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The formation of [5,6]- and [6,6]-open fulleroid structures

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Abstract. The experimental and theoretical data concerning the formation of open fulleroid structures (homofullerenes) upon chemical modifications of the fullerene spheroid are generalised. The bibliography includes 88 references.

I. Introduction

Cycloaddition is one of the best studied types of reactions in organic chemistry of fullerenes. The results of detailed studies of cycloaddition reactions involving fullerenes such as the Diels – Alder, 1,3-dipolar, [2 + 1] and others have been described in numerous publications. In the vast majority of cases, these reactions afford addition products at the fullerene C=C double bond, the so-called [6,6]-closed adducts. As expected for the normal cycloaddition, a π-bond is cleaved and all σ-bonds are maintained in these products. Meanwhile, many examples of the formation of [5,6]-open and [6,6]-open fulleroid structures in parallel, or in addition, to the expected [6,6]-closed adducts are presently available, which implies that it is σ-bonds between the carbon atoms of the fullerene sphere that are cleaved. In some particular cases, open fulleroids can spontaneously isomerise into closed fullerenes and *vice versa*. Various types of the cycloaddition reactions yield fulleroids, and the reasons for the formation of these unexpected structures among reaction products have not yet been completely established. Several authors speculated upon possible reasons for the formation of open adducts, whereas other authors merely described the experimental data obtained. Despite the fact that the formation of open fulleroid structures is undoubtedly of theoretical interest, no systematic review on this topic has been published so far.

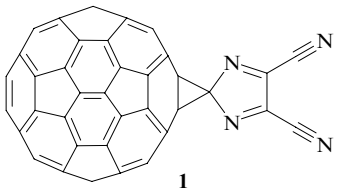
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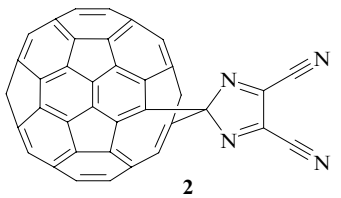
II. Reactions of diazo compounds with fullerene

Carbenes are known to readily add to the double bonds C=C to yield cyclopropanes. Diazo compounds are widely used as synthetic precursors of carbenes. However, the thermally induced addition of diazo compounds to C_{60} fullerene proceeds in a more complex way than the addition of singlet carbenes generated by other methods and affords mixtures of [6,6]-closed (fullerene) and [5,6]-open (fulleroid) isomeric cycloadducts. This is due to two possible mechanisms of the cyclopropane fragment formation in the thermally induced reactions of C_{60} with diazo compounds: the thermal decomposition of a diazo compound to a carbene followed by its synchronous addition to the [6,6] bond of fullerene giving rise to closed products and the 1,3-dipolar cycloaddition to fullerene followed by the extrusion of nitrogen from the pyrazoline intermediate, which can yield both isomers (Scheme 1).[1]

However, thermolysis of 2-diazo-4,5-dicyanoimidazole, which can afford two electrophilic intermediates, *viz*., carbene-type and zwitter-ionic species stabilised by two electron-withdrawing substituents in the heterocyclic ring in the presence of C_{60} does not yield isomeric fullerene and fulleroid spiromethanofullerenes (**1** and **2**, respectively),



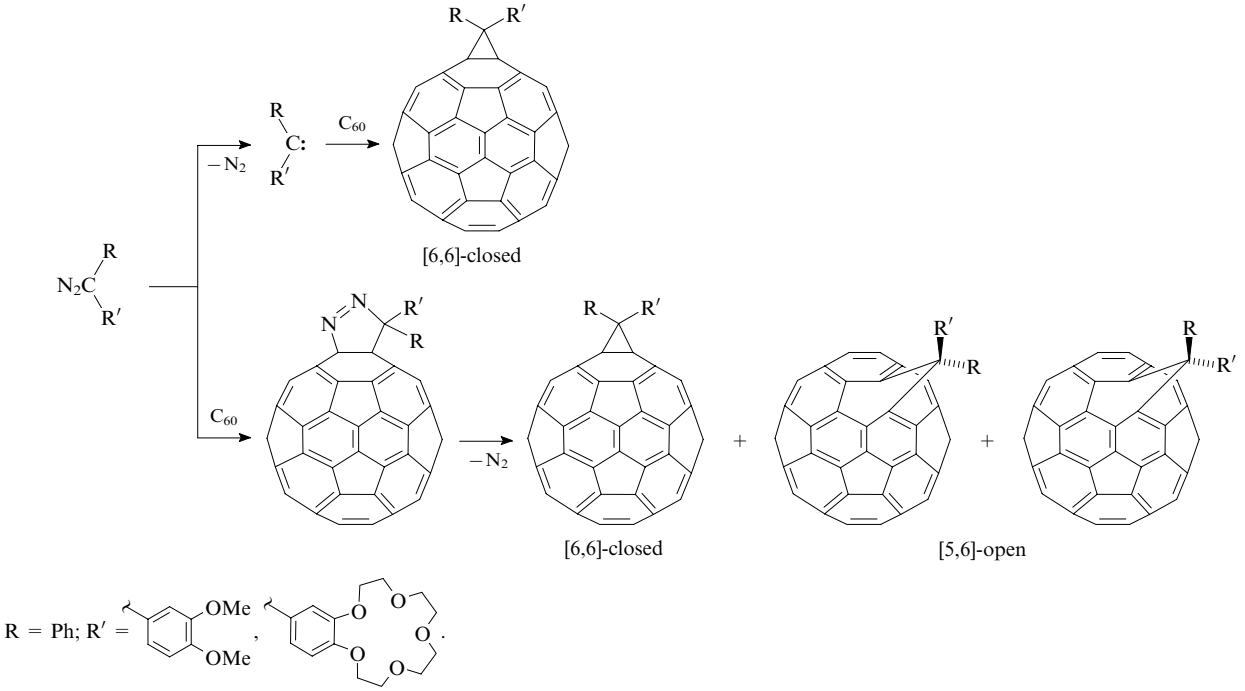
1



2

but rather an adduct **3**.[2] In our opinion, the radical 1,4-addition is a probable mechanism, since it is quite common in fullerene chemistry,[3] whereas no nucleophilic 1,4-addition to

Scheme 1



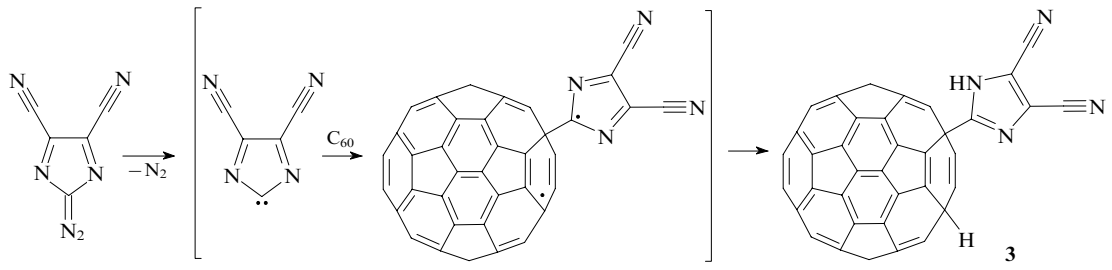
C_{60} has been described so far in the literature. Furthermore, the conversion of 2-diazo-4,5-dicyanoimidazole into a radical is by far more probable than into an anion, which requires the presence of a reducing agent (Scheme 2).

The thermal attachment of dimethyl diazomethylphosphonate $N_2CHP(O)(OMe)_2$ to C_{60} (110 °C, toluene) also yields a mixture of isomeric fullerene and fulleroid cycloadducts in a 3 : 1 ratio.[4]

Pellicciari *et al.*[5] reported the first addition of carbenoids to C_{60} catalysed by transition metals. In particular, the reaction of C_{60} with alkoxycarbonylcarbenoids generated from diethyl diazomalonate with $Rh_2(OAc)_4$ as a catalyst provides higher product yields and selectivity as compared to ordinary thermal reactions (Scheme 3, Table 1).

Unstable diazo compounds can be generated *in situ* from stable hydrazones and their derivatives using oxidation of hydrazones, *e.g.*, with MnO_2.[6,7] It was suggested[8,9] that the reaction proceeds through the initial 1,3-dipolar cycloaddition of the diazo compound to C_{60} followed by the extrusion of a nitrogen molecule from the pyrazoline intermediate formed. As a result, a mixture of [6,6]-closed (fullerene) and [5,6]-open (fulleroid) derivatives is obtained. This method was successfully used to introduce methylene bridges containing benzocrown ether fragments[6] or 3,5-bis[(dimethylamino)methyl]-phenyl (dmmph) group[7] aimed at studying the complexation properties of new fullerene derivatives. It is of note that the formation of only one of two possible [5,6]-open stereoisomers (**8** and **9**) in addition to [6,6]-closed adduct **7** is feasible for specific asymmetric methanofullerenes, according to calcula-

Scheme 2



Scheme 3

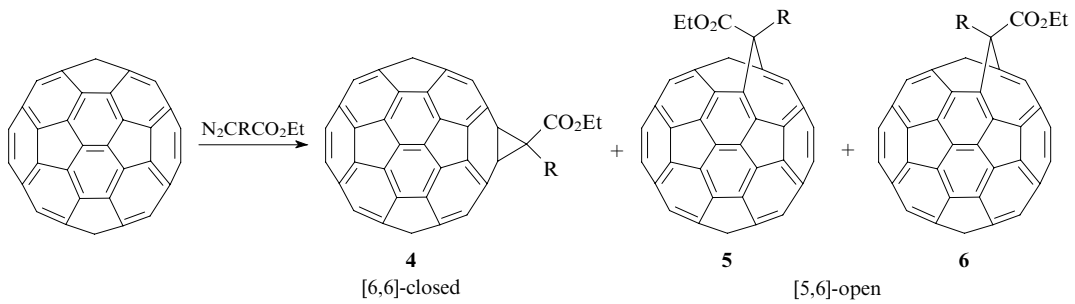
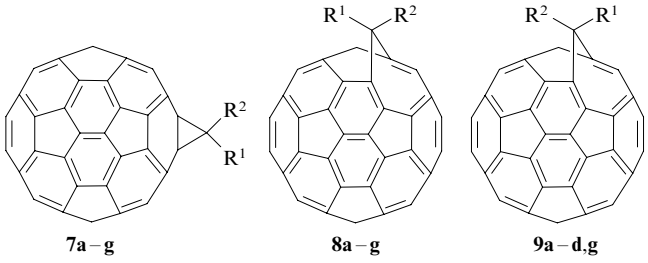


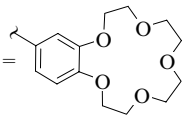
Table 1. Conditions, yields and product ratios for the reaction of C_{60} with diethyl diazomalonate.

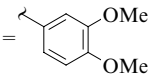
Catalyst	R	Solvent	T/°C	Reaction time/h	Yield (%)	Ratio of isomers		
						4	**5**	**6**
–	H	toluene	110	7	35	1	4	2
$Rh_2(OAc)_4$	H	toluene	20	20	21	14	1	1
$Rh_2(OAc)_4$	H	1-methylnaphthalene	20	8	42	52	1	–
–	CO_2Et	toluene	110	20	10	not determined		
$Rh_2(OAc)_4$	CO_2Et	1-methylnaphthalene	80	32	9	1	–	–

tions. In particular, isomers **8e**,**f** are feasible, whereas isomers **9e**,**f** are not.[6]



7a–g **8a–g** **9a–d**,**g**

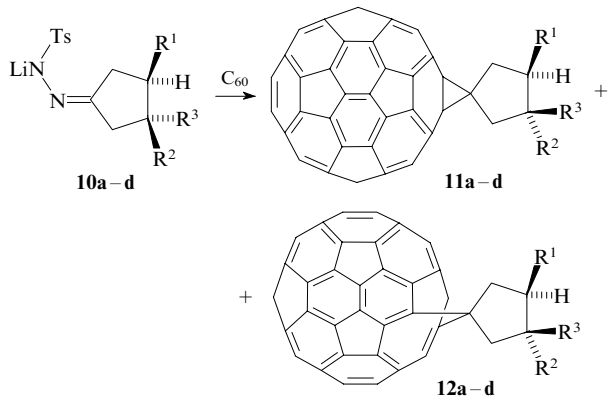
R^1 =  : R^2 = H (**a**), Me (**b**), Ph (**c**), R^1 (**d**);

R^1 =  : R^2 = H (**e**), Me (**f**), Ph (**g**).

For all other non-symmetrical methanofullerenes, both [5,6]-open isomers have been isolated. No rationale for this experimental fact has been given.[6]

Initially, the reaction of fullerene with diazo compounds bearing a dmmph group was found [7] to yield a mixture of [5,6]-open fulleroids and [6,6]-closed methanofullerene in a 9 : 1 ratio.

In addition to the aforementioned oxidation of unsubstituted hydrazones, thermolysis of *N*-tosylhydrazone anions **10** can be employed for the generation of diazo compounds.[8,10–16] Their addition also yields a mixture of [6,6]-closed and [5,6]-open isomeric cycloadducts (compounds **11** and **12**, respectively). Conditions of the thermolysis of the corresponding *N*-tosylhydrazone lithium salts in boiling toluene could be tuned so as to enable the preferred formation of fulleroid derivatives. This was accomplished by shortening the reaction time, which favours the formation of a kinetically controlled product.



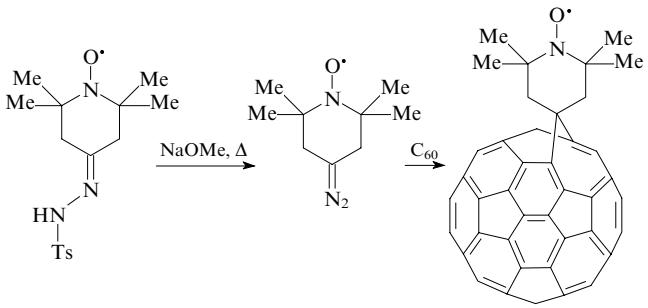
10a–d **11a–d** **12a–d**

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

The maximum yield of 67% and the maximum isomer ratio of [5,6]-open to [6,6]-closed (13.3 : 1) were achieved for compound **10c** and a reaction time of 25 min. With an increase in the reaction time to 90 min, the yield of monoadducts drops down to 23% and the isomer ratio, to 1.7 : 1. Most probably, such a change in the product ratio is due to the progressive accumulation of the product of thermal rearrangement of the initially formed [5,6]-open isomer into the [6,6]-closed isomer.

In contrast, the reaction of C_{60} with 4-[bis(4′-*tert*-butylbiphenyl-4-yl]benzaldehyde *N*-tosylhydrazone in *o*-dichlorobenzene in the presence of sodium methoxide even at a relatively low temperature (40 °C) yields selectively the thermodynamically more stable [6,6]-closed isomer.[17]

The reaction of fullerene C_{60} with 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl *N*-tosylhydrazone affords only the open isomer in a ~25% yield.[10]



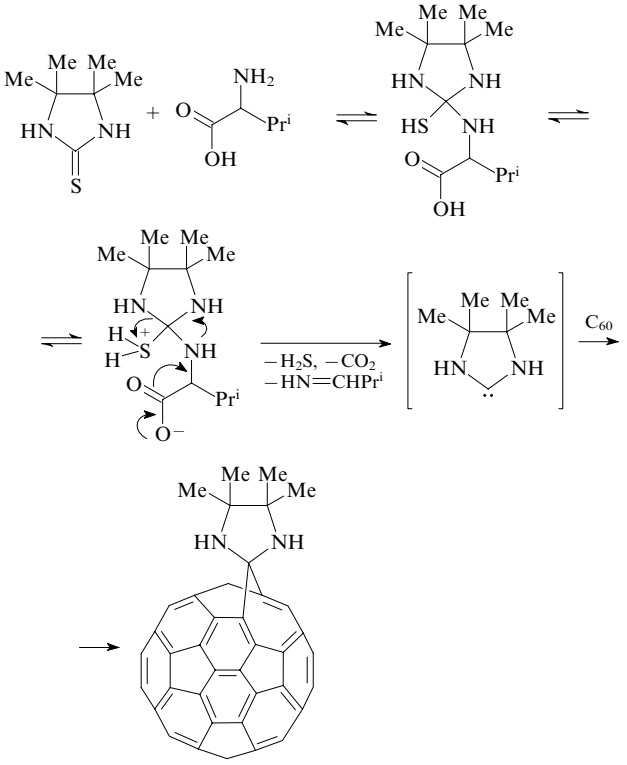
The kinetically controlled products, *viz*., [5,6]-fulleroids, were obtained in the reaction of fullerene with a diazo compound bearing a tetrathiafulvalene substituent [13] and a diazo compound generated *in situ* from 4-benzoylbutyric acid *N*-tosylhydrazone.[18]

An unusual method for the carbene generation has been found in the reaction of C_{60} with DL-valine and 4,4,5,5-tetramethylimidazoline-2-thione.[19] This reaction yields the respective spiro-fused fulleroid (Scheme 4).

As has been noted above, the reactions of C_{60} with carbenes afford [6,6]-closed methanofullerenes, whereas those with diazo compounds yield fulleroids (*i.e*., [5,6]-open isomers). This allows fullerenes to be used as specific probes to distinguish carbenes and diazo compounds. The nature of the adducts formed provides information on the reaction mechanism.[20]

However, it has to be noted that the thermal reaction of C_{60} with a dibromo derivative **13**, which involves a carbene intermediate, yields a symmetrical fullerene adduct **14**, dimers formed upon the reaction of two molecules of the carbene intermediate and an isomeric non-symmetrical adduct **15** comprising fullerene and fulleroid fragments in one molecule.[21] It was shown that the fulleroid **15** was the major reaction product (its yield varies from 5% to 10%), but no explicit ratio between the adducts **14** and **15** was given. According to calculations,[21] the isomer **15** is more stable than **14** (Scheme 5).

Scheme 4

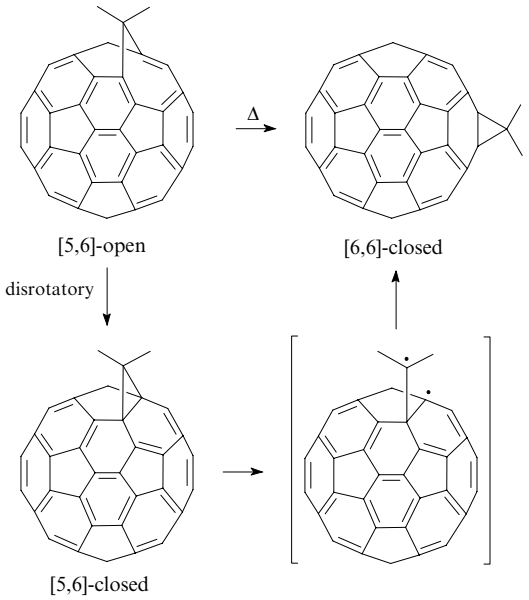


As has been shown by different groups,[6–8, 13, 18] [5,6]-open fulleroids synthesised in this way undergo a thermal rearrangement into thermodynamically more stable [6,6]-closed isomers. A number of [5,6]-open fulleroids bearing substituents stabilising radical species in the methylene bridge was proven to rearrange into [6,6]-closed fullerenes both in the zero-order (in terms of kinetics) photochemical process and in the high-energy unimolecular route, which involves the disrotatory ring closure into a [5,6]-closed fullerene followed by its rearrangment into the [6,6]-closed isomer *via* biradical intermediates.[22] Generally, this process is depicted in Scheme 6 (omitting substituents in the bridge). The energy parameters of various isomers of methanofullerenes and fulleroids calculated by the MNDO method are reported.[23]

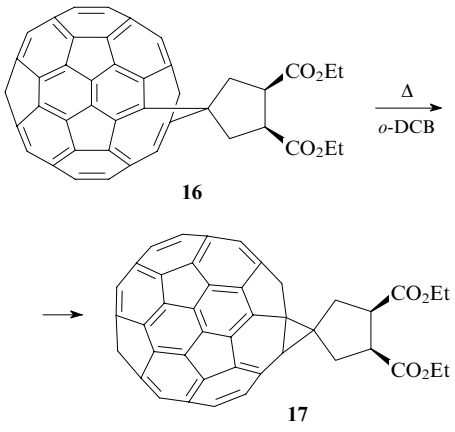
It has to be stressed that unsubstituted [5,6]-methanofulleroid is not thermally converted into methanofullerene.[24] This agrees with the radical mechanism of the rearrangement suggested above, since the formation of a biradical intermediate becomes thermodynamically unfavourable due to the absence of radical-stabilising substituents in the bridge.

The rearrangement of fulleroid **16** into methanofullerene **17** occurs in *o*-dichlorobenzene (*o*-DCB) at 153 °C, but all attempts to perform it in an NMR tube carefully protected

Scheme 6



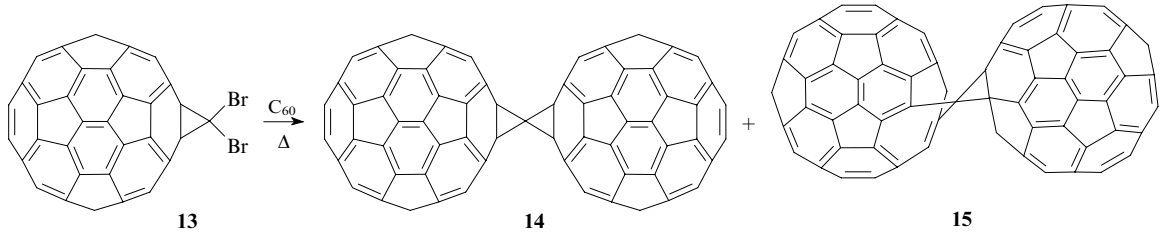
from light failed and the starting fulleroid **16** remained quantitatively intact.[25]



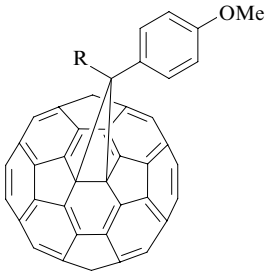
Thus, this rearrangement requires illumination. Indeed, compound **16** is converted into methanofullerene **17** quantitatively upon illumination of its solution with filtered light ($\lambda > 500$ nm, 200 W) for 16 h. Oxygen inhibits the reaction, which supports the suggested biradical mechanism of the isomerisation.

Prato *et al.*[23] also described experiments on the thermal rearrangement of fulleroids into methanofullerenes and presented calculations demonstrating higher thermodynamic

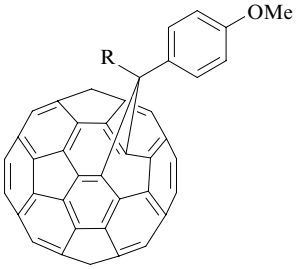
Scheme 5



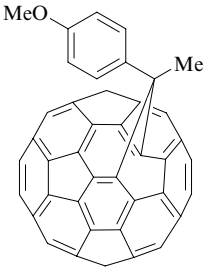
stability of methanofullerenes. It is of note that the reaction of fullerene with 1-(*p*-methoxyphenyl)diazoethane affords a mixture of [6,6]-closed (**18a**) and two [5,6]-open (**18b**,**c**) isomers in a 4 : 2 : 1 ratio, whereas the reaction with *p*-methoxyphenyldiazomethane yields only two isomers, *viz*., [6,6]-closed (**19a**) and one [5,6]-open (**19b**) adducts.



18a (R = Me), **19a** (R = H)



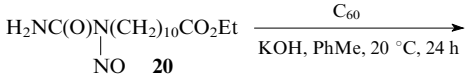
18b (R = Me), **19b** (R = H)

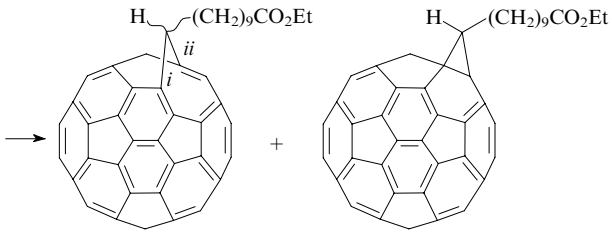


18c

According to calculations for a series of model systems containing fused six- and five-membered rings similar to those in the fullerene molecule (using MMPI, RHF/AM1 and UHF/AM1 methods with the geometry optimisation),[9] [5,6]-open isomers can become more stable than their [6,6]-closed counterparts with an increase in the degree of convexity.

The known instability of aliphatic diazo compounds makes the control over the process of their addition to C_{60} very difficult, the more so that the reaction occurs in extremely low yields. Zhu *et al*.[26] generated diazo compounds *in situ* from a stable precursor, compound **20**, which allowed them to overcome this problem.





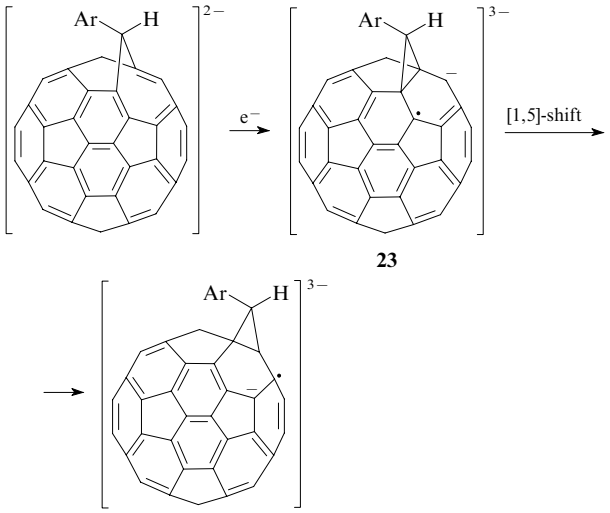
21 **22**

Since the addition of KOH to the nitroso compound results in the immediate nitrogen evolution and pyrazoline intermediates have never been observed among the reaction products, it was suggested that the reaction follows the carbene mechanism.

In this case, the [5,6]-open isomer **21** proves thermodynamically more stable. It is formed upon rearrangement of initially formed [6,6]-closed cycloadduct **22** (according to the data from NMR spectra), which was rationalised by the effect of a bulky aliphatic substituent in the bridge. On the one hand, the sp^2 carbon atoms *i* and *ii* of the fullerene cage in the open adduct are characterised by localised double bonds, which should induce strains in the cyclic structure, according to the Bredt rule. In the closed adduct, these carbon atoms are sp^3-hybridised and thus the total structural strain is substantially lower. On the other hand, the closed adduct contains a strained cyclopropane fragment, the strain in which is proportional to the steric bulk of the substituent in the methylene bridge. The distance between the carbon atoms *i* and *ii* is larger in the open adduct than in the closed one and thus the strain in the attached molecular fragment is lower. The relative stability of the two isomers, open and closed, is exactly determined by the interplay of these two factors. In the present case, the [5,6]-open adduct is more stable. Zhu *et al*.[26] stressed that the adduct isomerisation is strongly affected by solvents. They concluded that temperature, solvent and the nature of substituents are the three key factors governing the formation of a specific isomer. This conclusion on the reasons for a higher stability of open adducts with bulky substituents in the bridge agrees with the aforementioned experimental data[21] on higher stability of the open isomer with the fullerene molecule serving as the bulky substituent. This explanation, however, contradicts the results of other authors,[27] who showed that methanofullerenes bearing substituents of a comparable size [*viz*., $C(R)CH_2.C(O)OCH_2CMe_2CH_2OH$, R = H, Et, Ph] do not rearrange into open fulleroids even upon heating to 200 °C.

Eiermann *et al*.[28] reported the electrochemical isomerisation of a [5,6]-open fullerene synthesised by the addition of (*p*-methoxycarbonylphenyl)diazomethane to C_{60} into the respective [6,6]-closed methanofullerene. In this case, the generation of a radical anion **23** favours the isomerisation. The tentative mechanism is shown in Scheme 7.

Scheme 7

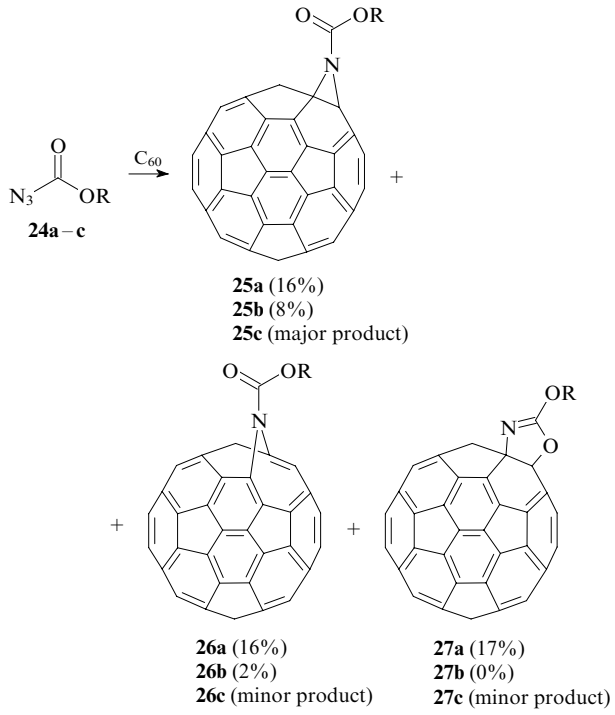


Ar = 4-$MeO_2CC_6H_4$.

As has been mentioned above, there are two possible mechanisms of the cyclopropanation upon thermal reactions of C_{60} with diazo compounds.[1,9] Wallenborn *et al*.[29] theoretically studied the possibility of the formation of methanofullerenes with the thermal extrusion of N_2 from the pyrazoline intermediate. According to *ab initio* calculations (using the B3LYP/6-31G* method) on benzene and pyracene as mimics for the fullerene core, the extrusion of a nitrogen molecule proceeds as a synchronous process with an energy barrier of 15–20 kcal mol^{-1}. The energy of biradical transition states corresponding to potential stepwise mechanism of the reaction is much higher, which makes this mechanism hardly probable.

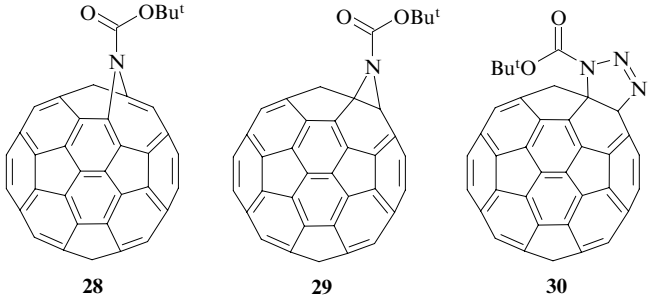
III. Reactions of azides with fullerene

Aza analogues of carbenes, *i.e.*, nitrenes, which can be generated *in situ* by the thermal decomposition of azides behave similarly in cycloaddition reactions, resulting in [6,6]-closed fulleroaziridines. However, it was found [30] that the reaction of fullerene with azidoformates **24** yields closed adducts **25** together with an appreciable amount of [5,6]-open isomers **26** (the reactions were accomplished under drastic conditions where azidoformates undergo thermal decomposition to nitrenes). Additionally, fullerooxazolines **27**, which are the thermal rearrangement products of alkoxycarbonyl fulleroaziridines, were isolated.



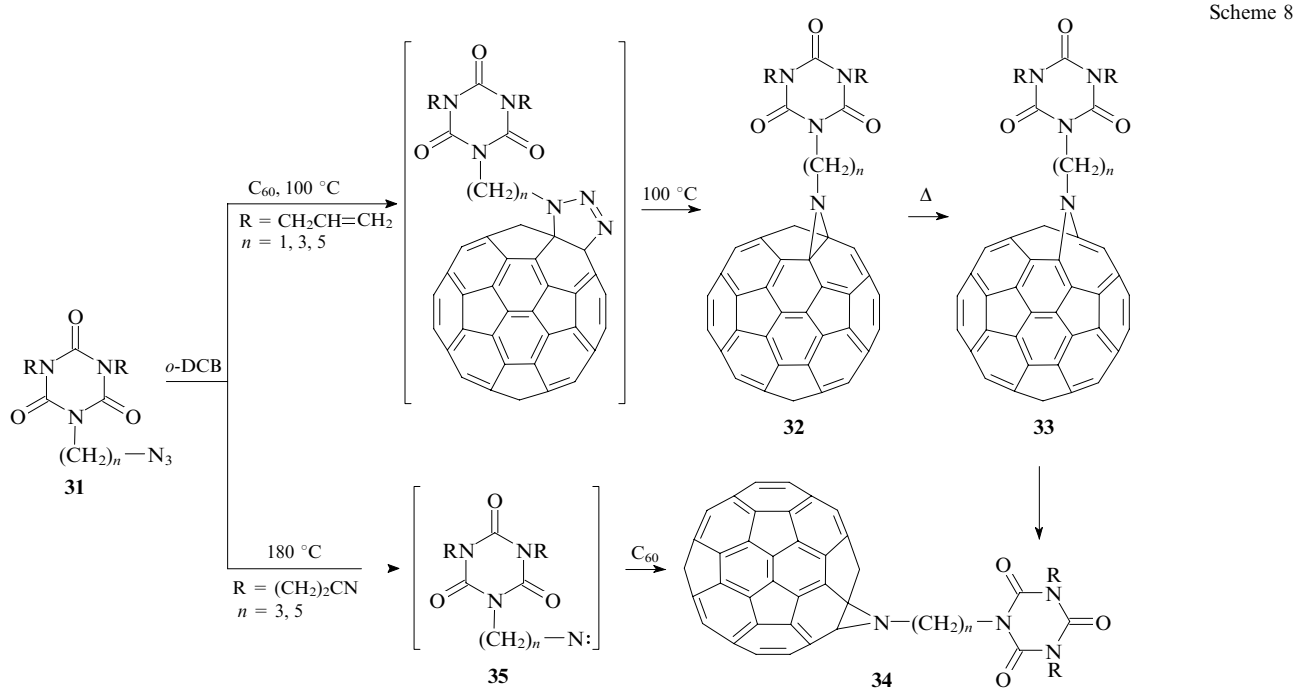
R = Et (**a**), Bu^t (**b**), 2,4,6-Bu$^t_3$C$_6$H$_2$ (**c**).

Schick *et al.* [31] reported the following synthesis. A concentrated solution of fullerene C_{60} in 1-chloronaphthalene was heated at 60 °C in the presence of $N_3CO_2Bu^t$ (1 equiv.); such conditions are typical of the formation of fullerotriazolines. Then the reaction mixture was diluted tenfold with toluene and heated at 120 °C to give a mixture of [5,6]-open and [6,6]-closed adducts (**28** and **29**, respectively) in a ratio 16 : 3. This result clearly demonstrates the preferred formation of the open fulleroid upon the thermal decomposition of fullerotriazoline **30**. Under the conditions of nitrene generation (*i.e.*, thermal decomposition of N_3CO_2Et), the [6,6]-closed aziridinofullerene is the major reaction product with fullerene.



The reactions with akyl azides typically afford [5,6]-open adducts, which can further rearrange into more stable [6,6]-closed isomers. Less stable acyl azides preferably yield [6,6]-closed adducts. This can be explained by the fact that the reaction of alkyl azides with fullerene follows the 1,3-dipolar cycloaddition mechanism giving rise to unstable triazolines that further decompose to [5,6]-open adducts. The thermal decomposition of acyl azides proceeds more readily, the resultant nitrenes react with fullerene to yield the [6,6]-closed adducts. Most probably, the nitrene attack occurs to the shortest and most reactive [6,6] bond of fullerene. This conclusion is supported by the fact that the addition of singlet carbenes and silylenes always occurs to the [6,6] bond yielding the respective closed adducts.[32, 33] Nevertheless, the reasons for the formation of [5,6]-open isomers in some reactions of fullerene with oxacarbonylnitrenes remain unclear.[34] Banks *et al.* [35] formulated two hypotheses. According to one of them,

Scheme 8



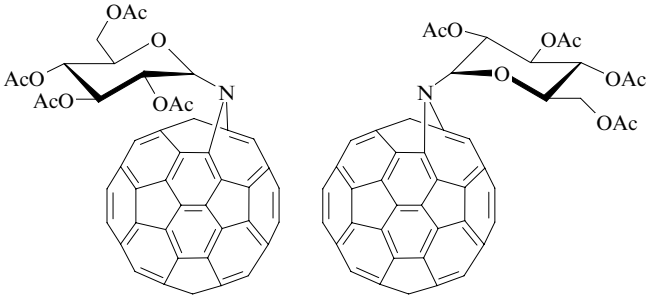
R = $CH_2CH{=}CH_2$, $(CH_2)_2CN$.

open adducts are formed directly upon the addition of a singlet nitrene to the [5,6] bond. According to another hypothesis, the addition of the remaining triplet nitrene to fullerene can result in a mixture of [5,6] and [6,6] regioisomers. The former hypothesis is supported by calculations,[36] which demonstrated that the [5,6] and [6,6] bonds are comparable in reactivities from both thermodynamic and kinetic viewpoints under the conditions of the nitrene addition to fullerene.

Within the context of investigations into the cycloaddition reactions of isocyanurate-substituted alkyl azides (**31**) to fullerene (Scheme 8), [5,6]-closed isomer **32** has been detected for the first time and convincing spectroscopic evidence for its existence has been gathered: in particular, its ^{13}C NMR spectrum revealed two signals assigned to the two sp^3-hybridised carbon atoms of the fullerene core.[37, 38]

The reaction of C_{60} with 5-(5-azidopentyl)-1,3-diallyl-1*H*,3*H*,5*H*-1,3,5-triazine-2,4,6-trione ($n = 5$) at 100 °C affords in a preparative yield [5,6]-closed isomer **32**, which is successively converted first into [5,6]-open isomer **33** and then into the thermodynamically most stable [6,6]-closed aziridinofullerene **34**. Under more drastic conditions (180 °C), the reaction with 1,3-bis(cyanoethyl)-substituted azide affords closed adduct **34** alongside with the dimerisation product of the intermediate nitrene **35**, which strongly supports the dominance of the nitrene mechanism at high temperature.

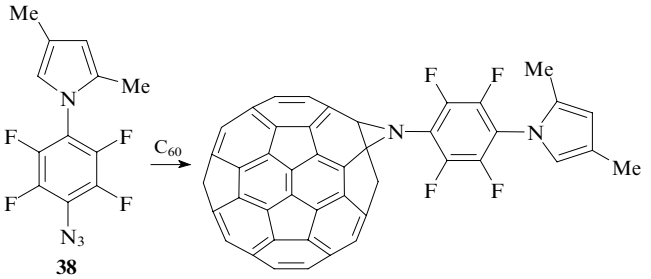
The cycloaddition of per-*O*-acetylglycosyl azides to C_{60} was used[39] for the preparation of fullerene glycoconjugates; this reaction yielded a mixture of open stereoisomers **36** and **37** in a ratio 2 : 1.



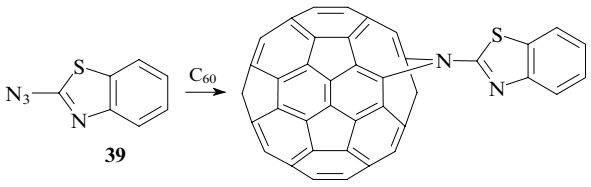
36 **37**

Compounds with fullerene and porphyrin moieties linked by a polyether linker were synthesised in a similar way.[40] The cycloaddition of azides was used to introduce a pharmacophore acridine group (known by its activity with respect to DNA) into fullerene.[41] Fulleroid cycloadducts were obtained in all these cases.

Jagerovic *et al.*[42] considered the dependence of the direction of cycloaddition on the azide structure using aryl and hetaryl azides. It is known that the nitrene addition occurs to the double [6,6] bond to yield closed fulleroaziridines, whereas the initial 1,3-dipolar cycloaddition yields triazoline intermediate, which converts into [5,6]-open π-azafulleroids upon subsequent extrusion of nitrogen. The [6,6]-closed and [5,6]-open cycloadducts are formed from aromatic and heterocyclic



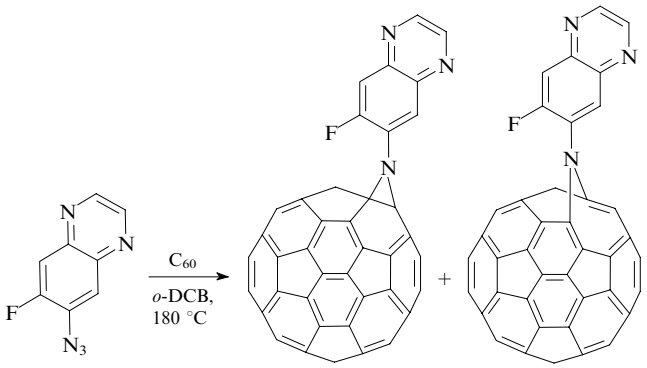
38



39

azides **38** and **39**, respectively. However, the authors did not comment this experimental result.

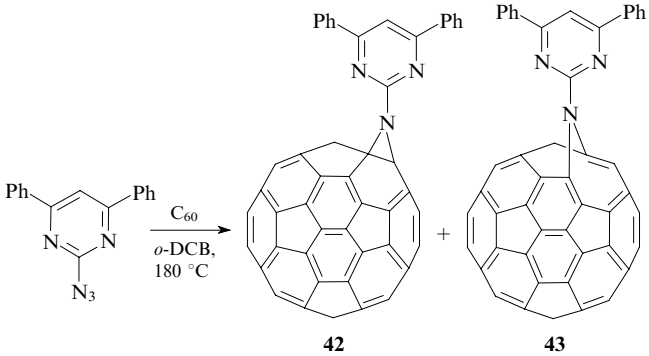
The reaction of C_{60} with 7-azido-6-fluoroquinoxaline in *o*-DCB at 180 °C yields a mixture of [6,6]-closed (**40**) and [5,6]-open (**41**) isomers with predominance of the former one.[43]



40 **41**

The structure of [6,6]-closed isomer **40** was reliably established by ^{13}C NMR spectroscopy. Unfortunately, the available amount of compound **41** was insufficient for the collection of NMR spectra and thus its assignment to the [5,6]-open isomer was made on the basis of the UV spectrum that revealed no narrow weak band at $\lambda_{max} = 425$ nm typical of the closed isomer **40**.

Similar results were obtained for the reaction of fullerene with 2-azido-4,6-diphenylpyrimidine.[44]

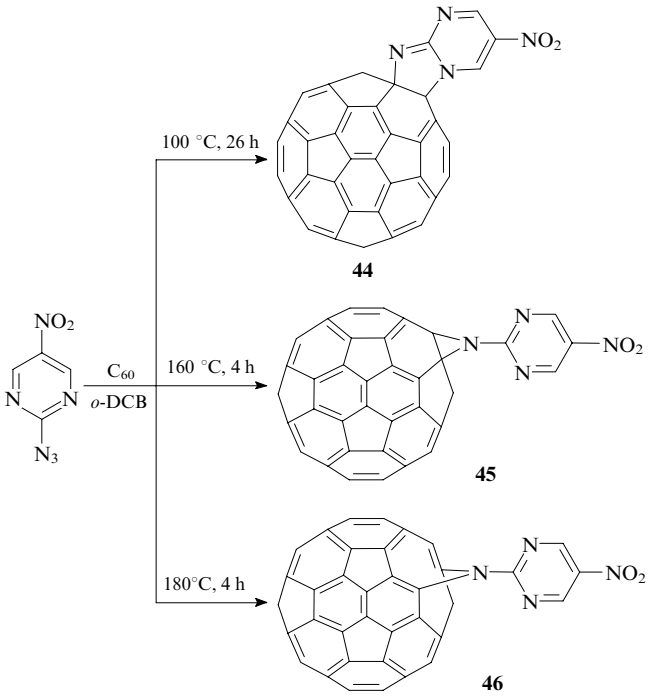


42 **43**

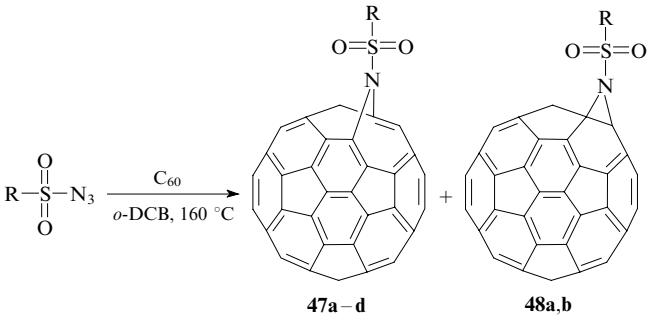
Studies of the electrochemical reduction of compounds **40**–**43** bearing quinoxaline and pyrimidine fragments by means of cyclic voltametry revealed that they represent first fulleroaziridines that are stronger electron acceptors than the parent fullerene.[43, 44]

Different products can be obtained in the reaction of fullerene C_{60} with 2-azido-5-nitropyrimidine, depending on the reaction conditions.[45, 46] In particular, 4-nitro[60]fullero[1′,2′ : 4,5]imidazo[1,2-*b*]pyrimidine (**44**) was obtained upon heating at 100 °C in *o*-DCB; [6,6]-closed 5-nitro-2-{[60]fullereno[1,2-*b*]aziridino}pyrimidine (**45**) was obtained in a 13% yield at 160 °C; and azahomofullerene **46** is formed at a higher temperature (Scheme 9). It is of note that the reaction products do not undergo thermal interconversions.

Scheme 9

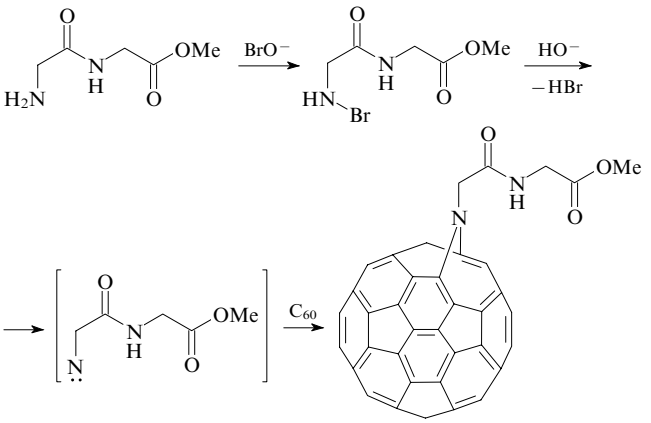


The reaction of alkylsulfonyl azides with fullerene yields a mixture of open (**47a**,**b**) and closed (**48a**,**b**) adducts, whereas that with arylsulfonyl azides affords exclusively open fulleroids **47c**,**d**. All open fulleroids synthesised in this way undergo the photochemical rearrangment into [6,6]-closed fulleroaziridines.[47]

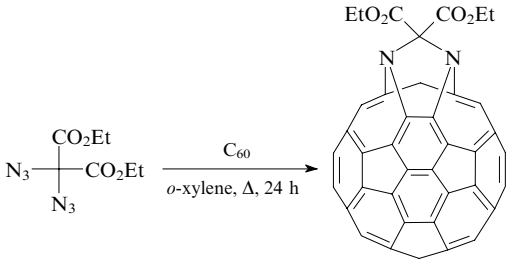


R = Me (**a**), Bn (**b**), 4-MeC$_6$H$_4$ (**c**), 4-MeOC$_6$H$_4$ (**d**).

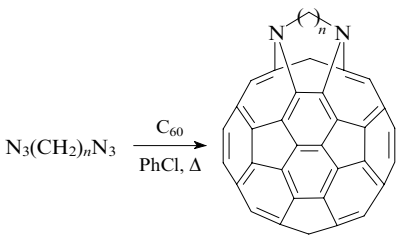
The possibility of oxidative generation of nitrene from glycylglycine methyl ester enabled the synthesis of a dipeptide with a fulleroid substituent.[48]



Bisazides are added to two fullerene [5,6] bonds giving rise to fulleroid structures. In particular, the reaction of C_{60} with diethyl diazidomalonate in boiling xylene affords a 1 : 1 adduct representing a bis(aza)fulleroid in a 65% yield.[49]

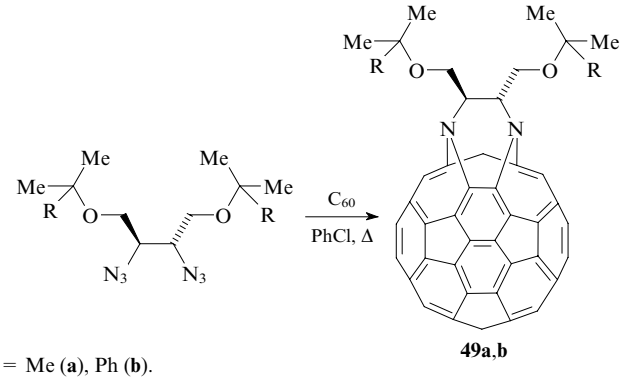


The bis-addition proceeds regioselectively: it still involves two [5,6] bonds of the same five-membered ring of fullerene even when the azido groups are separated by two or three methylene units.[50]



n = 2, 3.

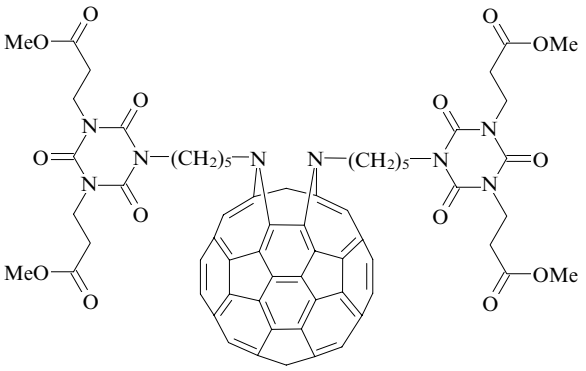
The reaction of C_{60} with chiral 1,4-di(*tert*-alkoxy)-2,3-bis(azido)butanes affords the respective chiral bis(aza)fulleroids (2*R*,3*R*)-**49a**, (2*S*,3*S*)-**49a**, (2*R*,3*R*)-**49b** and (2*S*,3*S*)-**49b** in yields of 54%, 49%, 56% and 51%, respectively.[51]



R = Me (**a**), Ph (**b**).

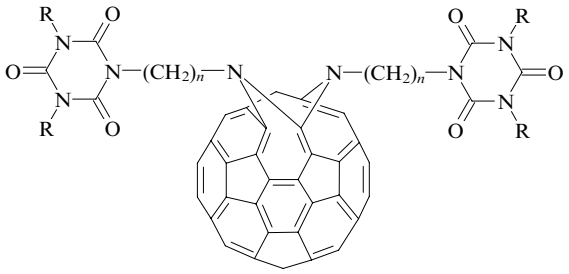
It turned out that the regioselective synthesis of azahomofullerene bisadducts is possible even with monoazides. In particular, the addition of isocyanurate-substituted alkyl azides to fullerene C_{60} can result in the regioselective formation of diverse azahomofullerene adducts, depending on the bulk and structure of organic substituents.[52] For instance, in the case of isocyanurate groups with methoxycarbonylethyl substituents at the nitrogen atom, an open bisadduct **50** similar to those described above is obtained owing to the azide addition to two [5,6] bonds.

Bisadducts with different structures were unexpectedly formed upon changes in the substituent R at the nitrogen atom in the isocyanurate-substituted alkyl azides virtually independent of the length of the methylene spacer between the azido group and the heterocycle. The structure of adducts **51a**,**b** was postulated [52] due to the presence of a signal at



50

δ = 160 in their ^{13}C NMR spectra, which is typical of carbon atoms bonded to two nitrogen atoms.

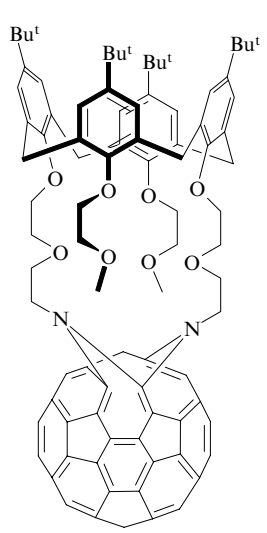


51a,**b**

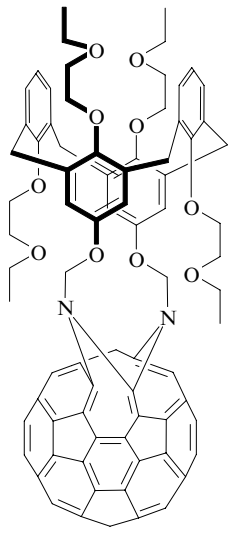
R = $CH_2CH{=}CH_2$: n = 2, 3, 5 (**a**); R = $(CH_2)_2CN$, n = 5 (**b**).

In our opinion, this single argument is insufficient for the unambiguous determination of the structure that has to be confirmed by X-ray crystallography. The possible pathway to various azahomofullerene bisadducts proposed by the researchers cited is shown in Scheme 10.

The similar bis(aza)fulleroid structure was proposed for fullerene-containing calix[4]arene derivatives (*e.g.*, compounds **52** and **53**) capable of exohedral complex formation with Li^+, Na^+ and Ag^+ cations. In the [5,6]-open structures formed, one carbon atom of the fullerene part of the adduct is bonded to two nitrogen atoms.[49, 53]



52

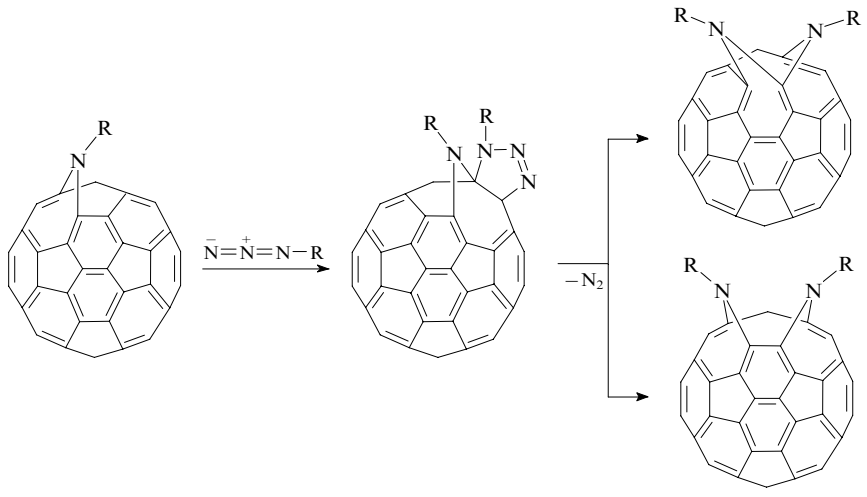


53

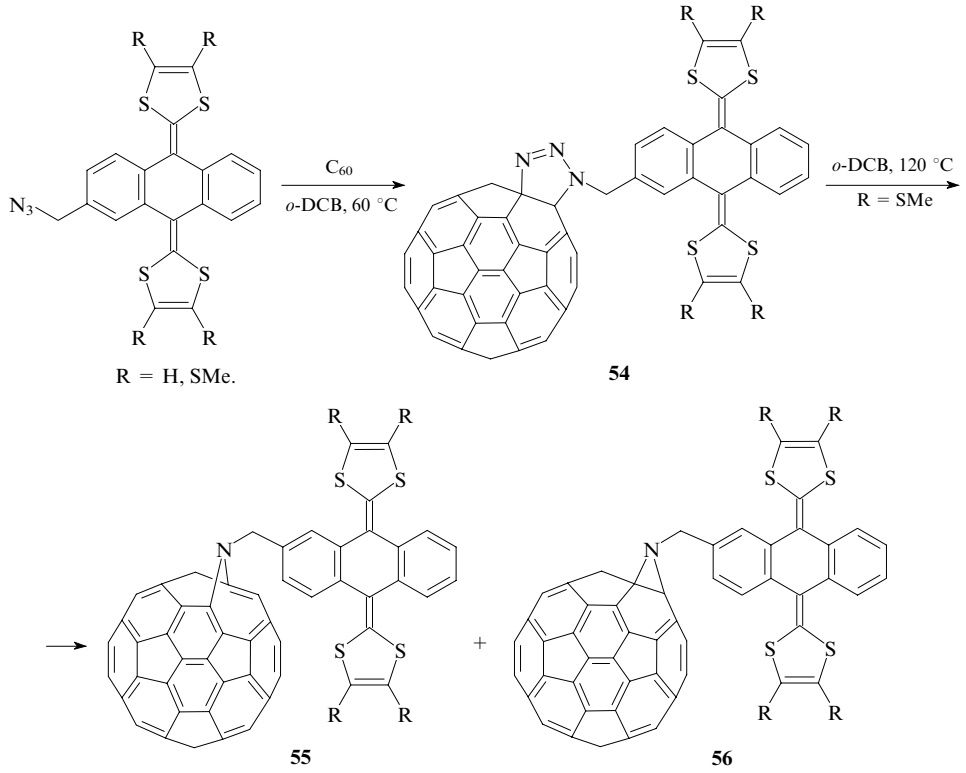
The reaction of C_{60} with tetrathiafulvalene-substituted methyl azides in *o*-dichlorobenzene with heating in an argon atmosphere for 4 h yields [60]fullero[1,2-*e*]-triazolines stable in the solid state at room temperature; the products include initially formed triazoline **54**, azafulleroid **55** (20%) and traces of fulleroaziridine **56** (Scheme 11).[54]

The mechanism of the reaction involving the 1,3-dipolar cycloaddition of methyl azide to fullerene C_{60} followed by the extrusion of a nitrogen molecule was theoretically substantiated using quantum chemical calculations at the semiempirical level and within the density functional theory.[55] According to the results obtained, the azide addition occurs to the [6,6] double bond to yield the triazoline intermediate, which is characterised by the energy barrier of $\sim$20 kcal mol^{-1} and an exothermic effect of $\sim$2 kcal mol^{-1} (according to B3LYP/6-31G*//AM1 calculations). The subsequent thermal extrusion follows the stepwise mechanism with the cleavage of an N–N single bond followed by the cleavage of a C–N bond with an overall activation energy of $\sim$45 kcal mol^{-1}. The N_2 elimination occurs simultaneously with the formation of a new C–N bond. During this process, the steric influence of the outgoing N_2 molecule prevents the nitrene addition to the [6,6]

Scheme 10

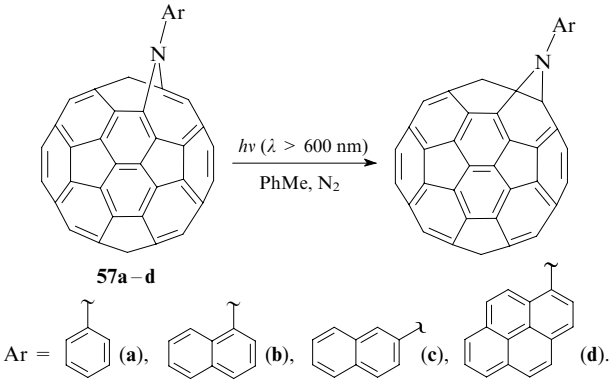


Scheme 11



bond thus enhancing the probability of the addition to the [5,6] bond.

It turned out that substituents at the azafulleroid nitrogen atom strongly affect the rate of the photochemical rearrangement into fulleroaziridines.[56]



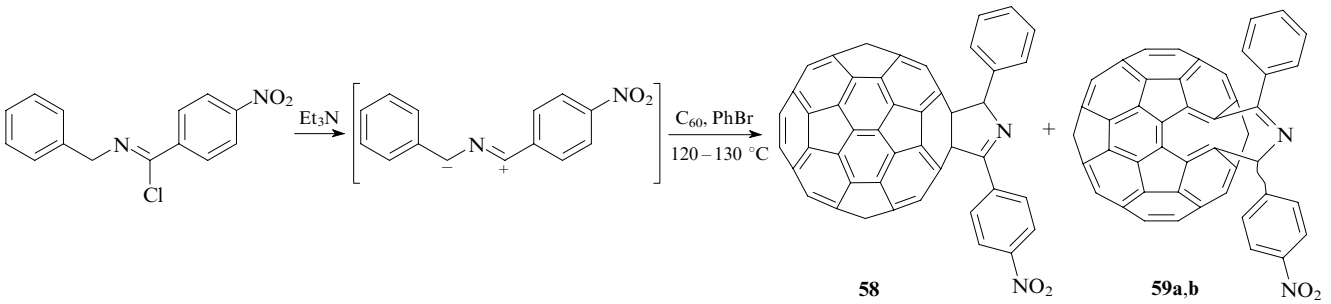
In particular, times for the completion of the reaction are 1440 : 1 : > 2160 : 360 for a series of derivatives **57a**–**d**. Thus, the rates of the photochemical rearrangement differ by a factor of more than 2000 between the most (**57b**) and least (**57c**) reactive compounds. Photolysis of compounds **57a**–**d** in air-saturated solutions proceeds much more slowly, which implies intermediacy of the triplet state of the starting azafulleroid.

IV. Reactions of nitrile ylides with fullerene

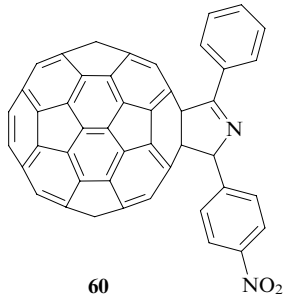
In all cases described in the early literature, only [6,6]-closed cycloadducts were obtained with fragments of five-membered heterocycles annulated to the fullerene spheroid. Unexpectedly, it was found [57] that the 1,3-dipolar cycloaddition of nitrile ylides to C_{60} can also yield [5,6]-open fulleroid isomers. Indeed, the cycloaddition of 1-(4-nitrophenyl)-3-phenylnitrile ylide generated *in situ* from *N*-benzyl-4-nitrophenylimidoyl chloride under the action of triethylamine at 130 °C yields [6,6]-closed [60]fullero[1,2-*c*]-5-(4-nitrophenyl)-2-phenyl-2*H*-3,4-dihydropyrrole (**58**) along with a mixture of diastereomeric [5,6]-open fulleroid cycloadducts **59a**,**b** in a ratio 2 : 1 (Scheme 12). The C=N double bond in the open cycloadducts **59** is in the α-position with respect to the unsubstituted phenyl group, whereas it is in the α-position with respect to the nitrophenyl substituent in the [6,6]-closed isomer.

Under milder conditions (toluene, room temperature), this reaction yields another set of cycloadducts with no open

Scheme 12



isomers.[58] In that case, isomeric compounds **58** and **60** differing in the position of a double bond were isolated.

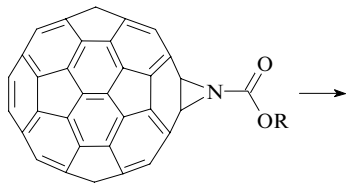


60

In our opinion, the nitro group can stabilise the biradical mesomeric form of the ylide, which enables the stepwise addition of the radical form to fullerene yielding open structures in addition to the concerted [6,6]-addition of the dipolar form yielding the closed adduct at high temperature.

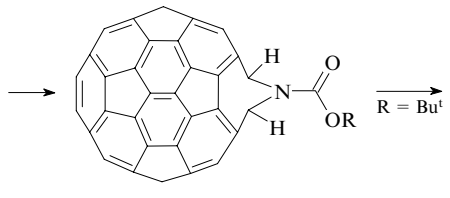
V. The formation of fulleroid structures with an open [6,6] bond

The unusual opening of the fullerene sphere has been discovered for the first time[59] in the reduction of *N*-alkoxycarbonyl[60]fullero[1,2-*b*]-aziridines (**61**) with zinc or magnesium in glacial acetic acid. This reaction yields fulleroids **62** with an open [6,6] bond. In the case of R = Bu^t, the removal of the *tert*-butoxycarbonyl protection with 50% aqueous CF_3CO_2H provides a convenient synthetic route to $C_{60}H_2NH$ (**63**), which is a parent compound of a new class of fulleroids. Under the action of a base (*e.g.*, 1,4-diazabicyclo[2.2.2]octane), compound **63** converts in several minutes into fulleroaziridine **64**.

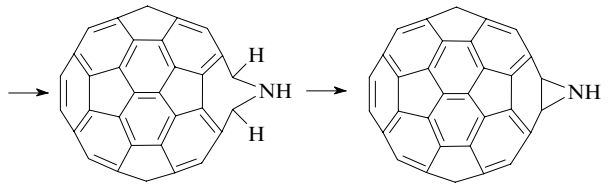


61

R = Et, Bu^t, CCl_3CH_2, 9-fluorenylmethyl



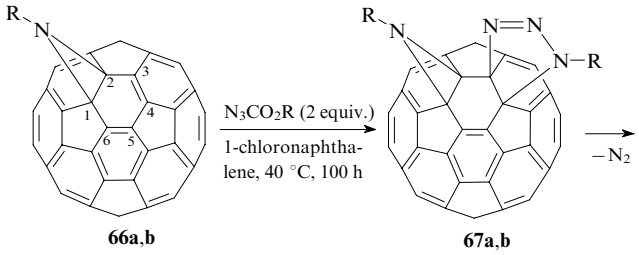
62



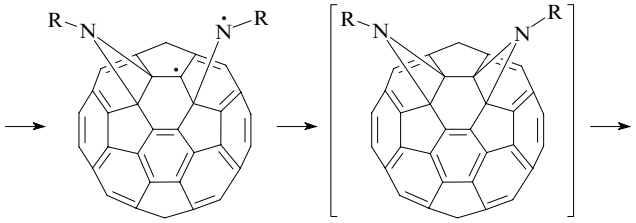
63 **64**

This reaction is of general character, compounds **61** bearing diverse substituents (R = Bu^t, Et, Cl_3CCH_2 or 9-fluorenylmethyl) can readily be reduced to derivatives **62** in yields of >90%.

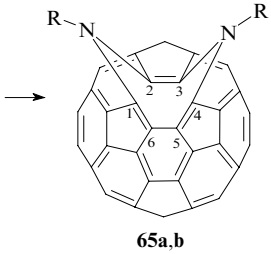
In addition to regioisomeric [6,6]-closed bis(imino)fullerenes, *cis*-1-isomeric bisadducts **65**, which represent the first example of fullerene derivatives with open [6,6]-transannular bonds, were isolated in the bisfunctionalisation of C_{60} with monoazides (*e.g.*, ethyl and *tert*-butyl azidoformates).[60]



66a,b **67a,b**



68a,b

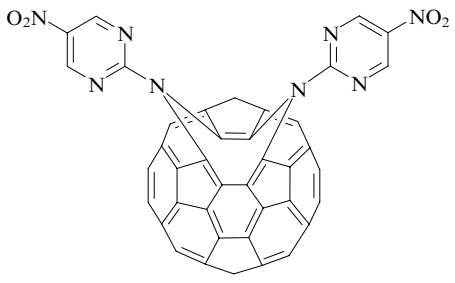


65a,b

R = Et (**a**), Bu^t (**b**).

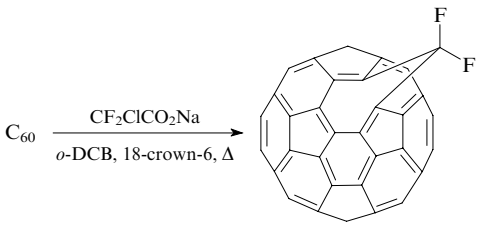
A relatively regioselective synthesis of compounds **65** was accomplished starting from monoiminofullerenes **66** *via* highly reactive intermediates **67** generated upon [3 + 2]-cycloaddition with a negatively polarised (R)N atom atached to a positively polarised C(4) atom of the adjacent non-functionalised [6,6] bond. Such a polarisation of bonds in the carbon cages of molecules **66** is supported by calculations using the AM1 method. The thermal extrusion of nitrogen gives rise to biradical intermediates **68**. Due to the localisation of the first addend at the same six-membered ring, normal spin density delocalisation over this ring [*i.e.*, spin density transfer to the C(5) atom] becomes impossible and thus the radical recombination can occur only for the radical site localised at the C(3) atom. Consequently, the formation of 1,2;3,4-bis(imino)[60]-fullerene isomer prevails. The subsequent retro-Diels–Alder reaction (or $2\pi - 2\sigma$ isomerisation) results in compounds **65**.

Similar formation of a bisadduct with [6,6]-open transannular bonds was also observed in the reaction of C_{60} with 2-azido-5-nitropyrimidine.[61]



It is of note that this adduct undergoes the electrochemical oxidation more readily than fullerene C_{60}.

It is well known that the reaction of C_{60} with dihalocarbenes (CCl_2 and CBr_2) yields closed [6,6]-dihalomethanofullerenes.[62–64] Nevertheless, as has been found recently,[65] [6,6]-difluoromethylene-homo[60]fullerene (**69**) can be synthesised by the reaction of C_{60} with CF_2ClCO_2Na in *o*-DCB in the presence of 18-crown-6.



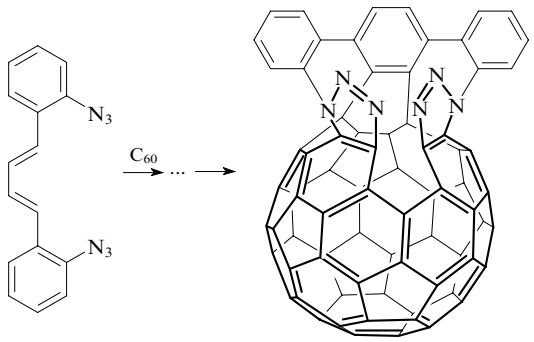
69

This open monoadduct is the major reaction product (the yield of pure compound is 19%), whereas polyadducts $C_{60}(CF_2)_n$ ($n = 2$, 3) and minor [5,6]-open isomeric monoadduct are formed as by-products. The structure of the adduct **69** was reliably established by mass spectrometry (MALDI), ^{19}F and ^{13}C NMR, UV and IR spectroscopy and further confirmed by quantum chemical calculations.

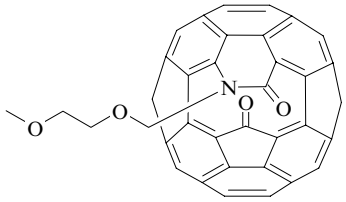
VI. The formation of miscellaneous fulleroid structures

The reaction of C_{60} with diazide **70** is also accompanied by the opening of the fullerene sphere. The oxidation of the intermediate yields bislactam **71** with an open carbon cage capable of accomodating foreign small molecules (He or H_2) (Scheme 13).[66, 67]

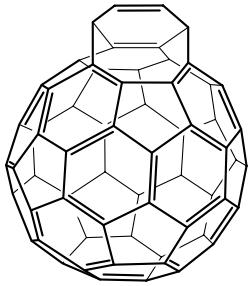
The addition of 1,4-bis(2-azidophenyl)buta-1,3-diene to fullerene is accompanied by complex rearrangements of both the fullerene cage and the addend finally resulting in an open derivative with two fused triazole rings.[68]



A fulleroid keto lactam containing an 11-membered ring was synthesised[69] by the reaction of C_{60} with methoxyethoxymethyl azide.



A fulleroid with an eight-membered ring in the fullerene cage is obtained from the fullerene adduct with 1,3-cyclohexadiene by the photochemical intramolecular [4 + 4]-cycloaddition followed by the ring opening.[70, 71]

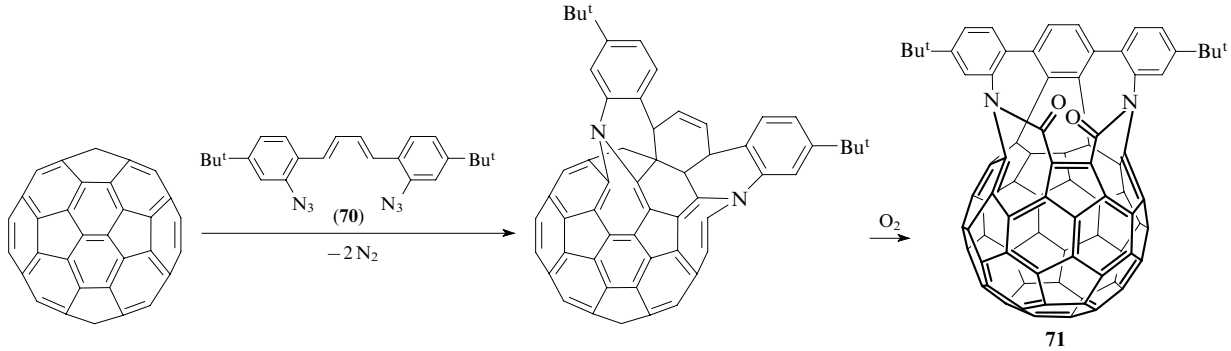


Fulleroid structures with eight-membered rings in the fullerene cages were synthesised in a similar way by the reaction of C_{60} with nickela-[72] and palladacyclopentadiene[73] derivatives and phthalazine.[74] The direction of the reaction of C_{60} with phthalazine (**72**) depends on the reaction conditions. In particular, a fulleroid structure **73** with an eight-membered ring in the fullerene cage is formed in 1-chloronaphthalene at 225 °C, whereas the mechanochemical solid-state synthesis yields fullerene dimer **74**. The authors argue that both processes start with the [4 + 2]-cycloaddition stage.[74, 75] A tentative mechanism of these reactions for di- and triazines is depicted in Scheme 14.[74–76] It involves the following principal stages: the [4 + 2]-cycloaddition of azines to the [6,6] bond of fullerene, the elimination of a nitrogen molecule, the radical [4 + 4]-cycloaddition[74] and finally the retro-[2 + 2 + 2]-process giving rise to the eight-membered ring.

Similarly, the thermal reaction of C_{60} with a 1,2,4-triazine derivative yields an open fulleroid **75** with an eight-membered ring.[75]

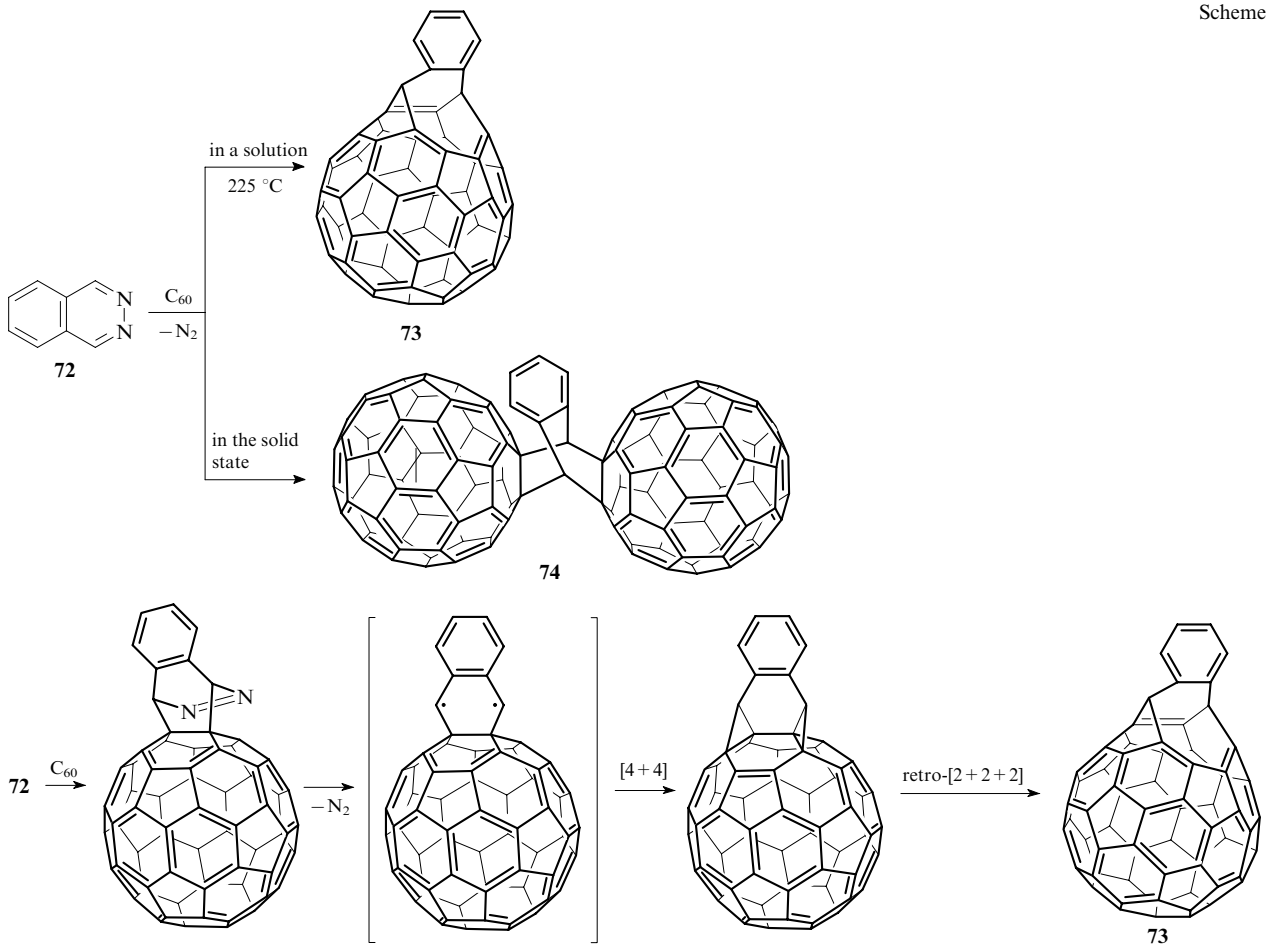
Oxidation of all aforementioned open fulleroids with an eight-membered ring in the cage gives rise to open structures

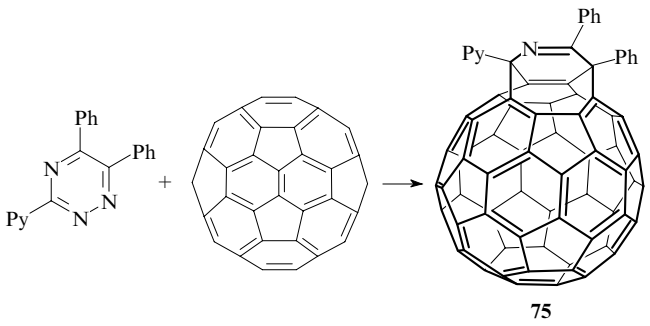
Scheme 13



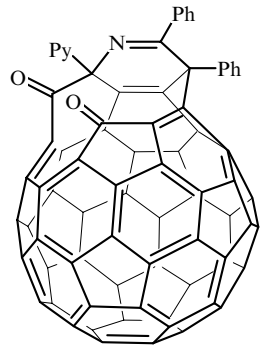
71

Scheme 14





with 12-membered rings [75–78] (compound **76** can serve as an example). In addition, open structures with 11- and 13-membered rings in the fullerene core were obtained as oxidation products.[75]



The reaction of fulleroperoxide $C_{60}(O)(OOBu^t)_4$ with aluminium chloride yields [5,6]- and [6,6]-oxahomo[60]fullerenes owing to the oxidative cleavage of the [5,6] and [6,6] bonds in the fullerene cage.[79]

There are experimental data [80–82] confirming the existence of fluoro derivatives of [6,6]-open oxahomofullerene, in which the oxygen atom is bonded to the fluorinated carbon atoms of the fullerene core.

As has unexpectedly been found, the fluorination of C_{60} with binary fluorides with the general formula $Cs_xPbO_yF_z$ in vacuum at 550 °C yields two stable polyfluorofullerenes $C_{58}F_{18}$ (**77**) and $C_{58}F_{17}CF_3$ (**78**), which represent open structures with a seven-membered ring (Fig. 1).[83]

The structures of these compounds were established using mass spectrometry and ^{19}F NMR spectroscopy. The authors suggested that the C_{60} molecules lose a carbon atom through the steps of fluorine atom addition to the single C—C and the

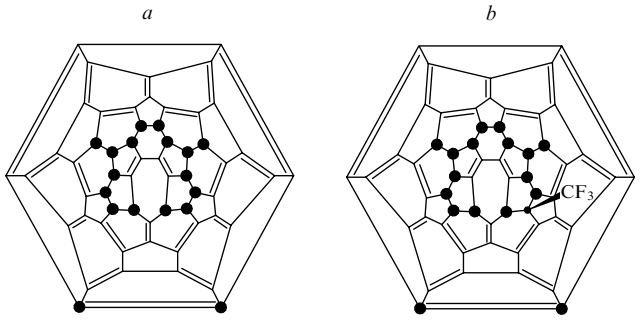


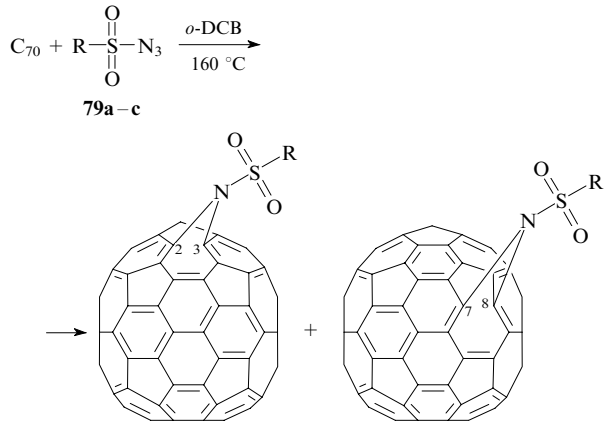
Figure 1. The Schlegel diagrams of open fullerene derivatives $C_{58}F_{18}$ (**77**) (*a*) and $C_{58}F_{17}CF_3$ (**78**) (*b*). Black circles denote the addition sites of F atoms.

conjugated double C=C bonds followed by elimination of difluorocarbene.

VII. The formation of open homo[70]fullerenes

Chemistry of fullerene C_{70} is studied in much less detail than that of fullerene C_{60} due to its lower accessibility. Nevertheless, there are some examples of the formation of open structures derived from fullerene C_{70}.

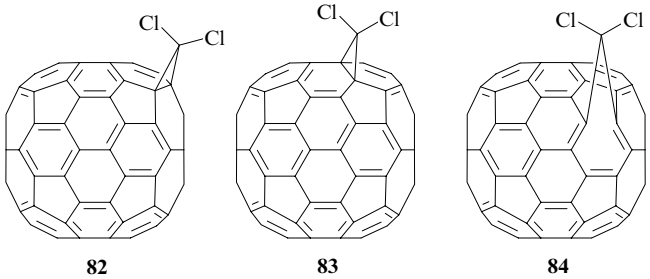
In contrast to fullerene C_{60}, even monofunctionalisation of C_{70} gives rise to mixtures of regioisomers due to its lower symmetry and larger differences in the reactivity of bonds. Four [6,6]-closed and four [5,6]-open isomeric adducts are possible.



R = 4-MeC_6H_4 (**a**), 4-$MeOC_6H_4$ (**b**), Me (**c**).

Ulmer and Mattay[47] studied the reaction of C_{70} with sulfonyl azides. It is of note that in this case, in contrast to the analogous reaction with C_{60}, only open adducts are formed. These reactions with azides **79a**,**b** afford two [5,6]-open isomers **80a**,**b** (in yields of 9% and 10%, respectively) and **81a**,**b** (in yields of 6% and 7%, respectively). Meanwhile, the reaction with azide **79c** yields only one fulleroid **80c** (12%).

The reaction of C_{70} with $PhHgCCl_2Br$, which produces dichlorocarbene upon heating, affords[84] three monoadducts (**82**, **83**, **84**) in a ratio of 35 : 37 : 29 along with polyadducts. Among the products, the adduct **84** is a [5,6]-open fulleroid.



The reaction of C_{60} with carbenes yields exclusively [6,6]-closed methanofullerenes, in contrast to the situation with C_{70}.

It is known that it is the [5,6] bond between the atoms C(7) and C(8) of fullerene C_{70} that is involved in the addition of dehydobenzene resulting in a [5,6]-closed adduct.[85] The authors suggested that the reaction of C_{70} with dichlorocarbene begins with the carbene addition to the [5,6] bond to form a [5,6]-closed methanofullerene, which subsequently undergoes the norcaradiene rearrangement to afford a [5,6]-open fulleroid.

VIII. Theoretical investigations into the possible formation of open adducts in the cycloaddition reactions

The mechanisms of the 1,3-dipolar cycloaddition of diazomethane, nitrile oxide and nitrone to fullerene C_{60} have been simulated[86] by *ab initio* calculations at the B3LYP/6-31G(d,p)//AM1 level. All four possible types of the addition giving rise to [6,6]-closed, [6,6]-open, [5,6]-closed and [5,6]-open adducts have been considered. According to the calculations, the cycloaddition processes resulting in [5,6]-closed and [6,6]-open adducts are endothermic, whereas those resulting in [6,6]-closed and [5,6]-open adducts are exothermic. Among all the aforementioned dipolar ylides, the formation of [6,6]-closed adducts is most favourable from both the kinetic and thermodynamic viewpoints. This process has to follow the concerted mechanism. Qualitatively, this theoretical result can be explained by three factors:

— open structures are more strained than closed ones;

— three and two double bonds in five-membered rings appear in [5,6]-closed and [6,6]-open adducts, respectively, which is energetically unfavourable;

— the [6,6] bonds are characterised by higher electron density than the [5,6] bonds, which enables more efficient overlap of the frontier orbitals upon the [6,6]-addition.

Similar to the case of methanofullerenes and their open isomers, [6,6]-closed aziridinofullerenes are calculated to be more stable than [5,6]-azafulleroids, whereas [6,6]-open and [5,6]-closed isomers should be least stable.[36, 87, 88]

IX. Conclusion

The literature data summarised in the present review suggest that the presently available experimental results and theoretical studies are insufficient for comprehensive understanding of the mechanisms governing the formation of fulleroids. Furthermore, some experimental facts and rationales for the formation of open structures contradict each other. Nevertheless, certain common regularities behind the cycloaddition processes resulting in open adducts can be revealed, which allows us to make some suggestions on the mechanism of the fulleroid formation.

1. With a high level of confidence it can be assumed that open structures are produced as a result of rearrangement or decomposition of an initially formed closed adduct in the majority of systems studied except for nitrile ylides and a few other nitrenes.

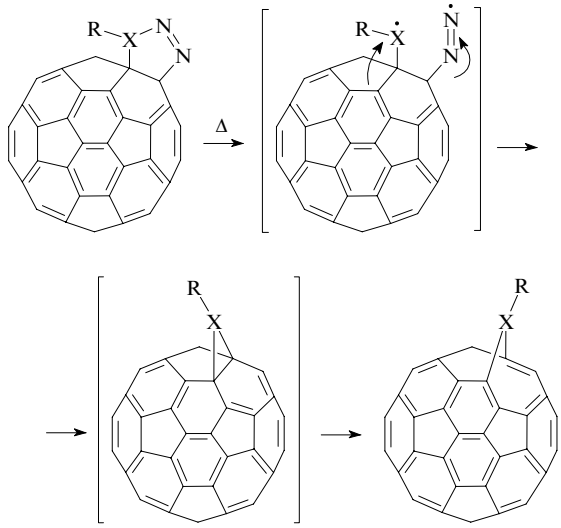
2. Very likely, synchronous addition to the [6,6] bond typically occurs, to yield closed fullerene adducts. This suggestion is supported by both theoretical calculations and numerous experimental data. The available data on the formation of open structures upon the addition of nitrenes, carbenes, diazo compounds, azides and dienes to fullerene suggest that a [6,6]-closed adduct is formed initially but then it is transformed into a fulleroid structure. Nevertheless, some theoretical calculations[35, 36] point to possible direct addition of nitrenes to the [5,6] bond to yield an open adduct.

3. Open and closed isomers are prone to interconversions, which often do not follow simple structure – stability relationships. In the majority of cases, [6,6]-closed isomers are thermodynamically most stable. Open adducts can transform into closed ones by thermal, photochemical or electrochemical isomerisations; for the opposite process, only thermal rearrangements have been described.

4. Hardly there is a single mechanism explaining the formation of any open structure; several routes to fulleroids can be envisaged.

The first, most common mechanism consists of the thermal decomposition of fulleropyrazolines and fullerotriazolines initially formed upon cycloaddition. The extrusion of a nitrogen molecule proceeds simultaneously with the formation of a new C—X bond, three-membered rings involving a [5,6] bond being preferably formed due to the steric effects of the outgoing nitrogen molecule, *i.e.*, [5,6]-closed adducts are formed. They undergo rapid rearrangements into more stable [5,6]-open fulleroids (Scheme 15).

Scheme 15



X = N, CR′.

An alternative is represented by thermal rearrangements of [6,6]-closed methanofullerenes bearing bulky substituents that induce substantial steric strains in the three-membered ring thus making [5,6]-open isomers thermodynamically more stable. The mechanism of such rearrangements remains unclear.

The third route consists of the formation of [5,6]-open adducts directly as a result of the 1,3-dipolar cycloaddition of specific nitrile ylides to fullerene. Probably, this reaction proceeds as successive addition of nitrile ylide in the biradical form, which gives rise to fulleroids.

There are a number of reactions resulting in the cleavage of a [6,6] bond in the fullerene sphere or even a few σ-bonds at once. These transformations follow different mechanisms that cannot be unified within a single principle. The C—C σ-bonds in a fullerene cage can be cleaved upon the oxidation, reduction or rearrangements.

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