing functional substituents, with fullerene C_{60}.

The addition of a nucleophilic glycosylidene carbene derived from the corresponding diazirine to C_{60} yielded optically active amphiphilic cyclopropafullerene **77**, which formed a stable monolayer at the air–water interface.[87–89]

Scheme 11

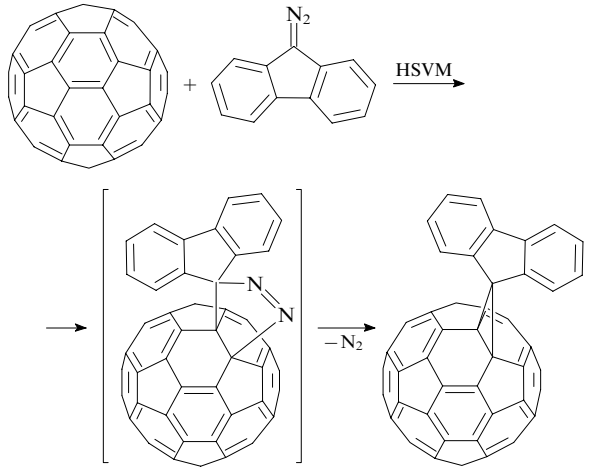




77

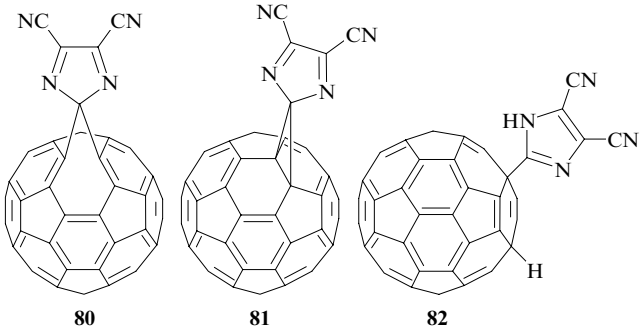
R = Bn, C(O)Bu^t.

The solid-state reaction of fullerene C_{60} with 9-diazofluorene in a high-speed vibration mill (HSVM) afforded the corresponding [6,6]-closed spiro compound **78** in ~ 50% yield; moreover, no substituted pyrazolinofullerene **79** was detected.[90]



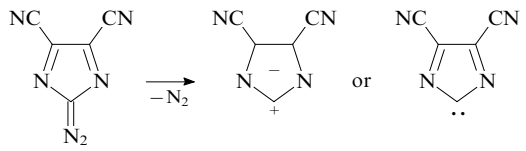
79 **78**

The reaction of C_{60} with 2-diazo-4,5-dicyanoimidazole[91] resulted, in addition to spirohomo- (**80**) and spirocyclopropafullerene (**81**), in an acyclic compound (**82**).

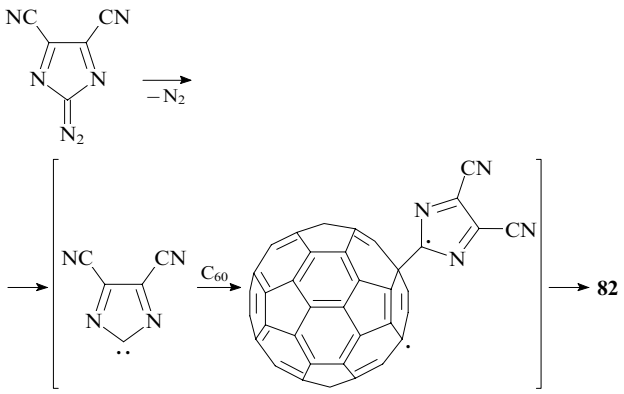


80 **81** **82**

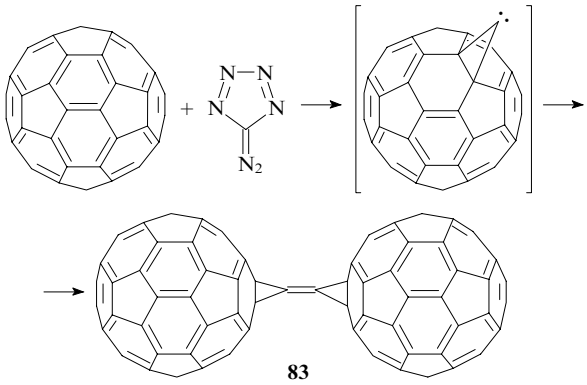
Adduct **82** was assumed to be the result of 1,4-addition of an anionic or radical intermediate, generated by the thermolysis of the starting 2-diazo-4,5-dicyanoimidazole, to C_{60}.



This reaction was assumed[9] to proceed as the 1,4-radical addition.

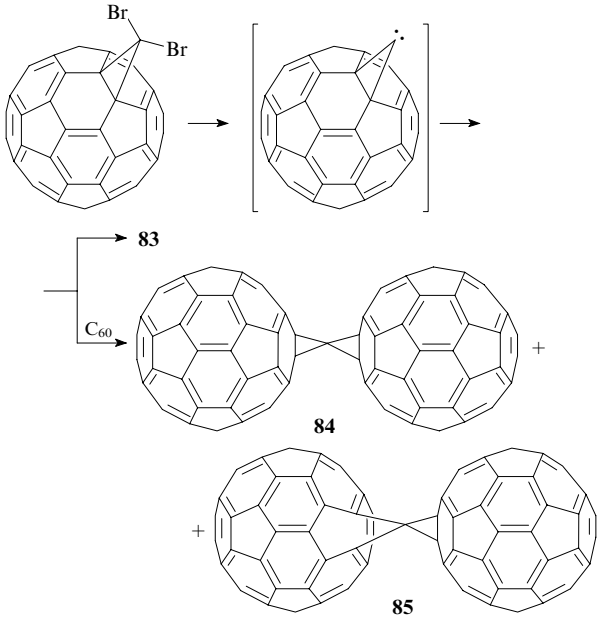


The reaction of C_{60} with diazotetrazole was studied.[92] This resulted, for the first time, in bisfullerene **83** containing a dispiro(dicyclopropane)ethylene bridge.



83

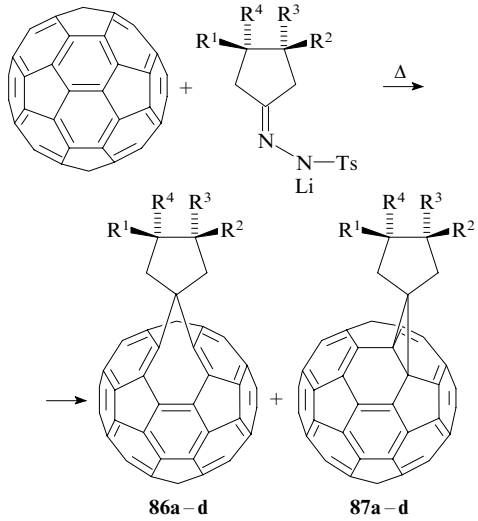
A mixture of the same compound (**83**) with symmetrical fullerene dimer **84** and its isomer **85** containing fullerene and fulleroid moieties was obtained by the Bingel reaction.[93–95] Dimer of fullerene **84** was also detected in the mass spectrum of a solution of C_{60} and $C_{61}H_2$ obtained by the Simmons–Smith reaction.[93]



84 **85**

The reactions of C_{60} with diazocycloalkanes generated *in situ* by the thermolysis of the corresponding tosylhydrazone lithium salts afforded mixtures of [5,6]-open and [6,6]-closed spiro isomers. Substituted and non-substitited

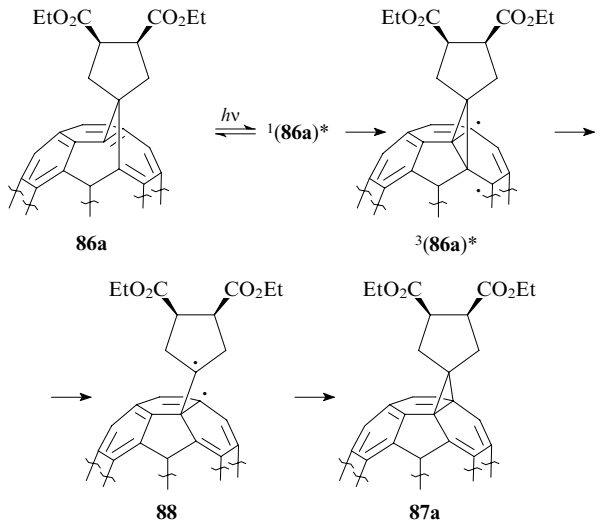
cyclobutanone, cyclopentanone and cyclohexanone tosylhydrazones were chosen as the starting compounds;[96] in the case of cyclopentanone derivatives, adducts **86a–d** and **87a–d** were obtained.



86a–d **87a–d**

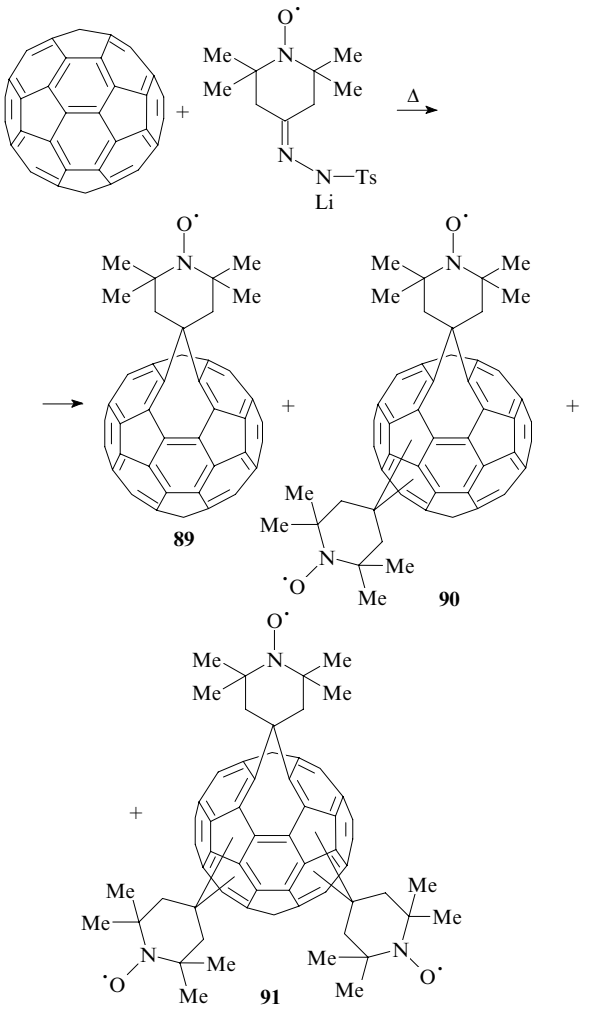
$R^1 = R^2 = CO_2Et$, $R^3 = R^4 = H$ (**a**); $R^1 = R^3 = CO_2Et$, $R^2 = R^4 = H$ (**b**); $R^1 = R^3 = CO_2Me$, $R^2 = R^4 = H$ (**c**); $R^1 = R^2 = R^3 = R^4 = H$ (**d**).

Later, it was found[37] that [5,6]-open adducts could exclusively be obtained as the reaction time shortened; however, this concerned only the compounds containing saturated rings. No open cycloadducts could be isolated if tosylhydrazones containing a double bond in the carbocycle were used. Studies on thermal isomerization of [5,6]-open adducts to methanofullerenes revealed that this reaction was inhibited in the absence of both oxygen and light, which suggested a triplet mechanism in which the isomerization rate at a given temperature depended only on the illumination intensity. According to the proposed mechanism, the transition from the triplet compound ^{3}(**86**)* to biradical **88** required thermal activation (the excited molecules are marked with asterisks).



86a ^{3}(**86a**)* **88** **87a**

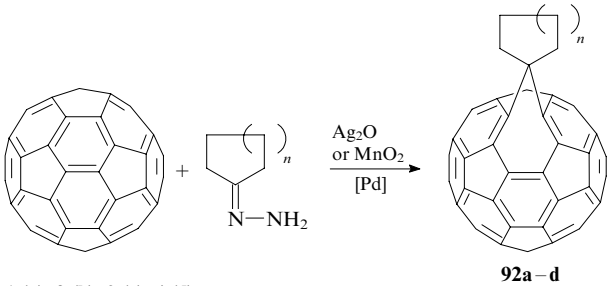
A similar approach was used in the synthesis of C_{60} derivatives bearing the TEMPO radical (2,2,6,6-tetramethylpiperidin-1-oxyl) (**89–91**). The reaction was non-selective and resulted in mono-, bis- and tris-adducts.[97]



89 **90** **91**

Besides thermal and photochemical initiation, the microwave radiation can also be used to induce cycloaddition of diazo compounds to C_{60}. It was shown that the thermal reaction of fullerene with diazoanthrone took 10–12 h, whereas under microwave radiation the corresponding spirocyclopropafullerene **67** formed in 1 h.[98]

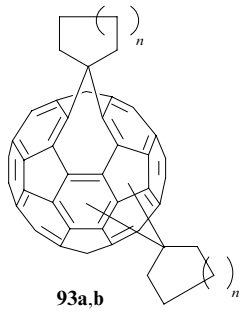
With the aim of developing an efficient method for the high-yield synthesis of fullerene spiroadducts and elucidating the effect of the ring size on the reaction efficiency and selectivity, cyclic diazo compounds generated *in situ* from hydrazones of corresponding cyclic ketones were added to C_{60} in the presence of a complex Pd-containing catalyst.[99] The reaction of fullerene with the corresponding hydrazones afforded [5,6]-open isomers **92a–d** in 30 min in high yields and with high selectivity. The yields of the target cycloadducts were reduced somewhat with the increase in the ring size in the original cycloalkanone hydrazone.



92a–d

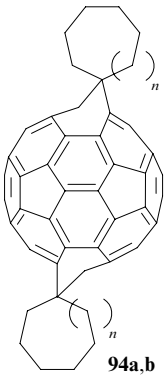
n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**).

The increase in the reaction time or in the starting hydrazone concentration led to the complete conversion of fullerene C_{60} with formation of the corresponding bis- (**93**, **94**) and tris-adducts. As followed from the ^{13}C NMR spectra of compounds **94a**,**b**,[99] the bisadducts possessed high symmetry, *i.e.*, the addends occupied the opposite poles of bishomofullerenes [in analogy with *trans*-1-bis(methano)fullerenes]. For hydrazones with smaller rings, the reaction proceeded with lower selectivity (adducts **93a**,**b**). At present, studies on the cycloaddition reactions of natural compounds and macrocycles are in progress.



93a,**b**

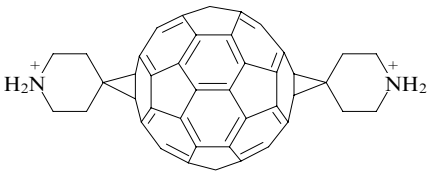
n = 1 (**a**), 2 (**b**).



94a,**b**

n = 1 (**a**), 2 (**b**).

According to computations, compound **95** with the *trans*-1-arrangement of addends could be the HIV-1-protease inhibitor.[100]



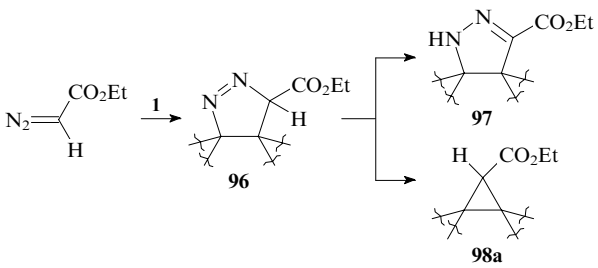
95

Spiro compounds were also synthesized by photochemical reactions of endofullerenes [$La_2@C_{72}$,[101] $La_2@C_{78}$ (Ref. 102) and $M_2@C_{80}$ (M = La, Ce)[103]] with spiroadamantanediazirine. The synthesized spiroendofullerenes were studied by mass spectrometry, NMR spectroscopy, optical and IR spectroscopy and by X-ray diffraction analysis. The adduct synthesized from $La_2@C_{80}$ was assumed to have the [6,6]-open structure.[103]

V. Fullerenes in reactions with diazocarbonyl compounds

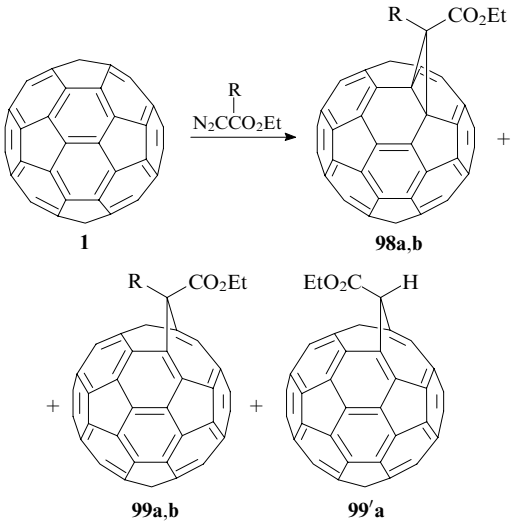
Attention paid to cycloaddition reactions of amino acid-derived diazo compounds to fullerene C_{60} was associated with the prospects of synthesizing water-soluble carboxyl-containing fullerenes that could be attached through the amide bond to oligopeptides with potential biological activity.

The simplest example of these reactions is the reaction of fullerene C_{60} with ethyl diazoacetate. Pyrazolinofullerene **96** formed was converted to isomeric pyrazolinofullerene **97** and [2 + 1]-cycloadduct **98**.[42] However, the structures of these products were not substantiated by spectral studies, which casts doubt on the reliability of the results obtained.



96 **97** **98a**

The Diederich group dealt with preparative synthesis of methanofullenecarboxylic acids.[104] The reaction of fullerene C_{60} with ethyl diazoacetate was chosen as the model process. It was shown that under the thermolysis conditions (110 °C, 7 h), the reaction afforded a mixture of [6,6]-closed **98a** and stereoisomeric [5,6]-open compounds **99a** and **99′**.



1 **98a**,**b** **99a**,**b** **99′a**

R = H (**a**), CO_2Et (**b**).

Although the corresponding pyrazolinofullerene has not been detected, it was assumed that the reaction of fullerene with ethyl diazoacetate proceeded as the 1,3-dipolar cycloaddition. In 2004, the synthesis of stable pyrazolinofullerene **97** at room temperature was reported.[105] However, this cycloadduct was transformed into target adducts **98a**, **99a**, **99′a** only on refluxing in *o*-dichlorobenzene, which suggested that they formed by the extrusion of nitrogen from isomeric unstable pyrazolinofullerene **96**. Similar results were obtained in the reaction carried out in a high-speed vibration mill (Scheme 12).[105]

The reaction of fullerene with ethyl diazoacetate in the presence of stoichiometric amounts of $Rh_2(OAc)_4$ made it possible to selectively synthesize not only compound **98a** in the same yield, but also the adduct of ethyl diazomalonate **98b** inaccessible by a common thermal reaction (Table 4). The dependence of the reaction selectivity on the solvent was studied.[106]

Probably, the mechanism of fullerene cyclopropanation in the presence of $Rh_2(OAc)_4$ is analogous to that of alkene cyclopropanation by diazo compounds, which involves the formation of a metallocarbenoid complex as the reactive intermediate.[106]

A more efficient catalyst of cycloaddition of ethyl diazoacetate[107] and α-substituted ethyl diazoacetates[108] to C_{60} proved to be a three-component system $Pd(acac)_2 - PPh_3 - Et_3Al$ (20 mol.%). In the presence of this catalytic system, adducts **98a**,**c**–**g**, **99a**,**c**–**g**, **99′a**,**e**,**f**

Scheme 12

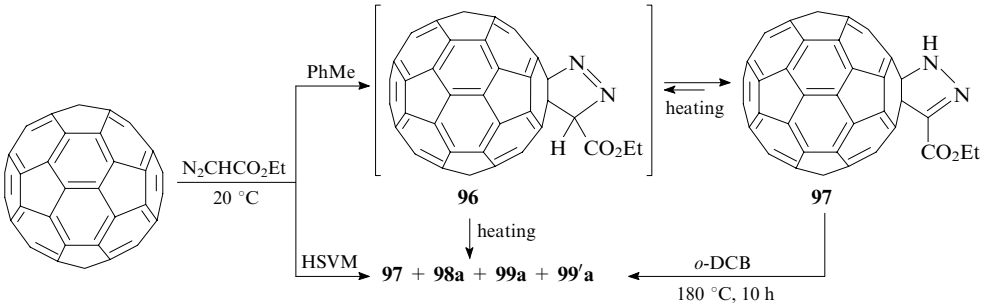
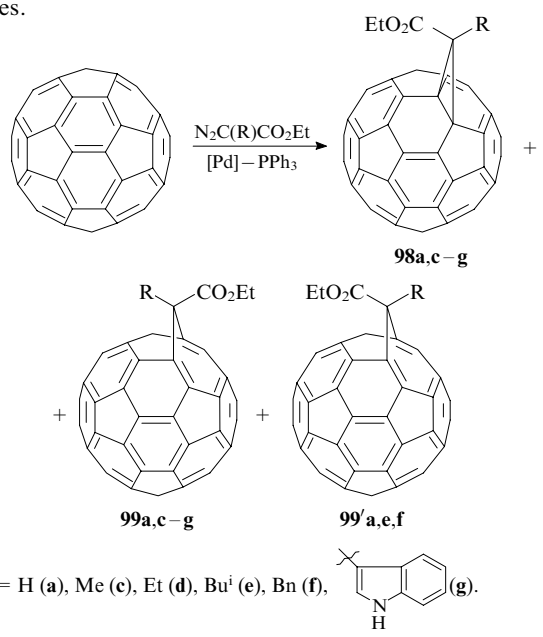


Table 4. Reactions of fullerene C_{60} with diazoacetate and diazomalonate [$N_2C(R)CO_2Et$].[106]

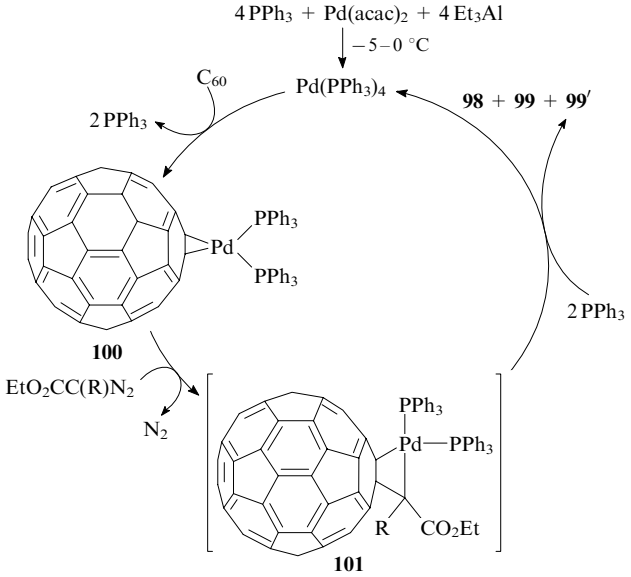
Reaction conditions	R	Solvent	*T* /°C	Time /h	Overall yield (%)	Product ratio **98** : **99** (:**99′a**)
Heating	H	PhMe	110	7	35	1 : 4 (:2)
$Rh_2(OAc)_4$	H	PhMe	20	20	21	14 : 1 (:1)
$Rh_2(OAc)_4$	H	1-$MeC_{10}H_7$	20	8	42	52 : 1 (:0)
Heating	CO_2Et	PhMe	110	20	10	—
$Rh_2(OAc)_4$	CO_2Et	1-$MeC_{10}H_7$	80	32	33	9 : 1

Note. $Rh_2(OAc)_4$ was taken in the stoichiometric amount.

were synthesized. It was shown that alkyl- and hetaryl-substituted ethyl diazoacetates easily reacted with fullerene C_{60} to give, in sufficiently high yields, [6,6]-closed or [5,6]-open isomers depending on the catalyst composition, the nature of the solvent and reaction conditions. At the same time, it was shown that the increase in the size of the α-alkyl substituent in the starting diazoacetate reduced the reactivity of the latter but increased the yields of methanofullerenes.

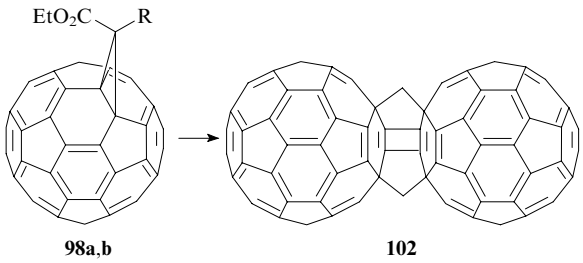


The role of the palladium catalyst was assumed[107] to consist of the activation of the C–C bond in the fullerene molecule through oxidative addition to form palladacyclopropane complex **100**. Ethyl diazoacetate reacted later with compex **100** at the polarized Pd–C bond with simultaneous elimination of the N_2 molecule to afford palladacyclobutafullerene **101**, which transformed into the products **98**, **99**, **99′** with the regeneration of $Pd(PPh_3)_4$.



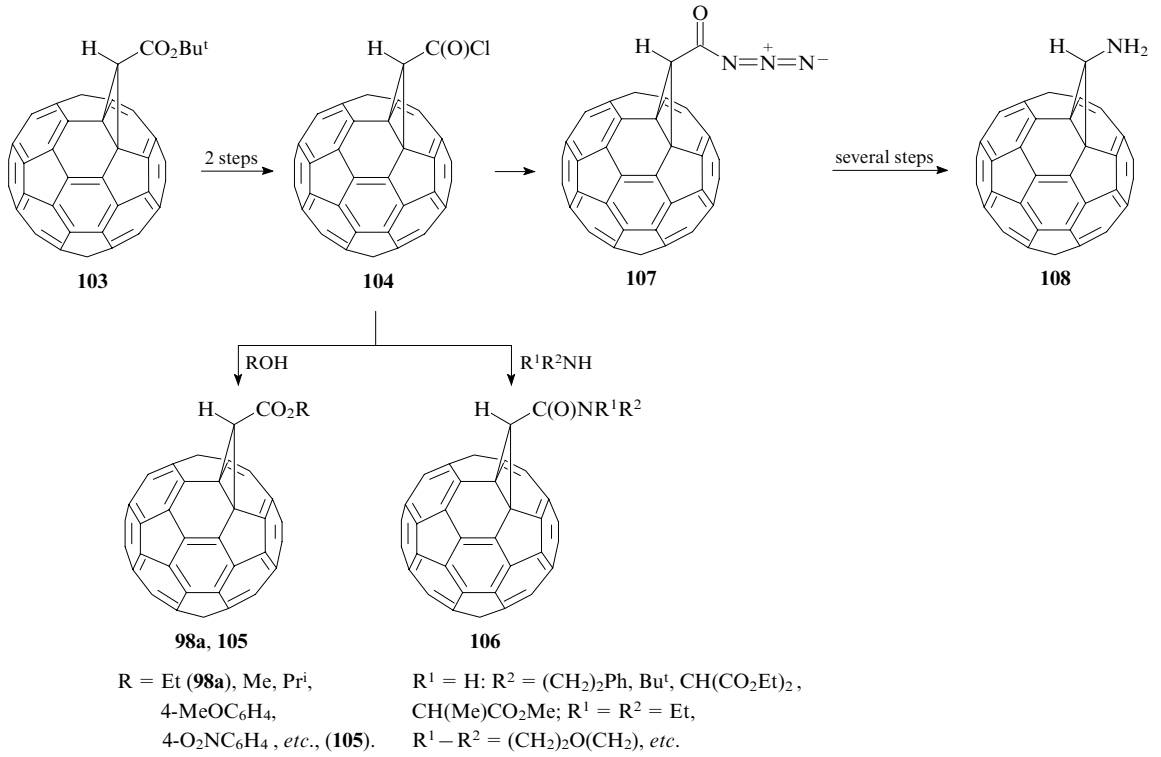
The solid-state reaction (HSVM) of fullerene with ethyl 2-diazopropionate produced a mixture of the corresponding [6,6]-closed **98c** and [5,6]-open compounds **99c** and **99′c**.[109] The overall yield and the ratio of products depended on the reaction conditions and duration. Note that in contrast to the catalytic reaction discussed above, this product mixture contained a stereoisomer with the methyl group located over the hexagon plane in the fullerene molecule. This reaction afforded no pyrazolinofullerene, as has been reported earlier[106] for the analogous reaction of C_{60} with ethyl diazoacetate.

Heating of methanofullerenes **98a**,**b** at high pressure produced new dimers of fullerene **102**, which were characterized by IR, UV and ^1H and ^{13}C NMR spectroscopy.[110]

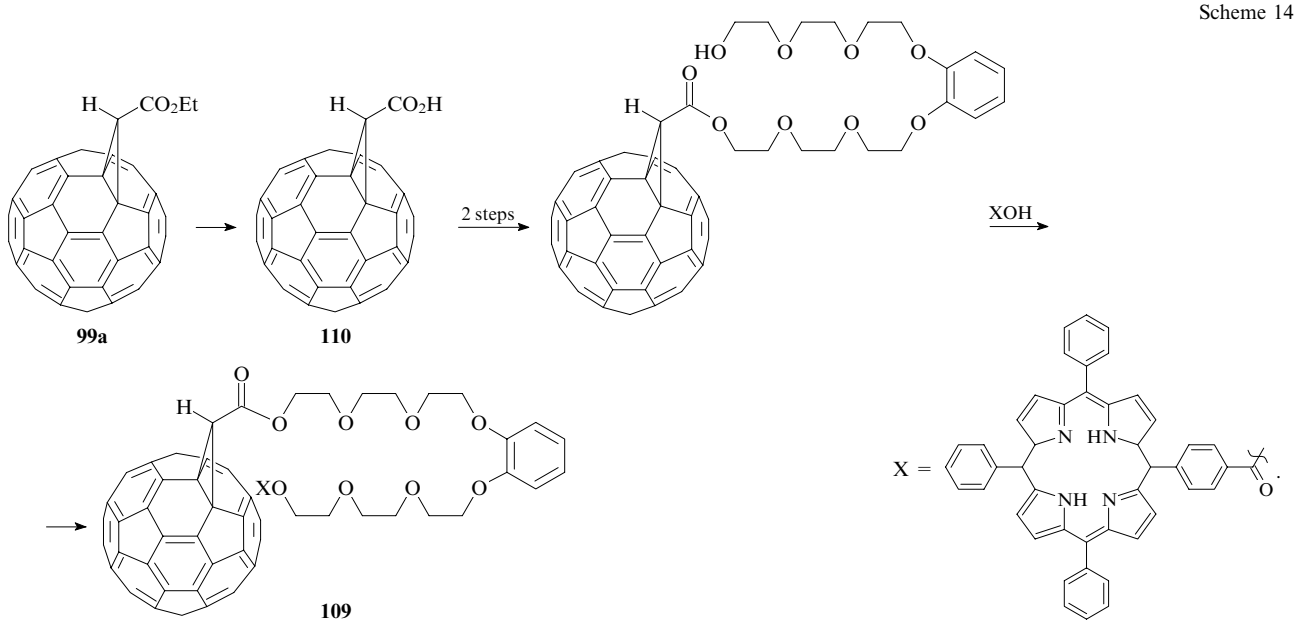


At the same time, according to other results,[79, 111] heating of the same methanofullerenes at atmospheric

Scheme 13



Scheme 14

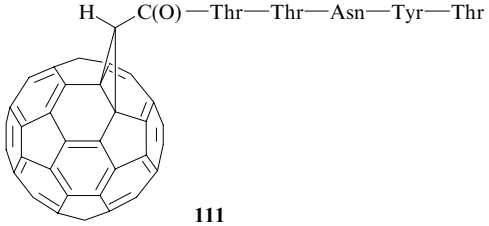


pressure favoured the formation of bisfullerenes **83** and **84** described earlier [77–80] (see Section V).

It was shown that *tert*-butyl methanofullerenecarboxylate (**103**) could be transformed into the corresponding acid chloride **104**; the latter served as the source of different esters **98a**, **105**,[112,113] amides **106**,[113] methanofullerenecarbonyl azide **107** (Ref. 114) and aminomethanofullerene **108** (Scheme 13).

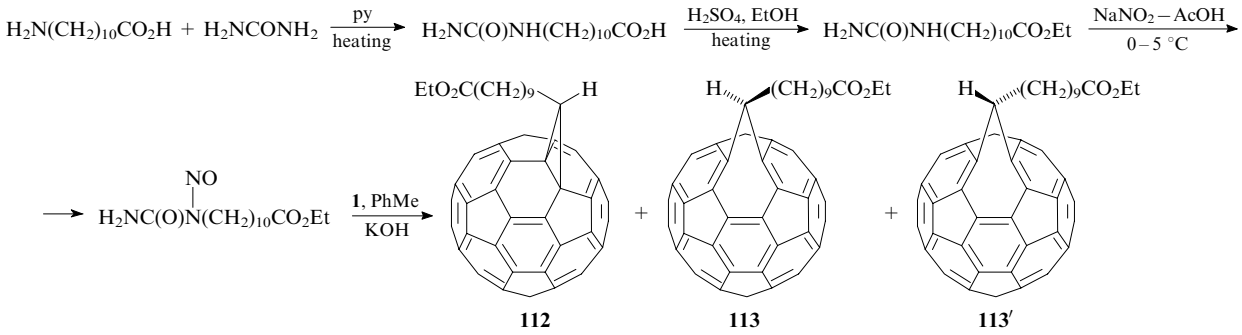
Based on ethyl methanofullerenecarboxylate (**98a**), a hybrid molecule was synthesized (**109**), which included the fragments of fullerene, oxyethylated pyrocatechol and triphenylporphyrin (Scheme 14).[115] Irradiation of compound **109** in air-saturated C_6D_6 was shown to afford singlet oxygen in high quantum yield.

Methanofullerenecarboxylic acid **110** served as a precursor for derivative **111** with the covalently linked fragment 4–8 of peptide T; this derivative was a weak inhibitor of HIV-1 protease.[116]



111

Scheme 15



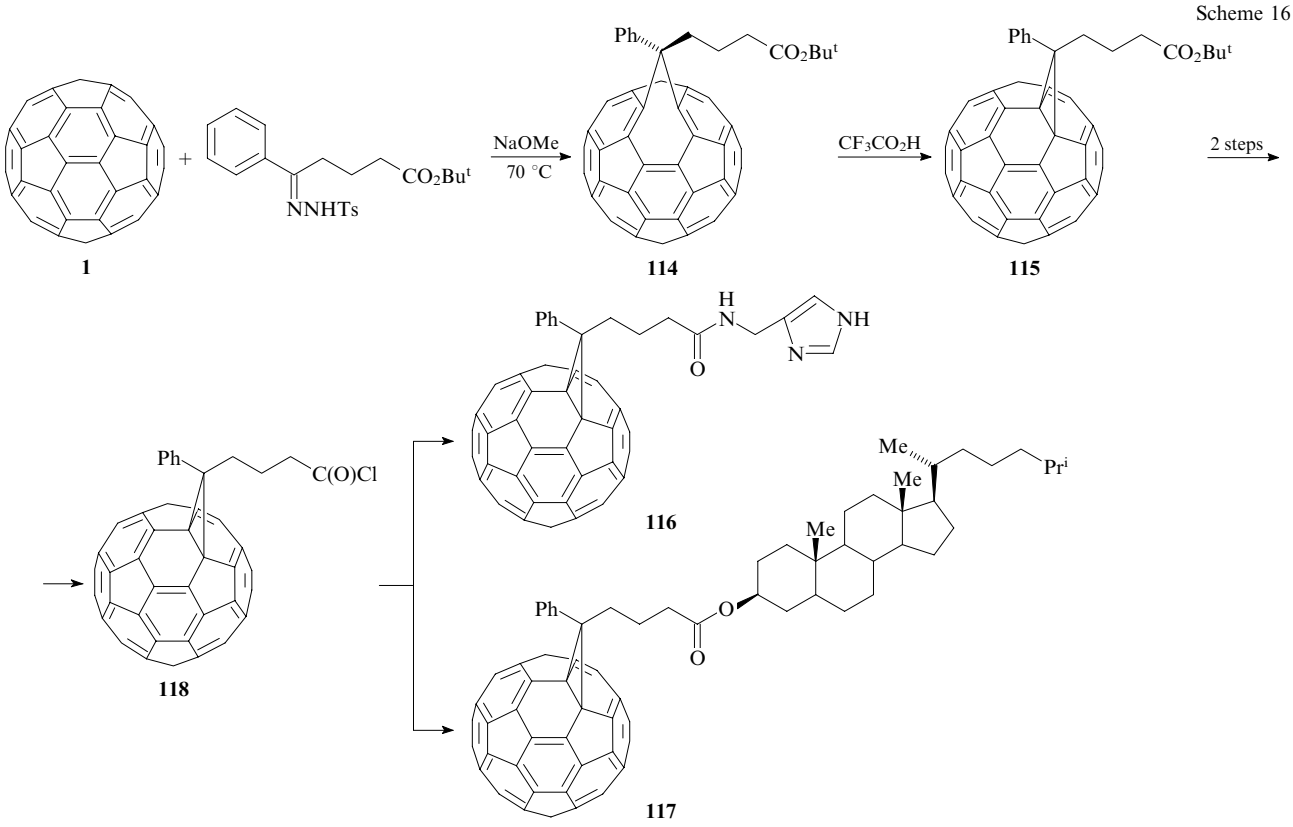
It is known that the farther the amino group from the carboxyl group in an amino acid the more problematic the synthesis of the corresponding diazo compound due to its instability. Therefore, it was proposed [117] to synthesize methanofullerenes *in situ* from the corresponding nitroso compounds. It was found that among isomers **112**, **113**, **113′**, the [5,6]-open isomer **113** was thermodynamically more stable. These compounds attracted attention in connection with the synthesis of the Langmuir – Blodgett films (Scheme 15).

Sufficiently stable diazo compounds of such a type were characterized by the presence of a phenyl substituent, which made it possible to synthesize homofullerene **114**. Its isomerization led to [6,6]-closed isomer **115** in quantitative yield [73, 74] (Scheme 16). In turn, methanofullerene **115** could be converted to derivatives **116** and **117** containing the histamine and cholestane fragments, respectively, *via* acid chloride **118**.[73] Compound **116** was tested for antiviral activity.

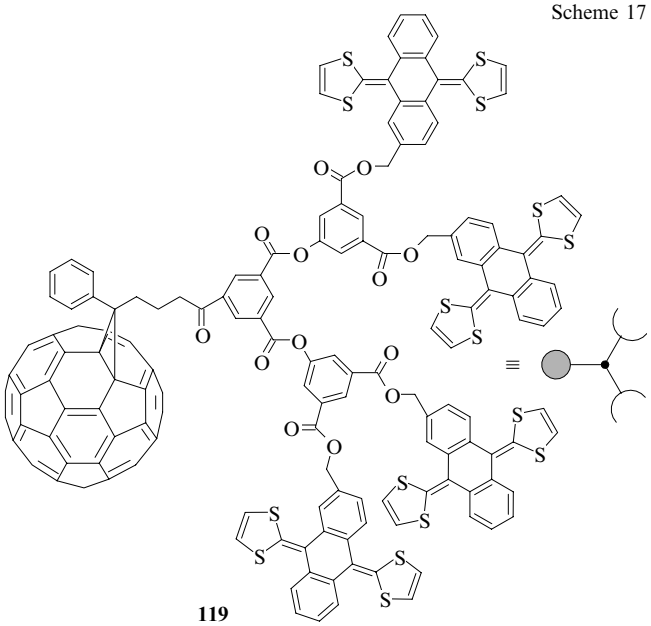
Compound **119**, which is an electroactive dynamically polydisperse supramolecular dendrimer, was synthesized by the analogous scheme (Scheme 17).[118]

It was reported [119] that the known [38] methyl ester **17** ([60]PCBM) in a combination with regioregular poly(3-hexylthiophene) is an efficient and promising material for the production of solar energy photoconverters.[86] Much effort has been spent to enhance the efficiency of such devices, which was found [120 – 122] to depend on the active layer morphology. Thus sulfur-containing analogues of [60]PCBM (compounds **120a – e**) were synthesized to improve the characteristics of such devices, of which only compound **120e** overperformed [60]PCBM in the required parameters.[123, 124]

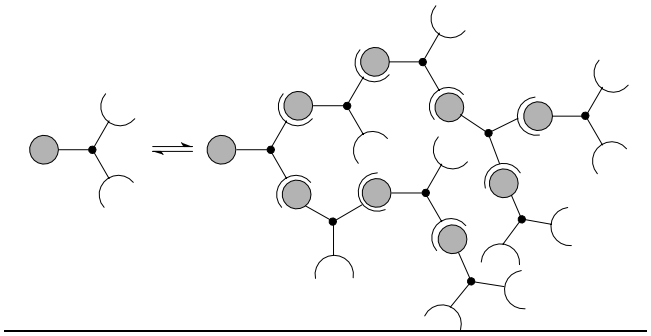
Scheme 16

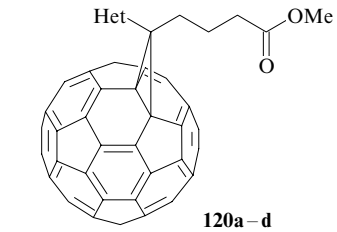


Scheme 17

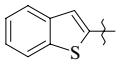
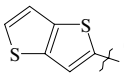


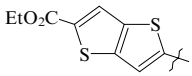
119



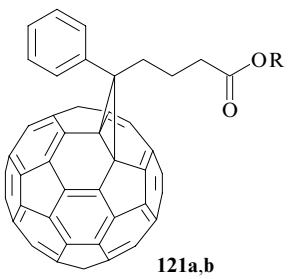


120a–d

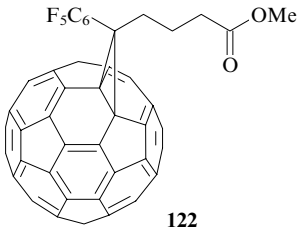
Het =  (**a**),  (**b**),  (**c**),  (**d**),

 (**e**).

In a similar way, the synthesis of fluorine-containing [60]PCBM derivatives **121a**,**b**, **122**, which are promising as organic transistors, were synthesized.[125]



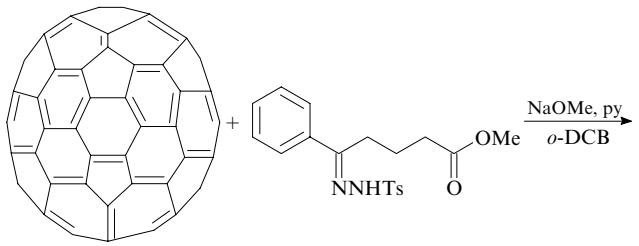
121a,**b**

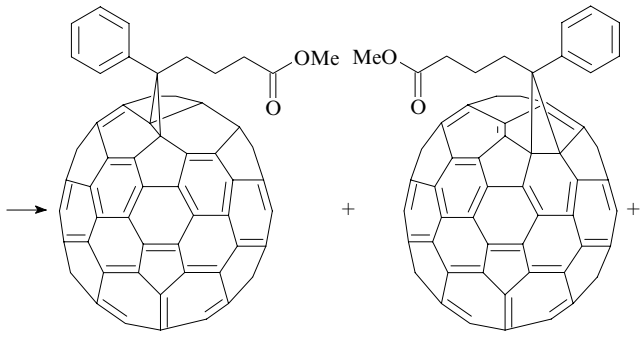


122

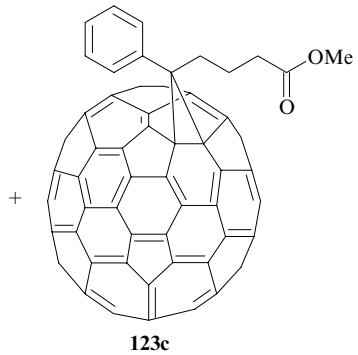
R = $CH(CF_3)_2$ (**a**), CH_2CF_3 (**b**).

Aimed at the practical use of functionally substituted fullerenes in the design of efficient materials for photovoltaic cells by a known procedure,[73] the derivatives of fullerenes C_{70} (Ref. 126) and C_{84} (Ref. 127), namely, [70]PCBM and [84]PCBM, were obtained. In both cases, mixtures of three isomeric [6,6]-methanofullerenes were obtained, *e.g.*, adducts **123a**–**c** for C_{70}. The electrochemical analysis has shown that [84]PCBM is better electron acceptor than compounds [60]PCBM and [70]PCBM.[127]





123a **123b**



123c

Comprehensive information on the possibility of using methanofullerenes as the solar energy photoconverters can be found elsewhere.[128]

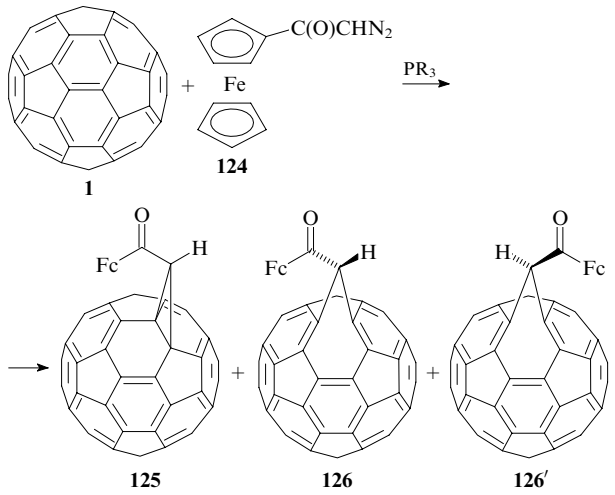
Analogues of [60]PCBM (**17**) were also synthesized for endofullerenes $M_3N@C_{80}$ (M = Sc, Y); in both cases, [6,6]-open structures formed.[129]

Thermal reaction of fullerene C_{60} with diazoacetylferrocene **124** in the presence of triphenylphosphine or tricyclohexylphosphine (PR_3) produced, depending on the initial reactant ratio, a mixture of methanofullerene **125** and stereoisomeric homofullerenes **126**, **126′** (Table 5).[130] The use of $Rh_2(OAc)_4$ as the stoichiometric catalyst led exclusively to [6,6]-closed structure **125**.

Table 5. Dependence of the yield of compounds **125**, **126**, **126′** on the ratio of the reactants.

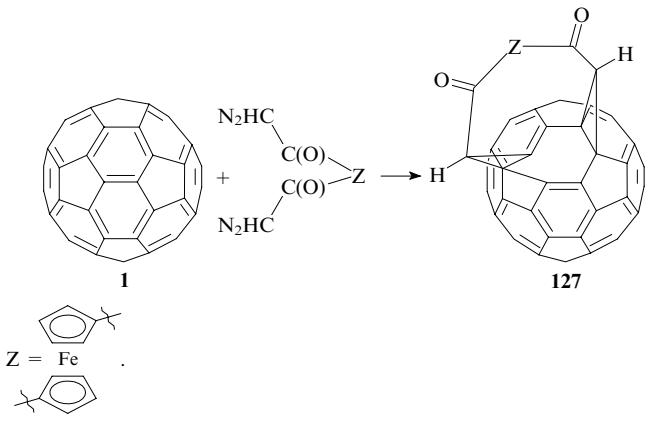
Ratio **1** : **124** : PR_3	Content of isomers in the mixture (%)		
	125	**126**	**126′**
1 : 3 : 0	85	15	0
2 : 1 : 0	60	37	3
1 : 1 : 1	14	79	7
1 : 1 : 0 [a]	100	0	0

[a] In the presence of $Rh_2(OAc)_4$.



R = Ph or cyclo-C_6H_{13}.

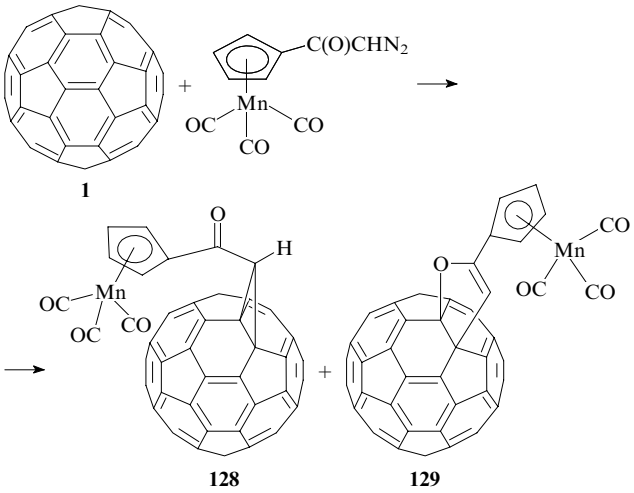
Later, metallocene-containing fullerene **127** was synthesized [131] as a candidate for building 'molecular wire' by the reaction of C_{60} with 1,1′-bis(diazoacetyl)ferrocene.



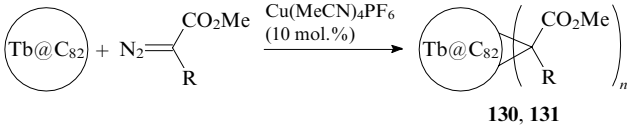
Z = Fe .

Based on spectral characteristics, it was shown that both carbenoid species derived from bis(diazoacetyl)ferrocene added to the [6,6] and [5,6] bonds of the same fullerene molecule. The *ansa*-structure was assigned to the adduct, which was virtually devoid of the conformational mobility, a fact unprecedented from the standpoint of the chemistry of fullerenes.[130, 131]

Thermolysis of diazoacetylcymantrene in the presence of fullerene C_{60} afforded methanofullerene **128** and dihydrofuranofullerene derivative **129** in the 1 : 1 ratio in the overall yield of 17%. Decomposition of the diazo compound under the action of the stoichiometric amount of $Rh_2(OAc)_4$ in the presence of C_{60} at room temperature afforded, as should be expected, only [6,6]-closed isomer **128**.[130, 132, 133]



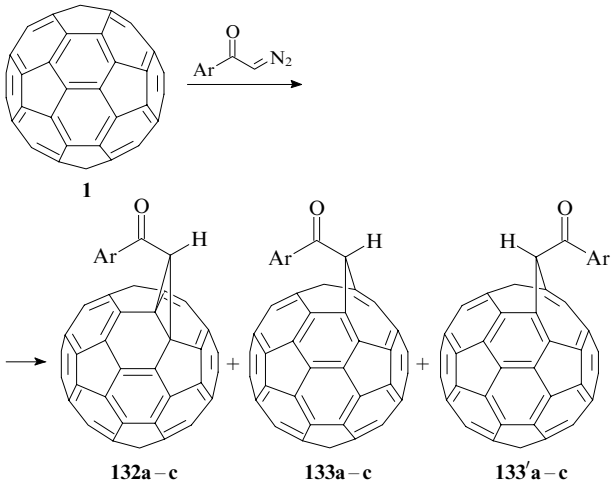
The use of a complex copper catalyst $Cu(MeCN)_4PF_6$ made it possible to carry out reactions of endomethallofullerene $Tb@C_{82}$ with aryl- and hetaryldiazoacetates to afford mixtures of compounds **130** and **131** containing from 1 to 6 added fragments. Such structures are interesting as the basis for new promising materials.[134]



130, **131**

R = Ph (**130**), naphthyl (**131**); n = 1–6.

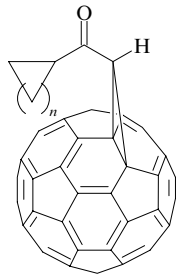
The reaction of C_{60} with diazoketones, as with diazoacetates, afforded mixtures of [6,6]-closed **132** and stereoisomeric [5,6]-open compounds **133** and **133′** in the yields not exceeding 30% with respect to the consumed fullerene. Similar results could be obtained in a shorter time interval (1 h) by carrying out this reaction under solid-phase conditions (HSVM) in the total yields not exceeding 45%.[135]



Ar = 4-$MeOC_6H_4$ (**a**), Ph (**b**), 4-BrC_6H_4 (**c**).

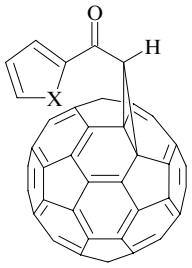
It should be noted that in the presence of a complex catalyst $Pd(acac)_2 - 2\,PPh_3 - 4\,Et_3Al$ this reaction was highly selective and resulted exclusively in methanoful-

lerenes **134**–**137** in yields of 40%–60%. The starting diazo compounds comprised a carbo- or a heterocycle.[136]



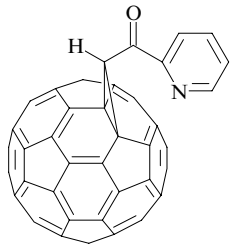
134a–**c**

n = 1 (**a**), 2 (**b**), 3 (**c**).

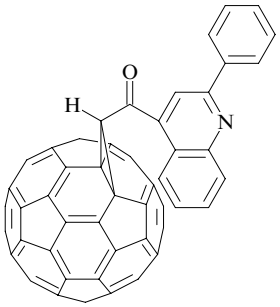


135a,**b**

X = O (**a**), S (**b**).

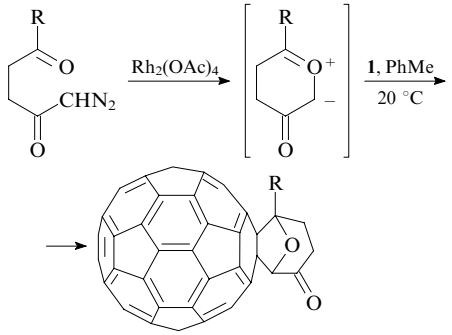


136



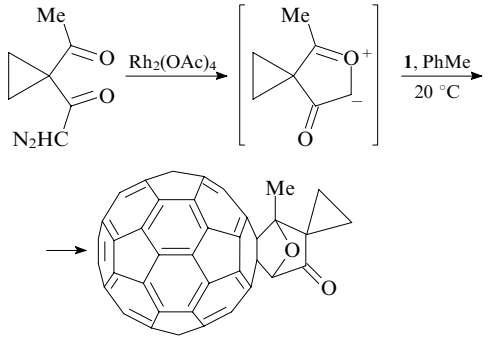
137

However, the reaction of C_{60} with diazoketones in the presence of $Rh_2(OAc)_4$ afforded intermolecular cyclization products **138** and **139** in place of the expected methanofullerenes.[137] It was found that upon insertion of an additional methylene group between two keto groups of the original diazoketone the latter did not react with fullerene.



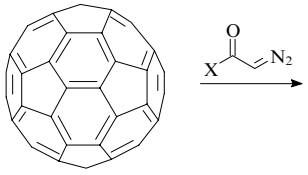
138 (31%–53%)

R = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, Me, Fc, 2-thienyl.

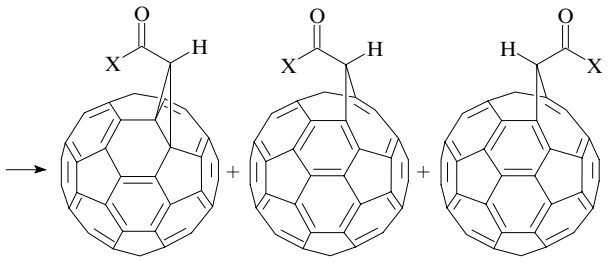


139 (54%)

Similar results were also obtained with diazoamides as the starting diazo compounds. Thus the reaction of C_{60} with simple diazoamides in boiling toluene afforded the corresponding methanofullerenes **140** and stereoisomeric homofullerenes **141** and **141′**.[138]



1



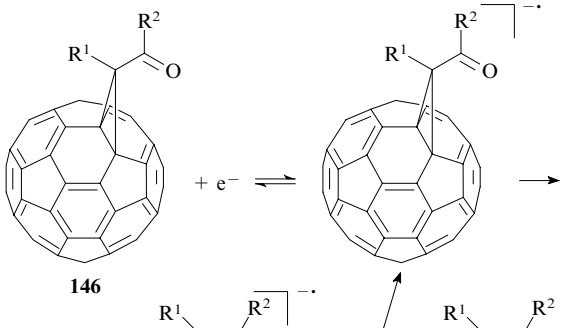
140a–**d** **141a**–**d** **141′a**–**d**

X = (**a**), NHBn (**b**), NHCH(Bn)CO_2Bn (**c**),

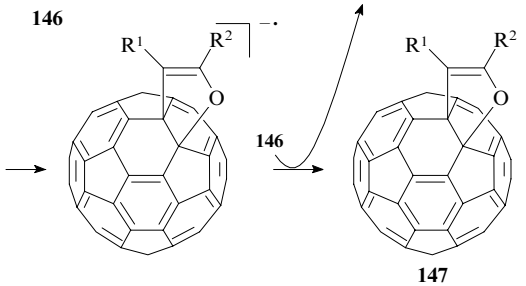
L-$NH(CH_2)_4CH(NH_2)CO_2Et$ (**d**).

The reaction of fullerene C_{60} with more complex diazoamides containing several carbonyl groups in the presence of $Rh_2(pfb)_4$ (pfb is perfluorobutyrate) as the catalyst afforded intramolecular cyclization products **142**–**145**. Upon thermolysis of compound **142**, this decomposed to the original C_{60} (Scheme 18).[139]

Under conditions of electrochemical reduction, methanofullerenes **146** containing a phosphonate or a phenyl group in the cyclopropane ring and an electron-withdrawing keto group transformed to the corresponding dihydrofurofullerenes **147**.[140–142] The electroreduction process was studied by the methods of cyclic voltammetry and EPR combined with *in situ* electrolysis.



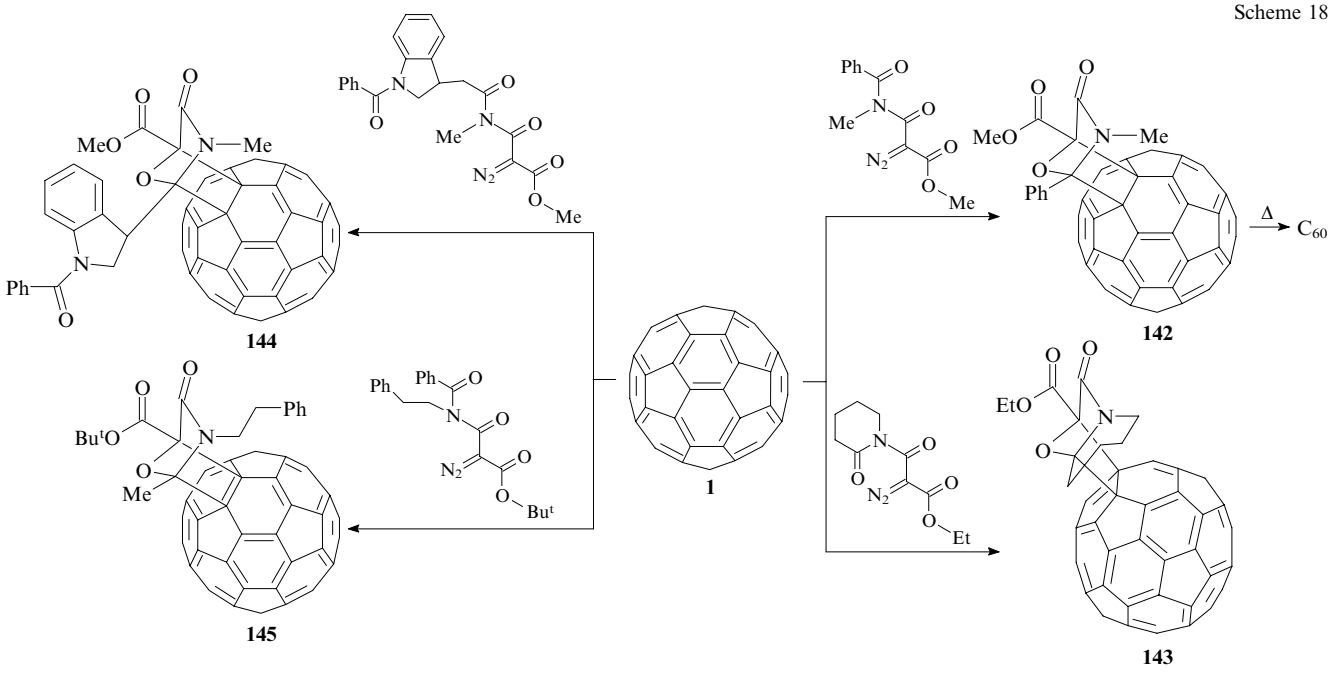
146



147

R^1 = $P(O)(OEt)_2$: R^2 = Me, $CH(OEt)_2$; R^1 = $P(O)(OPr^i)_2$, R^2 = Me; R^1 = Ph: R^2 = $C(O)Bu^t$, CO_2Me.

Scheme 18



Under the reaction conditions, the formation of a five-membered ring was stimulated by the functional groups with pronounced electron-withdrawing properties capable of efficient negative charge delocalization, which were present at the *exo*-carbon atom. This apparently was the reason for the cleavage of the C–C bond between the *exo*-carbon atom and the fullerene sphere as soon as in the radical anion stage. The presence of a keto group directly at the *exo*-carbon atom not only stabilized the three-membered ring opening products in the anionic intermediates but also allowed their cyclization to form the corresponding dihydrofuranofullerenes.

* * *

From the literature data presented it follows that the cycloaddition of diazo compounds to carbon clusters to form homo- and methanofullerenes may be considered among the first synthetic transformations in the chemistry of fullerenes once the latter became accessible in macroamounts. To date, several methods of carrying out this reaction under different conditions have been described. These are the generation of diazo compounds *in situ* from the corresponding nitroso compounds, unsubstituted hydrazones and tosylhydrazones, which react with fullerenes under thermal, photochemical and catalytic conditions and also under solid-state reaction conditions and at microwave irradiation. The use of the above methods allowed selective synthesis of both [6,6]-closed and [5,6]-open isomers.

The majority of published results in this field were obtained in thermal reactions of diazo compounds with carbon clusters and only few studies consider the use of stoichiometric or catalytic amounts of metal complexes or salts for these reactions.

It is quite evident that the introduction of methods of metal complex catalysis into the chemistry of carbon clusters, particularly, for reactions of diazo compounds with fullerenes, makes it possible to develop highly selective and efficient methods for the synthesis of homo- and methanofullerenes of the desired structure, which opens up wide prospects for using these compounds with unique structures and properties in different fields of science and technology.

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