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Organic chemistry of fullerenes: the major reactions, types of fullerene derivatives and prospects for their practical use

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Abstract. Data on the methods of functionalisation of C_{60} and C_{70} fullerenes published in the past 15 years are summarised. The general analysis of fullerene reactivity is performed. Reactions of nucleophilic and radical addition and cycloaddition are considered in detail. The prospects of using fullerene derivatives as medicinal drugs and photoactive materials in light converting devices are demonstrated. The bibliography includes 337 references.

I. Introduction

Directed synthesis of compounds aimed at their practical use is one of the challenges of organic chemistry. The use of fullerenes as 'building blocks' made it possible to design a large number of various molecules with valuable properties.

Thus their application in medicine seems very promising. Some compounds of [60]fullerene were employed in the photodynamic therapy of malignant tumours, others proved to be sufficiently effective bacteriostatic and fungicidal agents and the third exhibited antioxidant properties and might be useful in curing neurodegenerative diseases, for example, Parkinson's disease. Attention is focused on fullerene derivatives capable of HIV inhibition. Such compounds are already the objects of clinical trials as anti-AIDS drugs.

Fullerene compounds with alkali and alkaline earth metals (fullerides) turned out to be high-temperature organic superconductors with the transition temperature (T_c) < 40 K, while an ionic complex $[C_{60}]^-TDAE^+$ [TDAE is tetrakis(dimethylamino)ethylene] represents the only known organic ferromagnet that contains neither d- nor f-atoms.

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Various supramolecular dyads, triads and polyads based on fullerene molecules and different organic donors, namely, tetrathiafulvalenes, metallocenes, porphyrins, phthalocyanines, *etc*., attract keen attention of scientists. These systems are interesting subjects for studying the intramolecular photoinduced electron transfer. The use of fullerene as the acceptor allows the lifetime of charge-separated states to be increased by several orders of magnitude as compared with other known donor-acceptor systems. Special attention is drawn to noncovalently bonded systems built of derivatives of fullerenes and metalloporphyrins that resemble natural photosynthethetic antennas in many parameters.

Composites based on C_{60} and C_{70} derivatives with polyconjugated polymers (polyphenylenevinylenes, polythiophenes, *etc*.) serve as the materials for plastic organic solar cells with the power conversion efficiency reaching 5.0%. This field of organic photovoltaics was actively elaborated in the past decade in both research institutes and commercial firms in the USA, Germany, Austria, Japan, *etc*. The obtained results instil confidence that fullerene-based light-transforming plastics will soon find their place among the most important structural materials to be widely used in different fields of human activity.

In the years ahead, fullerene organic derivatives will become common materials to be employed both in organic electronics and as the components of pharmaceutical and makeup preparations with the production volume of hundreds and thousands of kilograms annually. An important role is given to the development of new effective approaches towards functionalisation of fullerenes by different organic compounds that would provide high yields of target products and easy introduction of required functional groups to the carbon cage.

In this review, we made an attempt to systematise information on the known methods of chemical functionalisation of C_{60} and C_{70} fullerenes and formulate the mechanisms of their major reactions. Reactions of radical and nucleophilic addition and cycloaddition are considered in most detail. The list of examples shown for each reaction type should by no means be considered as complete — we confine our consideration to examples that provide the largest amount of information and are unusual. Special attention is drawn to publications of 2005 – 2007. Unfortunately, the scope of this review did not

allow us to consider a large body of information devoted to the synthesis and studies of coordination and ionic compounds of fullerenes with metals as well as of endometallofullerenes and fullerene halides and hydrides. Several reviews devoted to fullerene fluorination,[1–3] bromination and chlorination reactions are known.[4–9] The literature on organic chemistry of fullerenes is represented by the reactions of cycloaddition [10] and the syntheses of compounds with the open fullerene cage.[11] Several new monographs on chemistry of fullerenes were published,[12,13] including that devoted to the prospects of their practical application.[14]

II. Structure of fullerenes

In contrast to diamond, graphite and carbyne, fullerenes are a molecular form of carbon. A fullerene molecule consists of sp^2-hybridised carbon atoms bound together to form a three-dimensional cage. There are 12 five-membered rings separated from one another by six-membered rings in the fullerene molecules (Fig. 1). Among fullerenes, the most widespread are C_{60} and C_{70} each representing a single structural isomer. Fullerenes C_n with $n \geqslant 76$ are called the higher fullerenes, each of them has several isomers.[15]

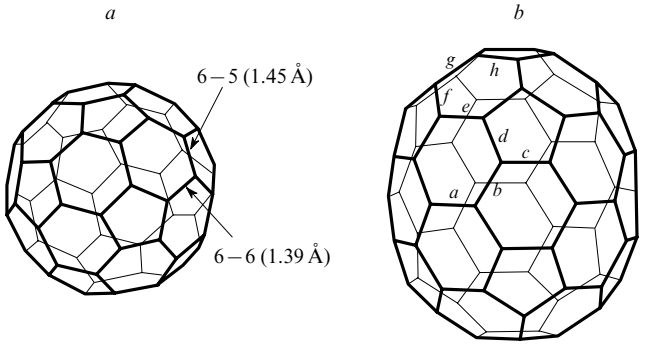


Figure 1. Carbon cages of C_{60} (*a*) and C_{70} (*b*) molecules.

The molecule of [60]fullerene possesses icosahedral symmetry (symmetry group I_h) with all carbon atoms equivalent to one another. At the same time it contains bonds of only two types, namely, between two six-membered rings (6–6 bonds) and between a six-membered and a five-membered ring (6–5 bonds) (see Fig. 1 *a*). According to the results of experimental studies and calculations,[16–19] 6–6 bonds (bond distance of 1.39 Å) in the C_{60} cage are much shorter than 6–5 bonds (1.45 Å); this is why the former are conditionally considered as double bonds and the latter are considered as single bonds in the conjugated polyene system of the carbon cage.

The C_{70} molecule (symmetry group D_{5h}) is less symmetrical as compared with C_{60}; it has 5 symmetrically non-equivalent carbon atoms and 8 types of bonds (see Fig. 1 *b*). In the C_{70} cage, the bond distances lie in the same interval as in [60]fullerene. Thus according to X-ray diffraction data,[20] a C_{70} molecule in the $C_{70} \cdot 2\,TiCl_4$ crystal structure has the following bond distances:

Bond type	Bond distance /Å	Bond type	Bond distance /Å
a	1.476	*e*	1.372
b	1.418	*f*	1.461
c	1.437	*g*	1.377
d	1.450	*h*	1.456

The presence of a large number of non-equivalent bonds in the C_{70} molecule usually leads to the formation of a mixture of isomeric products in functionalisation reactions; isolation of these products is challenging even by HPLC. This is why the chemistry of [70]fullerene is being developed rather slowly.[21]

Insofar as C_{60} fullerene has the higher symmetry and is more accessible than C_{70} and, at the same time, is virtually as good as the latter in the physical characteristics *etc*., electron affinity), it became an attractive object for chemical transformations. Of all fullerenes, only C_{60} was widely used as the 'building block' in the synthesis of functional derivatives of fullerenes.[22]

III. Analysis of fullerene reactivity

1. Specific features of multiple bonds and the major types of fullerene reactions

The main reaction mechanisms of C_{60} molecules can be extended to C_{70} fullerene with allowance made for the larger number of isomeric products formed when different reagents add to the less symmetrical cage of the latter. Below, the fullerene reactions are shown mainly by the example of C_{60} molecules.

As was mentioned above, 6–6 bonds in the C_{60} cage are substantially shorter than 6–5 bonds and assumed to be double. Thus, in their structure, six-membered rings resemble a rarely encountered cyclohexatriene with localised multiple bonds, while five-membered rings are topologically related to [5]radialene (Fig. 2 *a*, *b*).[23]

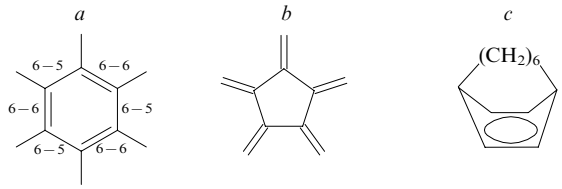
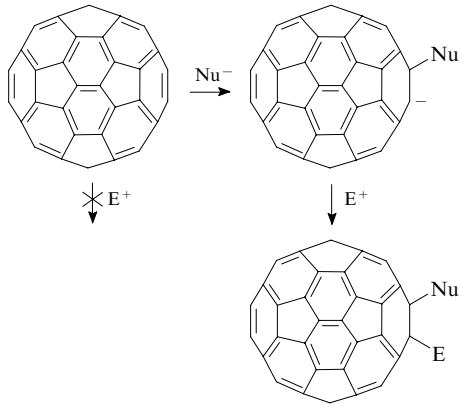


Figure 2. Structural fragments of [60]fullerene: cyclohexatriene (*a*) and [5]radialene (*b*). The structure of [6]paracyclophane (*c*).

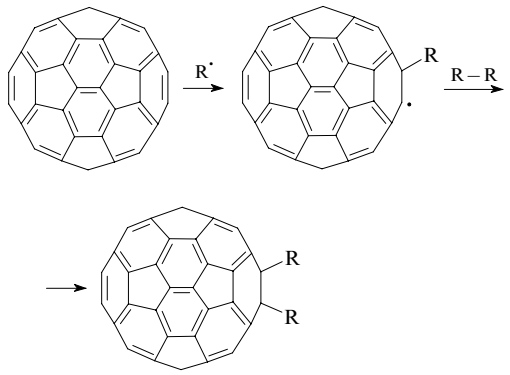
The non-aromaticity in the six-membered fragments of the [60]fullerene cage is a consequence of the substantial deviation of the double bond geometry from the normal planar one (*i.e*., the result of pyramidalisation). Such deviations were thoroughly studied by the example of [*n*]paracyclophanes with non-planar benzene rings (see Fig. 2 *c*), which is the reason for the appearance of properties non-typical of arenes.[24] Due to rigidity of the fullerene cage, cyclohexatriene fragments in the C_{60} molecule remain planar despite the considerable pyramidalisation of multiple bonds. The pyramidisation-induced strain is the reason for the high reactivity of fullerenes compared to other carbon forms.

It is known that a C_{60} molecule is a sufficiently strong electron acceptor capable of accepting from one to six electrons to form the corresponding anions.[25] Thus, multiple bonds in the fullerene cage are strongly electron-deficient. There is a certain analogy in the reactivity of multiple bonds in fullerene, on the one hand, and in perfluoro- or perchloroethylene, acrylonitrile, maleic anhydride, *etc*., on the other hand. [60]Fullerene readily reacts with nucleophiles but does not virtually undergo electrophilic addition reactions typical of simple alkenes.[23]

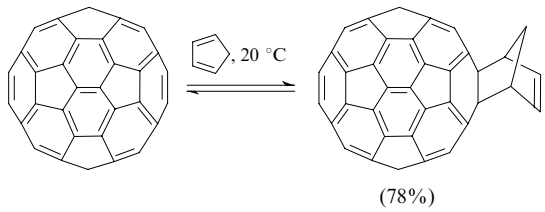


Nu is nucleophile, E is electrophile.

Reactions of C_{60} with typical electrophiles such as halogens proceed by the radical mechanism. [60]Fullerene easily adds other radical species.[21] In the simplified form, a reaction of radical addition can be presented as follows:



Apart from nucleophilic and radical addition, the C_{60} molecule undergoes various cycloaddition reactions.[6, 23] The [2 + 4] cycloaddition of cyclopentadiene was among the first discovered reactions of this type.[26]



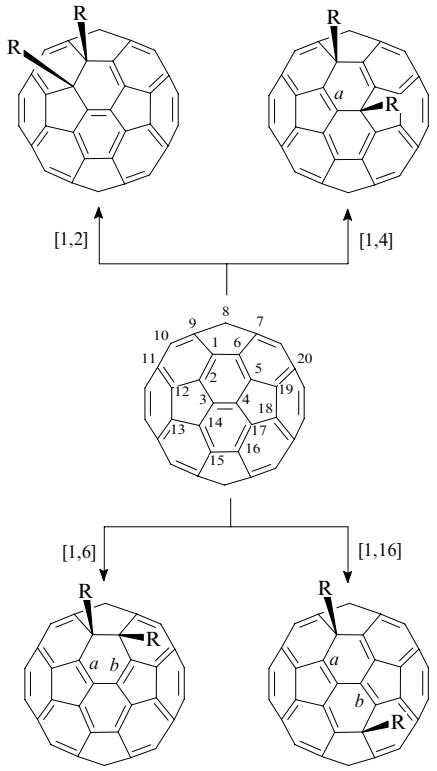
2. Regiochemistry of the formation of dihydro[60]fullerenes

In accordance with the IUPAC nomenclature, dihydrofullerenes are fullerene derivatives formed as a result of addition of reactive species to only one of multiple bonds in the carbon cage, irrespective of the nature and position of addends.

An important aspect of addition reactions of different substrates to the fullerene cage is associated with regiochemistry. As was mentioned above, double bonds in the C_{60} cage are localised to a considerable degree. Hence, it can be expected that the reactive species will add to the C_{60} cage virtually exclusively at 6 – 6 bonds ([1,2]-addition). Nonetheless, the conjugated [1,4]-cycloaddition occurs sufficiently often.

Scheme 1 shows the possible versions of [1,2]-, [1,4]-, [1,6]- and [1,16]-additions. The first reaction involves only one of 6 – 6 bonds of the cage; the other reactions afford new 6 – 5 double bonds (one or two, designated as *a* and *b*) as a result of alteration.[23]

Scheme 1



According to theoretical calculations,[27] the appearance of a new 6 – 5 multiple bond requires the consumption of approximately 8.5 kcal mol^{-1}. Hence, the [1,2]-addition should be more advantageous for the energy reasons than [1,4]-addition, while the latter is more advantageous than [1,6] and [1,16]. This trend usually holds; however, some exceptions exist (for example, the fulleroid $C_{60}CF_2$ contains three 6 – 5 multiple bonds).[28]

Yet another important factor is the steric repulsion between addends. Due to the rigidity of the fullerene cage, the attached groups are inevitably in the shielded conformation (*i.e.*, opposite to one another). Obviously, a strain that arises between them is stronger for groups located closer to one another and having larger van der Waals radii. From this standpoint, an adduct to positions 1 and 16 is the most advantageous, the 1,4-isomer is less advantageous and 1,2- and 1,6-isomers are the most strained.[28]

Thus, the regiochemical result of a particular reaction is determined by the relative contributions of two factors, namely, the emergence of energetically disadvantageous 6 – 5 double bonds and the appearance of steric strains. For small addends, the 1,2-addition is always observed, whereas for more bulky groups, 1,4-isomers or their mixtures with 1,16-adducts are formed.[29] As a rule, no 1,6-addition products are formed, because they are sterically hindered and contain two destabilising 6 – 5 double bonds.

The direction of addition also depends on the reaction mechanism. For example, cycloaddition almost always affords 1,2-cycloadducts, while radical species usually add to positions 1 and 4 of the C_{60} cage.

3. Regiochemistry of the formation of dihydro[70]fullerenes

The literature data make it possible to draw conclusions about the regiochemistry of nucleophilic addition and cycloaddition reactions to the C_{70} cage. It was shown that a bond between C(1) and C(2) is the most reactive in the [70]fullerene cage, the next are C(5)–C(6) and C(19)–C(20) (Fig. 3).

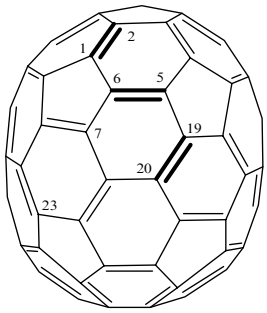


Figure 3. Possible positions of nucleophilic addition and cycloaddition to C_{70} fullerene.

As a rule, nucleophilic addition reactions to C_{70} afford a mixture of three isomers, more rarely, their number is reduced to two [30, 31] and in exceptional cases, a single isomer is formed.[32] The formation of three isomers was observed in hydrogenation of C_{70} to $C_{70}H_2$,[33] its RuO_4-induced hydroxylation to $C_{70}(OH)_2$ (Ref. 34) and in some other reactions non-related to the nucleophilic addition and cycloaddition.

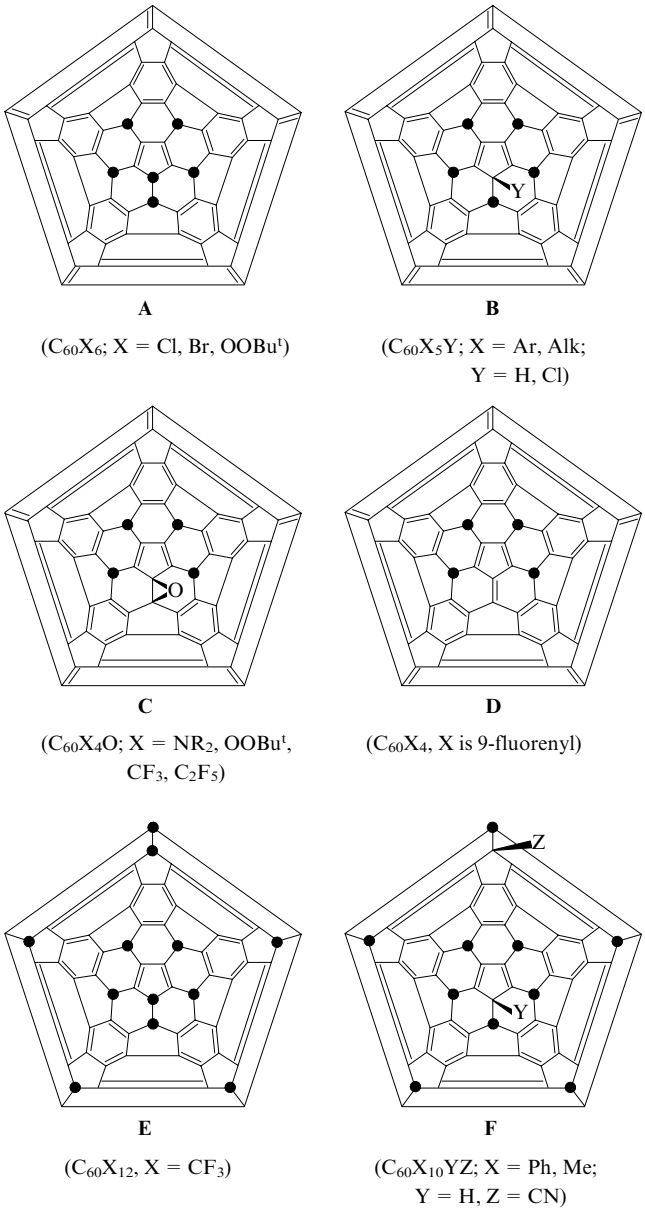
The direction of radical addition reactions to [70]fullerene is somewhat different, because the addition to neighbouring carbon atoms competes with conjugated 1,4-addition. This reaction was studied in most details by the example of synthesis of *tert*-butyl peroxide derivatives $C_{70}(OOBu^t)_2$. Apart from 1,2- and 5,6-isomers, the reaction produces 2,5- and 7,23-adducts (see Fig. 3).[35]

4. Regiochemistry of polyaddition to C_{60} and C_{70} cages

Polycycloaddition reactions (*i.e.*, reactions that involve more than one multiple bond of the cage) to C_{60} and C_{70} fullerenes proceed with a high selectivity only under thermodynamic control. Otherwise, complex mixtures of products are formed. Non-equilibrium trifluoromethylation,[36] chlorination [37] and fluorination of fullerenes,[38] *etc.* can serve as the examples. Under thermodynamic control, isomerically pure products or mixtures of several isomers with similar energies were formed as a rule.

a. Cyclopentadiene mode of addition to the C_{60} cage

If three multiple bonds in the [60]fullerene cage are involved in the addition, this proceeds according to the so-called cyclopentadiene mode (Fig. 4). This is typical of bromination,[39] chlorination,[40] addition of a peroxide [41] and aminyl radicals [42, 43] and of alkyl, perfluoroalkyl [44] and aryl groups.[45, 46] Apparently, all these reactions proceed by the radical mechanism. Chlorination and bromination of C_{60} fullerene afforded products with the composition $C_{60}X_6$, which correspond to the structural type **A** (see Fig. 4). If the introduced groups were sufficiently bulky, only four addends were attached (type **D**) and an oxygen atom in place of the remaining two addends (type **C**), or five addends added and the sixth represented a small atom (H or Cl) (type **B**).



A ($C_{60}X_6$; X = Cl, Br, $OOBu^t$)

B ($C_{60}X_5Y$; X = Ar, Alk; Y = H, Cl)

C ($C_{60}X_4O$; X = NR_2, $OOBu^t$, CF_3, C_2F_5)

D ($C_{60}X_4$, X is 9-fluorenyl)

E ($C_{60}X_{12}$, X = CF_3)

F ($C_{60}X_{10}YZ$; X = Ph, Me; Y = H, Z = CN)

Figure 4. The Schlegel diagrams of C_{60} derivatives with the cyclopentadiene addition mode (from hereon, dark circles designate X group addition sites).

Moreover, double cyclopentadiene mode is possible to afford $C_{60}X_{12}$ (type **E**) or $C_{60}X_{10}YZ$ (type **F**).[47] Particularly, the compound $C_{60}(CF_3)_{12}$, which pertains to the structural type **E** was synthesised, as confirmed by the X-ray diffraction analysis.[48]

b. Equatorial mode of addition to the C_{70} cage

Reactions that afford cyclopentadiene mode addition products in the case of C_{60}, for C_{70} fullerene lead to the addition along the 'equator' of a fullerene cage (equatorial mode). The complete division of the π-system of the C_{70} molecule in two parts takes place upon addition of ten addends. This kind of derivatives include $C_{70}H_{10}$,[49] $C_{70}Cl_{10}$,[50] $C_{70}Me_{10}$,[51] $C_{70}Ph_{10}$ [52] and $C_{70}Br_{10}$ [53] (type **A**, Fig. 5). In some cases, compounds containing eight addends (type **B**) were formed as the major or minor products; $C_{70}H_8$,[54] $C_{70}Br_8$,[55] $C_{70}Ph_8$,[52] $C_{70}Me_8$,[51]

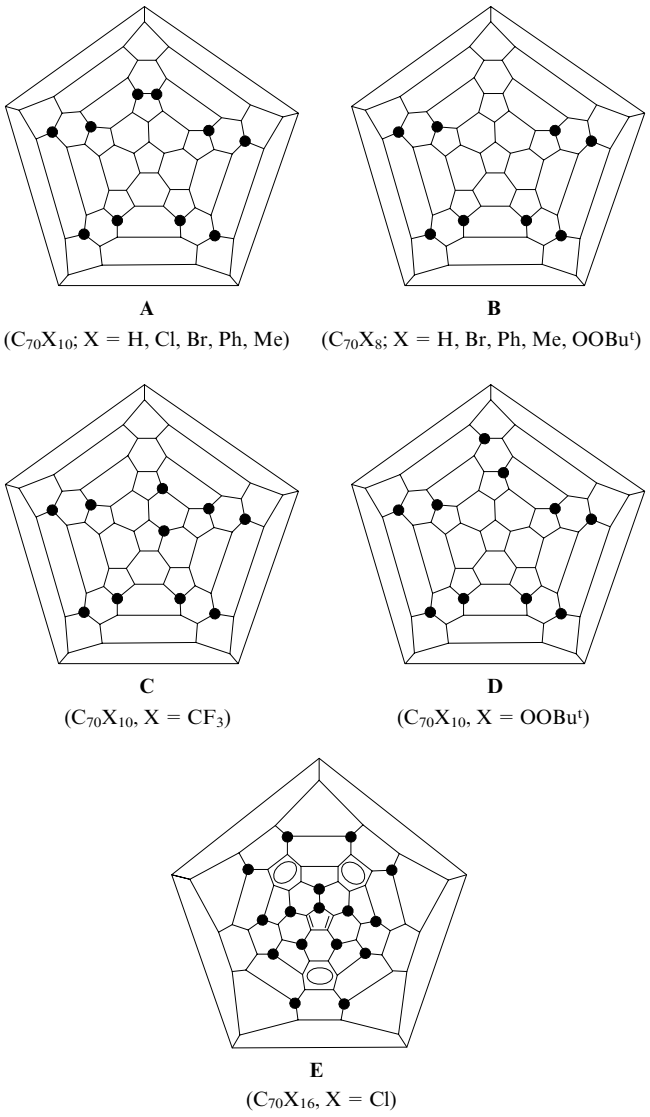


Figure 5. The Schlegel diagram of C_{70} derivatives with the equatorial addition mode.

$C_{70}(CF_3)_8$ [56] and $C_{70}(OOBu^t)_8$ pertain to this structural type.[35] Derivatives $C_{70}X_{10}$ of the type **A** contain two addends at neighbouring carbon atoms. For bulky groups, the formation of such moiety is hindered; hence, structural types **C** and **D** were formed.[35, 57] A combination of cyclopentadiene and equatorial addition modes was recently observed for chlorofullerene $C_{70}Cl_{16}$ (type **E**).[58]

c. Trend towards the increase in the degree of aromaticity for C_{60} and C_{70} derivatives

The presence of three aromatic six-membered rings in the cage of polychlorofullere $C_{70}Cl_{16}$ (recall that parent fullerenes C_{60} and C_{70} contain no aromatic fragments) points to another important factor that determines the regiochemistry of multiple addition to fullerenes, which will be called below as a 'trend to increase the aromaticity of the carbon cage'.

By the degree of aromaticity (α) of a carbon cage in fullerene derivatives is meant the ratio of carbon atoms involved in aromatic systems to the total number of sp^2-hybridised carbon atoms in a given compound. For instance, a hypothetical $C_{60}X_{20}$ molecule has totally forty sp^2-hybridised carbon atoms. If twenty of them belong to aromatic systems, the degree of aromaticity of this compound is $\alpha = 20:40 = 0.5$.

Under thermodynamic control, the halogenation and hydrogenation reactions of fullerenes afford products in which sp^2-hybridised carbon atoms constitute partially or entirely isolated aromatic structural fragments, for example, *T*- and C_1(or C_3)-isomers of $C_{60}X_{36}$ (X = H, F) [59–62] the cages of which contain 4 ($\alpha = 1$) and 3 ($\alpha = 0.75$) aromatic six-membered rings, respectively (Fig. 6).

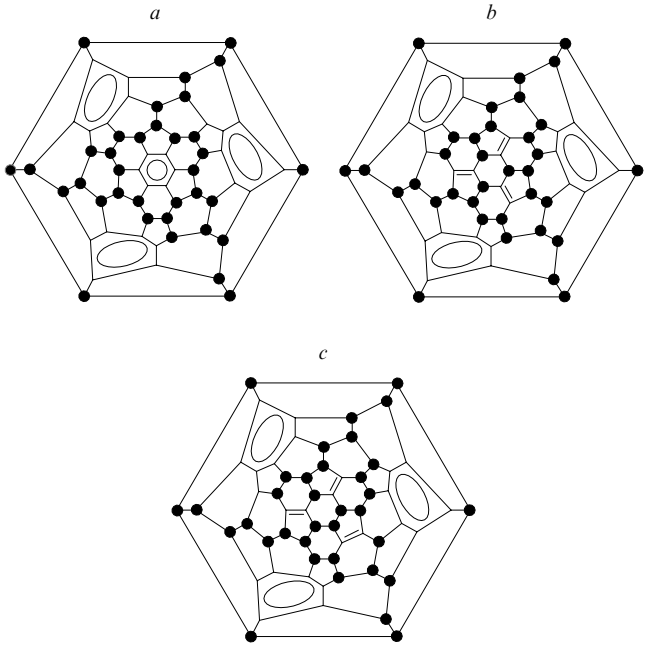


Figure 6. The Schlegel diagrams of $C_{60}X_{36}$ isomers (X = H, F) with symmetry groups T (*a*), C_3 (*b*) and C_1 (*c*).

Analogous trends were also observed for C_{70} derivatives. Particularly, isomers of polyfluorofullerene $C_{70}F_{38}$ with three ($\alpha = 0.56$) and four ($\alpha = 0.75$) aromatic six-membered rings (Fig. 7 *a*, *b*),[63, 64] polychloro derivatives $C_{70}Cl_{28}$ with four aromatic rings ($\alpha = 0.57$, see Fig. 7 *c*–*e*) [65] and $C_{70}Cl_{16}$ containing three aromatic rings ($\alpha = 0.33$) [58] were isolated.

Among fullerene C_{60} derivatives, the recently synthesised [66] polychlorofullerene $C_{60}Cl_{30}$ demonstrated the strongest trend towards the increase in the degree of aromaticity of the carbon cage. In its molecule, all sp^2-hybridised carbon atoms are involved in aromatic systems ($\alpha = 1$). Two planar aromatic six-membered rings are located at poles of the molecule, and an 18-membered annulene fragment is located on the equator. Such a structure of the molecule $C_{60}Cl_{30}$ determines its drum-like shape (Fig. 8). The aromatic 18-membered macrocycle in the $C_{60}Cl_{30}$ cage differs from the known planar [18]annulene with *cis*- and *trans*-configurations of conjugated double bonds. All double bonds on the equator of a polychlorofullerene molecule are in the *trans*-configuration; hence, the 18-membered aromatic ring in the fullerene carbon cage is called the trannulate ring and its derivatives are referred to as trannulenes.[67, 68]

The formation of aromatic, particularly, trannulene fragments is the driving force of not only such reactions as high-temperature halogenation, but also of the reactions of poly-

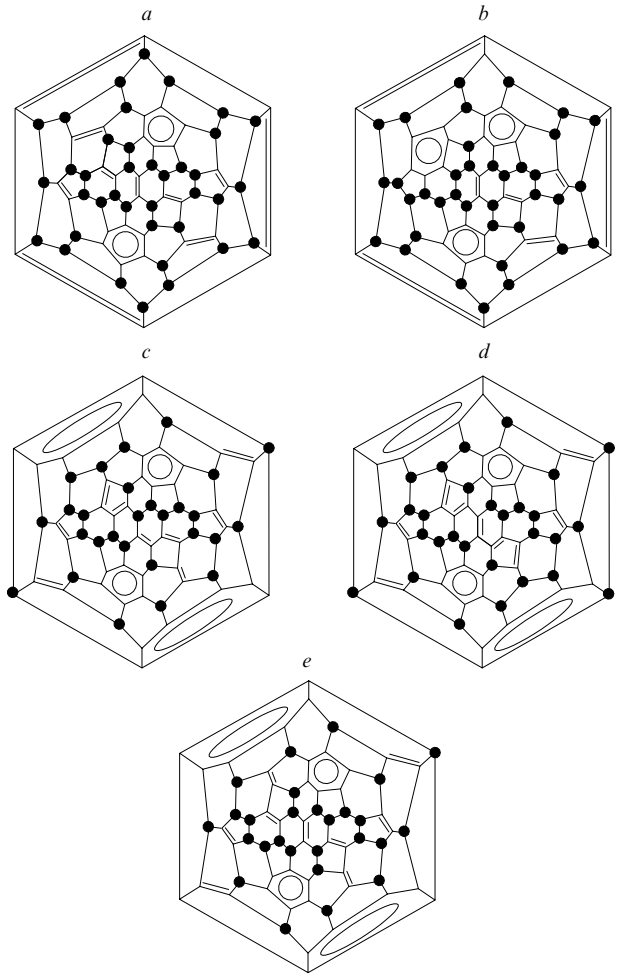


Figure 7. The Schlegel diagrams of isomers of $C_{70}F_{38}$ (*a*, *b*) (the aromatic system of the 'external' hexagon is not shown) and $C_{70}Cl_{28}$ (*c*–*e*).

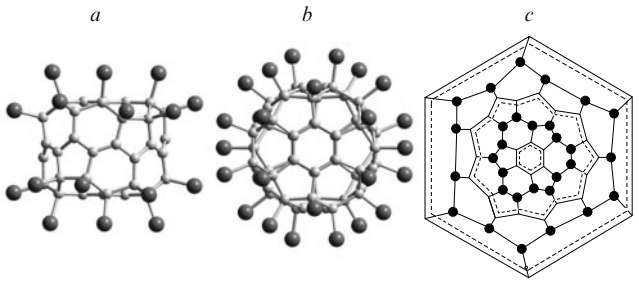


Figure 8. Two projections of a polychlorofullerene $C_{60}Cl_{30}$ molecule (*a, b*) and its Schlegel diagram (*c*).

fluorofullerene $C_{60}F_{18}$ with carbanionic nucleophiles to afford trannulenes $C_{60}F_{15}R_3$ ($\alpha = 0.57$) with addends $R = CX(EWG)_2$, where X is any substituent and EWG is an electron-withdrawing group (Fig. 9 *a*). A nucleophile attacks a position located two conjugated multiple bonds away from the leaving group; hence, this reaction mechanism was named the 'S_N2''-substitution'.[67, 69]

Trannulenes $C_{60}[CMe(CO_2R)_2]_6$ (R = Et, Bu^t) ($\alpha = 0.33$) were synthesised in a reaction of $BrCMe(CO_2R)_2$ with fullerene hexaanion $[C_{60}]^{6-}$ (Ref. 70). The latter is generated in the reduction of C_{60} with sodium naphthalenide $[C_{10}H_8]^-Na^+$.

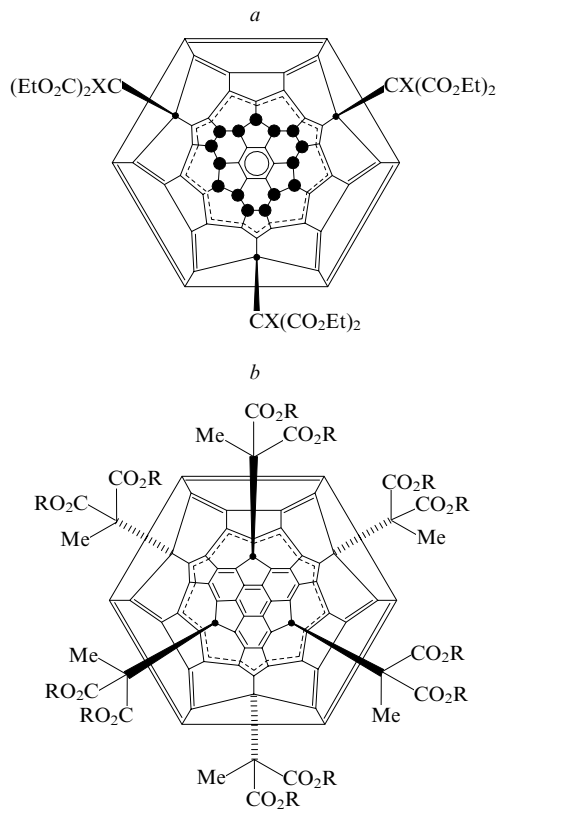


Figure 9. The Schlegel diagrams of trannulenes $C_{60}F_{15}[CX(CO_2Et)_2]_3$ (X = Cl, Br, NO_2, CO_2Et) (*a*) and $C_{60}[CMe(CO_2R)_2]_6$ (R = Et, Bu^t) (*b*). Large circles designate the fluorine atom addition sites.

The product contained three organic addends in each fullerene hemisphere and a trannulene moiety on the equator of this molecule (see Fig. 9 *b*).

Trannulenes $C_{60}Cl_{30}$, $C_{60}F_{15}[CX(CO_2Et)_2]_3$ and $C_{60}[CMe(CO_2R)_2]_6$ are characterised by the presence of intense absorption bands in the visible part of spectrum (400–900 nm), which determines their colouring untypical of fullerene derivatives. Particularly, solutions of $C_{60}[CMe(CO_2R)_2]_6$ are emerald-green.

d. Symmetry enhancement as the key factor that determines the regiochemical outcome of fullerene reactions

Thermodynamically controlled fullerene reactions usually afford sufficiently symmetrical products. As a rule, a trend for enhancement of the molecule symmetry is coupled with the increase in the degree of aromaticity of carbon cages of fullerene derivatives. However, several compounds are known that are symmetrical according to X-ray diffraction analysis but contain no aromatic fragments. Among polyhalofullerenes, these are $C_{60}Hal_{24}$ (Hal = F,[71] Cl,[72] Br[73]) and $C_{60}F_{20}$ (Fig. 10).[74] Molecules of $C_{60}Hal_{24}$ have T_h symmetry, *i.e.*, all 24 addends are symmetrically equivalent. According to NMR spectroscopy, all fluorine atoms in $C_{60}F_{20}$ are also equivalent and arranged in a chain along the fullerene cage equator (symmetry group D_{5h}). The molecule $C_{60}F_{20}$ resembles the planet Saturn and is known as 'saturnene'.

Addition reactions of organic groups to the C_{60} cage carried out under thermodynamic control afford hexaadducts of the octahedral structure (see below). This was observed for the reactions of [2 + 3] (Ref. 75) and [2 + 4] cycloaddition [76] and for nucleophilic cyclopropanation.[77]

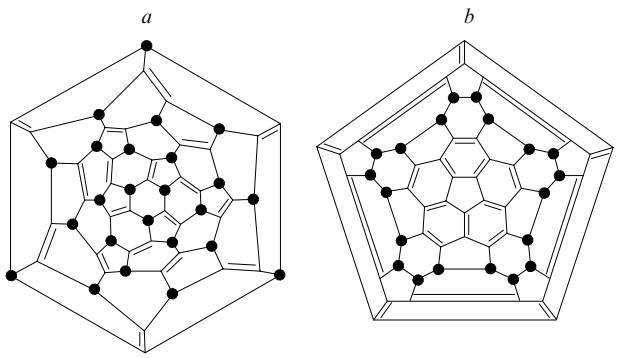
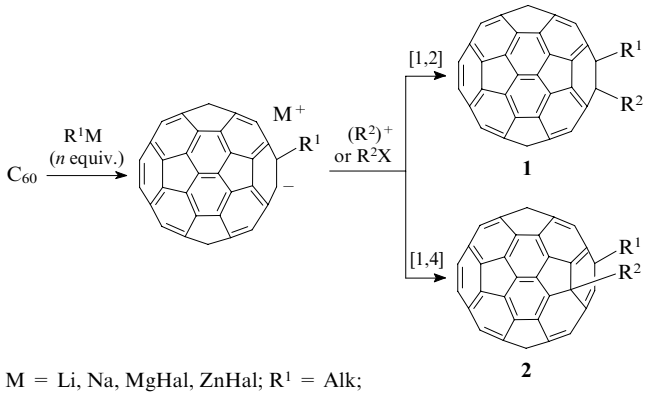


Figure 10. The Schlegel diagrams of polyhalofullerenes $C_{60}Hal_{24}$ (Hal = F, Cl, Br) (*a*) and $C_{60}F_{20}$ (*b*).



M = Li, Na, MgHal, ZnHal; R^1 = Alk; R^2 = H, Alk, AlkC(O), CN *etc.*

IV. Nucleophilic addition reactions

Below, the main reactions of fullerenes C_{60} and C_{70} are shown with the exception of halogenation, hydrogenation and the reactions with organometallic reagents that involve the formation of π-complexes.

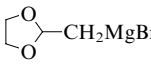
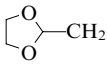
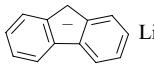
1. Conjugate addition of carbanionic nucleophiles and electrophiles

Fullerene C_{60} readily reacts with organolithium, -magnesium and -zinc reagents to form ionic intermediates unstable in air. These compounds are introduced *in situ* in reactions with various electrophiles.

Depending on the nucleophile and electrophile steric volumes, the reaction preferentially or exclusively affords 1,2- (**1**) or 1,4-adduct (**2**). Particularly, 1,2-isomers **1** were formed when a proton served as the electrophile. Surprisingly, the optimum yields are achieved with a large excess (5–27 equiv.) of organomagnesium or -zinc compounds as nucleophiles.[21,23] An unusual example of such reactions is the addition of the cyanide anion to the fullerene cage followed by 'capture' of the formed intermediate by appropriate electrophiles.[78]

Conjugate addition reactions of carbanionic nucleophiles and various electrophiles to activated carbon–carbon bonds are a powerful tool in organic synthesis.[79] However, in chemistry of fullerenes, this field is insufficiently elaborated. Apparently, this is caused by the existence of more convenient methods of [60]fullerene functionalisation based on diverse cycloaddition reactions. Table 1 lists examples of nucleophilic addition reactions to the C_{60} cage.

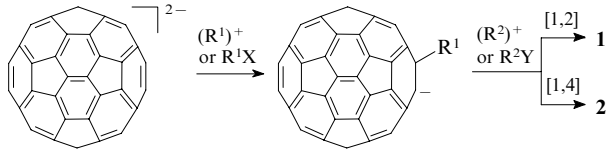
Table 1. Examples of reactions of conjugate addition of organometallic nucleophiles and electrophiles to fullerene C_{60}.

Nucleophile	*n* [a]	Electrophile	Product				Ref.
			R^1	R^2	No.	yield (%)	
MeLi	1.2	H^+	Me	H	**1a**	47	80, 81
Bu^tLi	1.2	H^+	Bu^t	H	**1b**	51	80, 81
	11.9	H^+		H	**1c**	52	80, 81
PhMgBr	9.2	H^+	Ph	H	**1d**	74	80, 81
HexC≡CLi	6	H^+	HexC≡C	H	**1e**	75	82
	2.1	H^+	9-fluorenyl	H	**1f**	41	83
$NCCH_2ZnBr$	25	H^+	$NCCH_2$	H	**1g**	34	84
EtO_2CCH_2ZnBr	25	H^+	EtO_2CCH_2	H	**1h**	51	84
$Bu^tC(O)CH_2ZnBr$	25	H^+	$Bu^tC(O)CH_2$	H	**1i**	27	84
$MeO_2CCH{=}CHCH_2ZnBr$	25	H^+	$MeO_2CCH{=}CHCH_2$	H	**1j**	10	84
NaCN	1	H^+	N≡C	H	**1k**	29	78
$Me_3SiC{\equiv}CLi$	3	BnBr	$Me_3SiC{\equiv}C$	Bn	**1l**	31	85
		CH_2O [b]	$Me_3SiC{\equiv}C$	$HOCH_2$	**1m**	57	85
HexC≡CLi	6	MeI	HexC≡C	Me	**1n**	98	85
			HexC≡C		**1o**	37	82
					2o	35	82
		PhC(O)Cl	HexC≡C	PhC(O)	**2p**	94	82
NaCN	1	MeOTf	N≡C	Me	**1q**	10	78
		TsCN	N≡C	N≡C	**1r**	61	78
		$4\text{-}Bu^tC_6H_4CH_2Br$	N≡C	$4\text{-}Bu^tC_6H_4CH_2$	**1s**	11	78

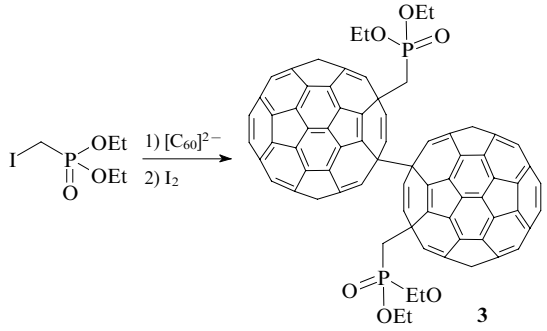
Note. The following abbreviations are used: Hex = $n\text{-}C_6H_{13}$, Tf = CF_3SO_2; [a] number of equivalents of an organometallic compound; [b] gaseous formaldehyde was used.

2. Formation of a $[C_{60}]^{2-}$ dianion and its reactions with electrophiles

In the previous Section, we considered the addition of carbanionic nucleophiles to a [60]fullerene cage to form an $[R^1C_{60}]^-$ anion that can react with different electrophiles (see Table 1). A similar result was obtained in consecutive reactions of dianion $[C_{60}]^{2-}$ with two electrophiles.

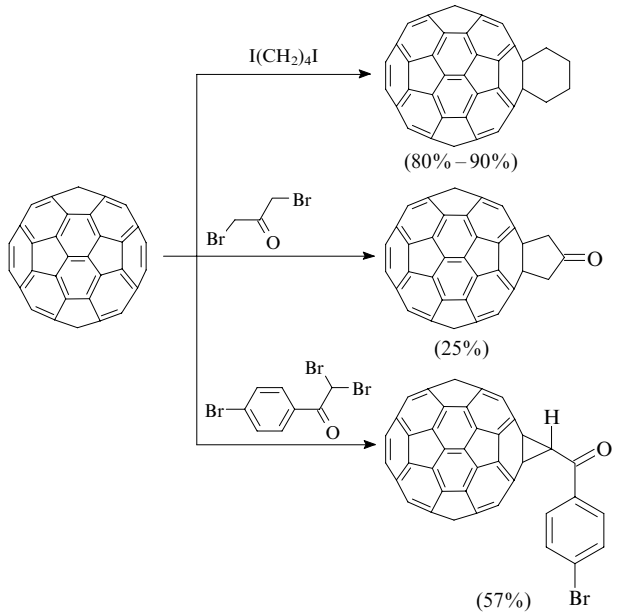


Depending on the volume of electrophiles, 1,2- (**1**) or 1,4-adducts (**2**) were preferentially formed. This reaction is not yet sufficiently studied; however, the examples documented in the literature unambiguously point to the prospects of its synthetic use.[86–92] In certain cases, fullerene dimers bonded by a single C–C bond were formed. Addition of an electrophile to the dianion $[C_{60}]^{2-}$ produced an $[EC_{60}]^-$ anion; reaction of the latter with, *e.g.*, molecular iodine afforded the dimer $EC_{60}–C_{60}E$ rather than $EC_{60}I$ (the C–I bond is extremely weak). Thus dimer **3** containing two phosphonate groups was obtained.[93]



The parent dianion is easily generated electrochemically or with the use of various reducing agents (metallic K in THF, a $Pr^nSH–K_2CO_3$ system, AlkSNa in acetonitrile). The most feasible synthesis of the dianion $[C_{60}]^{2-}$ is the reaction of fullerene with an excess of sodium alkanethiolate (*e.g.*, EtSNa) in anhydrous acetonitrile or dimethylformamide in an inert atmosphere.[90] Table 2 exemplifies products formed from the dianion $[C_{60}]^{2-}$ in a two-step addition of electrophilic reagents.

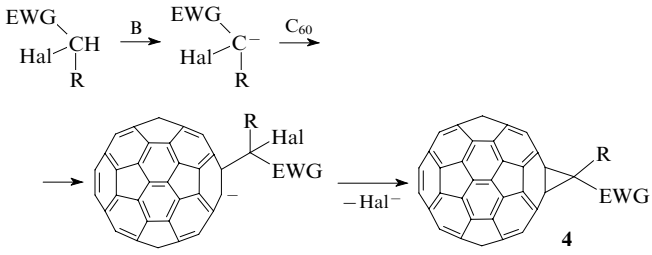
The use of biselectrophiles afforded carbocycle-annulated fullerenes. Examples [90, 92, 96] are presented below



3. Addition of α-halocarbanionic nucleophiles. The Bingel–Hirsch reaction.

In chemistry of fullerenes, the most important reaction is that of C_{60} with compounds of the RCH(Hal)EWG type in the presence of strong bases.[97] In the first step, the reagent is deprotonated to form a reactive nucleophile RC^-(Hal)EWG which then reacts with fullerene. The ionic intermediate is stabilised by intramolecular elimination of a halogen anion to afford a cyclopropane derivative of fullerene **4** (Scheme 2).[21]

Scheme 2



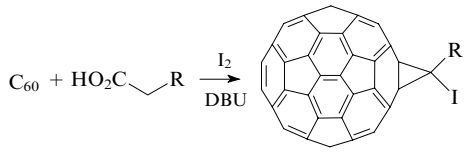
B is a base

Table 2. Examples of reactions of consecutive addition of two electrophiles to the $[C_{60}]^{2-}$ anion.

Electrophiles		Product				Ref.
1 step	2 step	R^1	R^2	No.	yield (%)	
H^+	H^+	H	H	**1t**	–	94
Cp*Mo(CO)$_3$Cl [a]	Cp*Mo(CO)$_3$Cl	(CO)$_3$Cp*Mo	(CO)$_3$Cp*Mo	**2u**	–	95
MeI	MeI	Me	Me	**1v**	80	90
				2v	10	90
EtI	EtI	Et	Et	**1w**	10	90
				2w	80	90
Bu^nI	Bu^nI	Bu^n	Bu^n	**2x**	90	90
$(EtO)_2P(O)CH_2I$	H^+	$(EtO)_2P(O)CH_2$	H	**1y**	24–33	91
	MeI	$(EtO)_2P(O)CH_2$	Me	**1z** + **2z**	10–20	91
	$(EtO)_2P(O)CH_2I$	$(EtO)_2P(O)CH_2$	$(EtO)_2P(O)CH_2$	**2aa**	10	93

[a] Cp* = η^5-C_5Me_5.

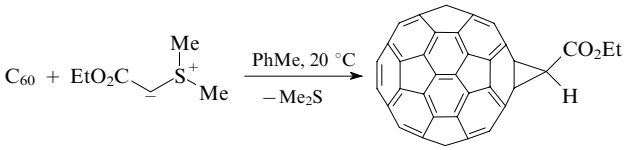
A convenient version of this method consists of generating RCH(Hal)EWG *in situ* from compounds of the RCH_2EWG type and halogenating agents (CBr_4 or I_2 in the presence of a strong base), which reacts with C_{60}.[98–100] For substrates containing an α-carboxyl group, the reaction is accompanied by decarboxylation to form halogen-substituted cyclopropanofullerenes **4a**.[101]



4a

DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene

Yet another version of nucleophilic cyclopropanation of fullerenes is based on the reaction of C_{60} with sulfonium ylides. In this case, a neutral dimethyl sulfide molecule acts as the leaving group.[102]



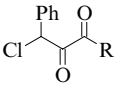
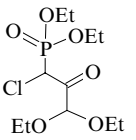
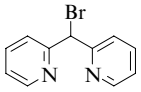
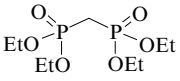
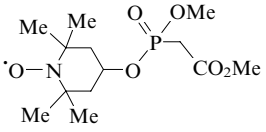
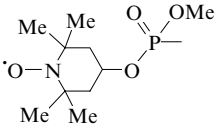
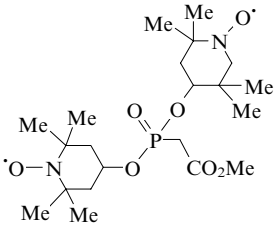
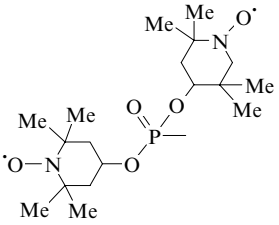
4b

The use of this method for functionalisation of C_{70} fullerene is of great importance because the reaction proceeds in a regioselective manner to form only the 1,2-isomer.[32]

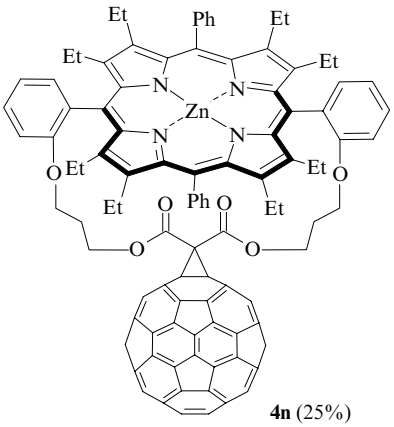
The nucleophilic cyclopropanation of fullerenes is known as the Bingel–Hirsch reaction.[10] Examples of its synthetic use are so numerous that it is difficult to consider them within the framework of this review. Table 3 shows certain examples of such reactions.

This method makes it possible to synthesise cyclopropanofullerene **4n** with a porphyrin fragment [reaction conditions: DBU, I_2] [110] and fullerene derivatives with highly branched [**4o** (DBU, CBr_4) [111]] and dendrimeric addends [**4p** (DBU, CBr_4)] from C_{60} and the corresponding 1,3-dicarbonyl compounds.[112]

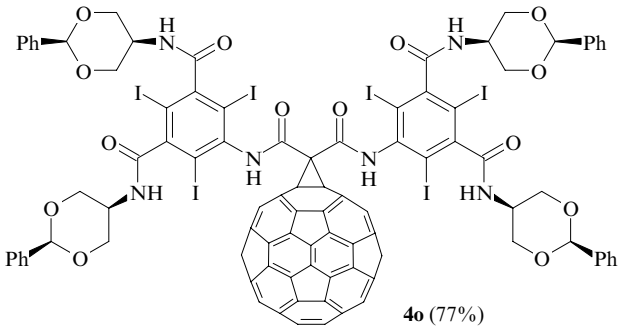
Table 3. Examples of nucleophilic cyclopropanation of fullerene C_{60}.

Reagent	Base	Product				Ref.
		R	EWG	No.	yield (%)	
$BrCH(CO_2Et)_2$	NaH	CO_2Et	CO_2Et	**4c**	35	97
$BrCH_2C(O)Ph$	DBU	H	C(O)Ph	**4d**	29	97
 (R = OMe, Bu^t)	DBU or NaH	Ph	C(O)C(O)R	**4e**	30–50	103
	the same	$C(O)CH(OEt)_2$	$P(O)(OEt)_2$	**4f**	30–50	103
$CHBr_3$	LDA [a]	Br	Br	**4g**	40	104
$BrCH_2CN$	LDA [a]	H	CN	**4h**	15	104
$BrCH_2NO_2$	Et_3N	H	NO_2	**4i**	32	105
	DBU	2-pyridyl	2-pyridyl	**4j**	32	106
	DBU, I_2	$P(O)(OEt)_2$	$P(O)(OEt)_2$	4**k**	38 47	107 108
	DBU, CBr_4	CO_2Me		**4l**	16–23	109
	the same	CO_2Me		**4m**	16–23	109

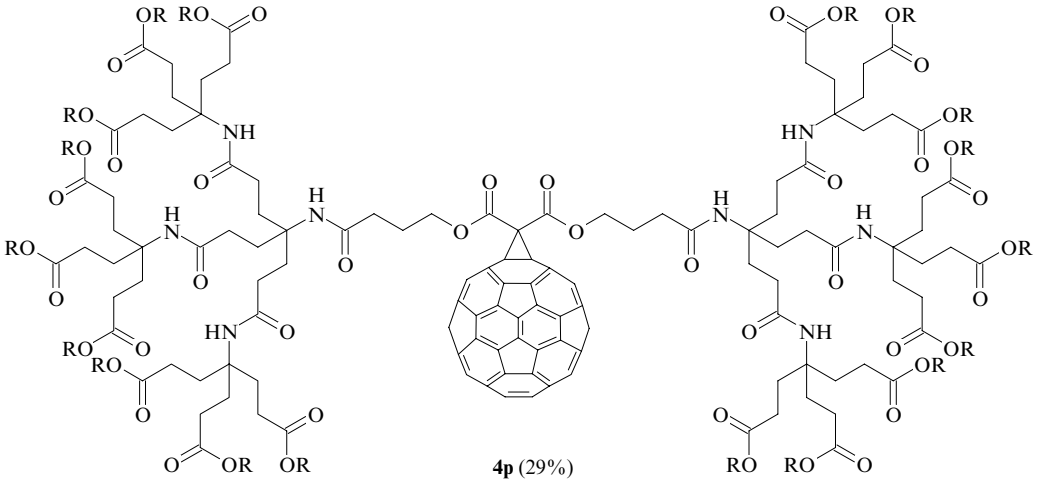
[a] LDA is lithium diisopropylamide.



4n (25%)



4o (77%)



4p (29%)

R = Bu^t, H.

4. Regiochemistry of polycyclopropanation of [60]fullerene

As was shown above, the reaction of C_{60} with α-halocarbanionic nucleophiles results in annulation of the cyclopropane fragment to a 6—6 bond of the cage. The resulting cycloadduct **4** has relatively low symmetry (C_{2v} or lower); hence, its further cyclopropanation yields mixtures of isomeric products. Monoadduct **4** with the C_{2v} symmetry contains 9 types of 6—6 bonds accessible for the attack (Fig. 11); their number and designations are shown below.[21,23]

Bond type	Number	Bond type	Number
cis-1	4	*trans*-1	1
cis-2	4	*trans*-2	4
cis-3	4	*trans*-3	4
e'	2	*trans*-4	4
e''	2		

In the general case, nine isometric bisadducts can be formed. For compounds with two identical addends, this number decreases to 8, because they have only one equatorial isomer (in this case, the equatorial positions e' and e'' are equal).[23]

Experimental studies of regiochemistry of double cyclopropanation of [60]fullerene made it possible to reveal certain trends.[113]

1. Under moderately drastic conditions, cyclopropanation is irreversible; hence, the observed isomer ratio reflects the kinetics of formation of products.

2. Cyclopropanation is not a random process.

3. Equatorial and *trans*-3-isomers are formed as the major products.

4. *cis*-1-Isomer forms only if the steric parameters of addends allow them to occupy the positions close to one another.

5. An attack on the e'' bonds is more favourable than on the e' bonds.

6. Reactions conducted under drastic conditions do not exhibit high regioselectivity.

Addition of three and more cyclopropane addends to the C_{60} cage obeys the same rules. Thus cyclopropanation of an

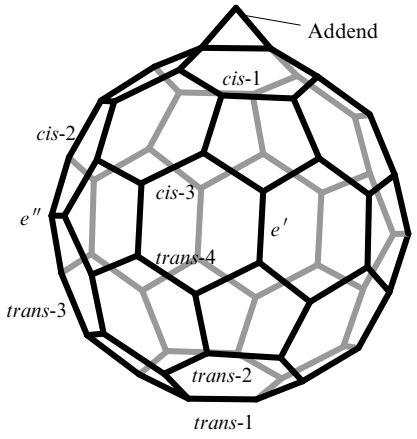
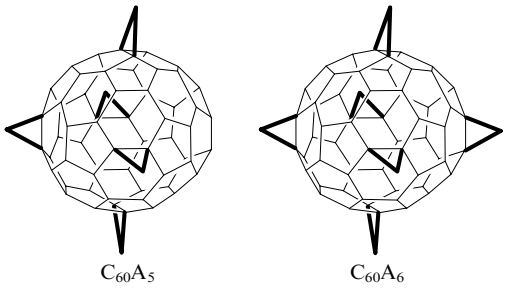


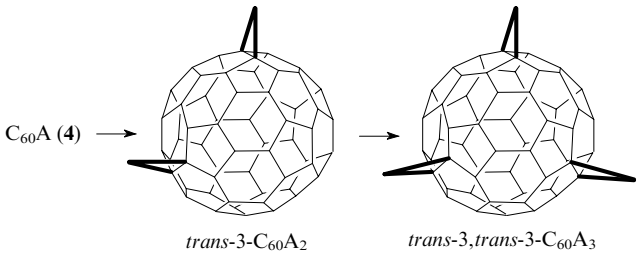
Figure 11. Types of 6—6 bonds in the C_{60}A monoadduct (**4**) cage and their designations.

equatorial bisadduct preferentially affords equatorial tris-, tetrakis-, pentakis- and hexakisadducts. Products $C_{60}A_n$ ($n = 2-4$) include several isomers with addends in equatorial positions, while for $C_{60}A_5$ and $C_{60}A_6$ only one isomer is possible with addends located at the octahedron vertices.



$C_{60}A_5$ $C_{60}A_6$

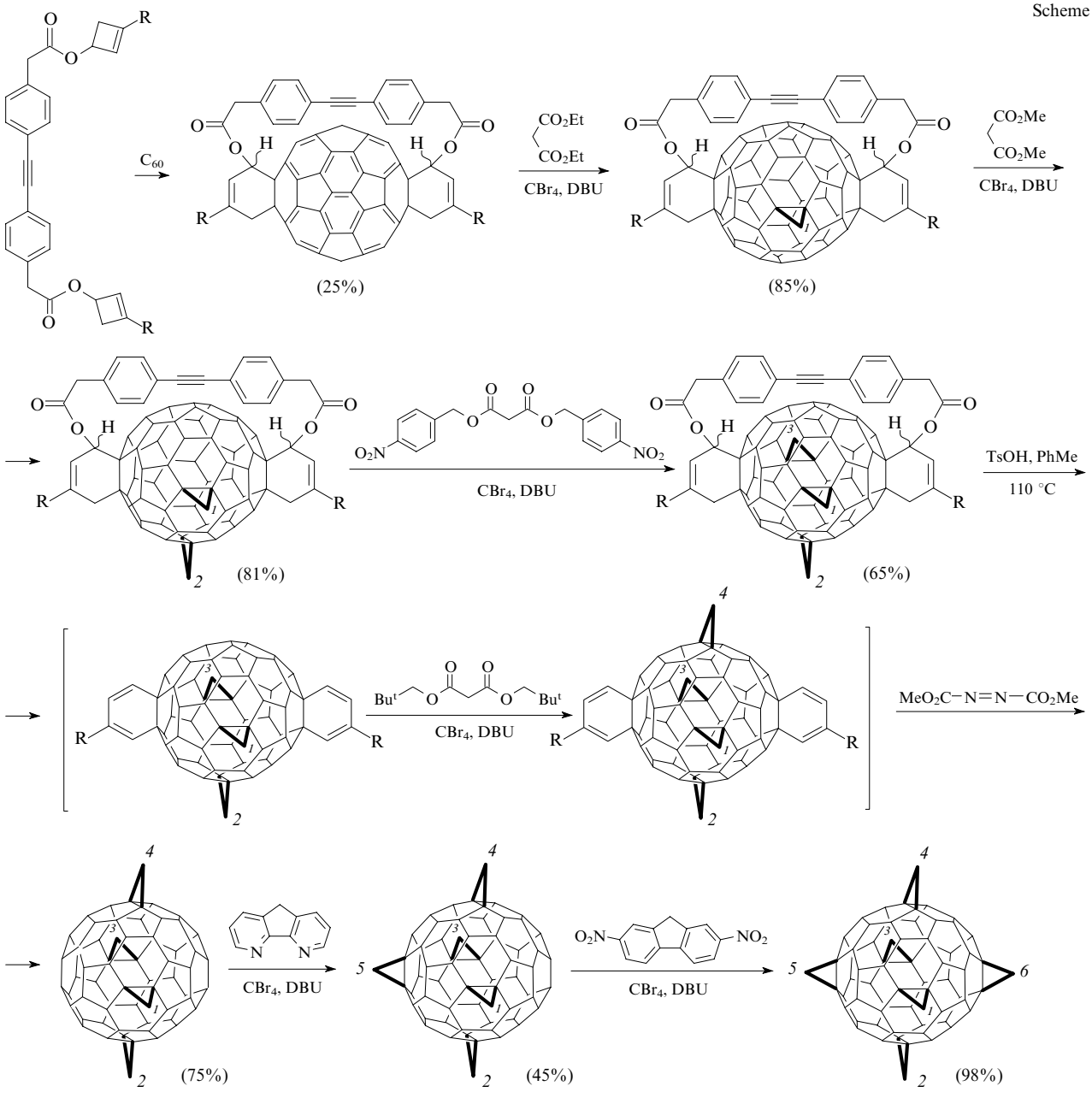
At the same time, cyclopropanation of a *trans*-3-bisadduct (*trans*-3-$C_{60}A_2$) results in the preferential formation of a *D*$_3$-symmetrical trisadduct, *trans*-3,*trans*-3-$C_{60}A_3$, in which all three addends were in *trans*-3-positions. It is of note that no further cyclopropanation of highly symmetrical hexakis- and trisadducts occurred even under relatively drastic conditions.[114]



$C_{60}A$ (**4**) → *trans*-3-$C_{60}A_2$ → *trans*-3,*trans*-3-$C_{60}A_3$

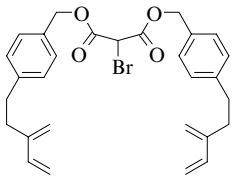
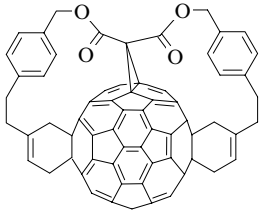
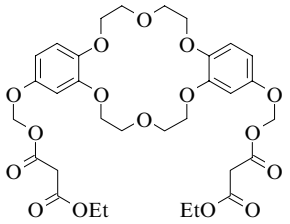
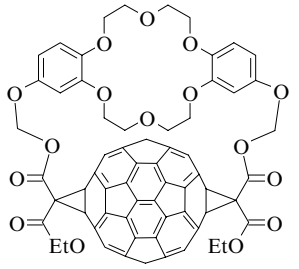
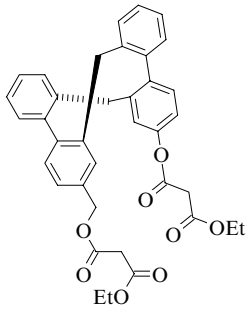
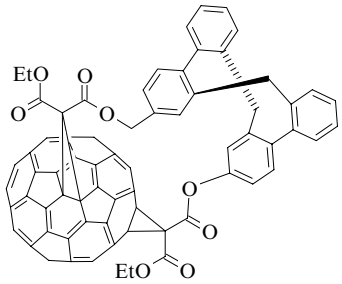
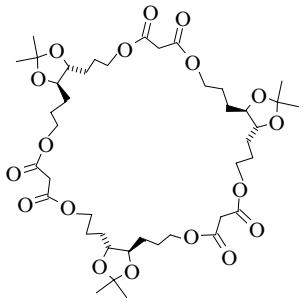
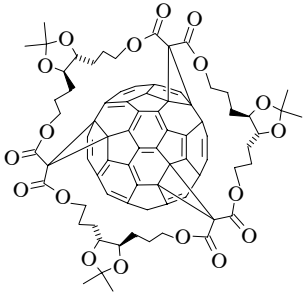
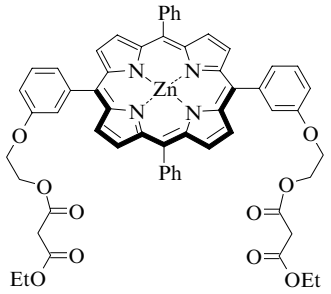
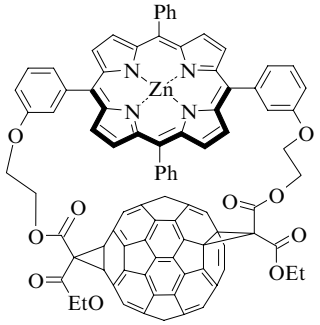
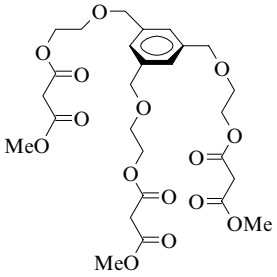
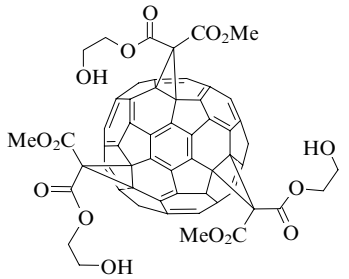
Note that the aforementioned modes of cyclopropanation to the C_{60} cage are sufficiently general and are also manifested in the formation of π-complexes with transition metals and in various cycloaddition reactions.[10, 115]

Scheme 3

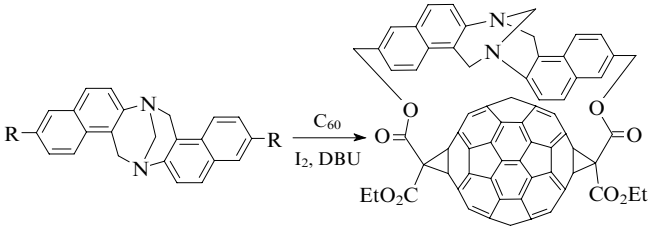


R = Ph.

Table 4. Template functionalisation of C_{60}.

Reagent	Conditions	Product	Yield (%)	Ref.	Reagent	Conditions	Product	Yield (%)	Ref.
	DBU, 20 °C, 12 h		60	122		DBU, I_2, 20 °C		15	125
	DBU, I_2, 20 °C		44	123		DBU, I_2		50	126
	the same		41	124		1) DBU, I_2 2) BBr_3		25	127

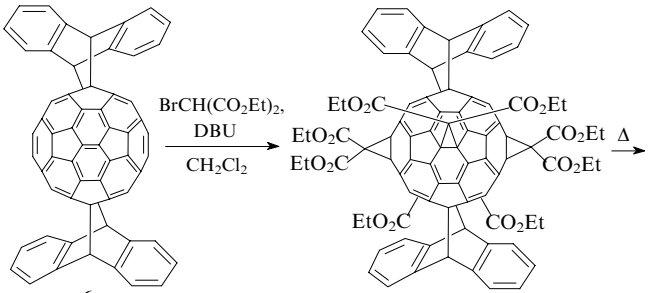
Recently, methods that use different 'guiding' spacers to provide the regioselective formation of bis- and trisadducts of fullerenes have been actively elaborated.[116] Thus the selective synthesis of *trans*-1-isomeric adduct **5** in which the cyclic diamine served as the template was carried out.[117]



5 (58%)

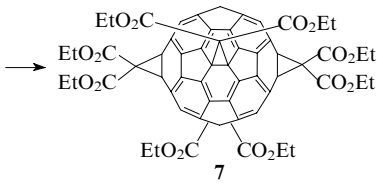
R = $EtO_2CCH_2CO_2CH_2$

Template molecules are often removed either by the hydrolysis [118] or in a retro-Diels–Alder reaction.[119] The latter reaction may be illustrated by the conversion of bisanthracene adduct to fullerene **6** into the compound *e*,*e*,*e*,*e*-$C_{60}[C(CO_2Et)_2]_4$ (**7**).



6

$C_{60}[C_{14}H_{10}]_2[C(CO_2Et)_2]_4$



7

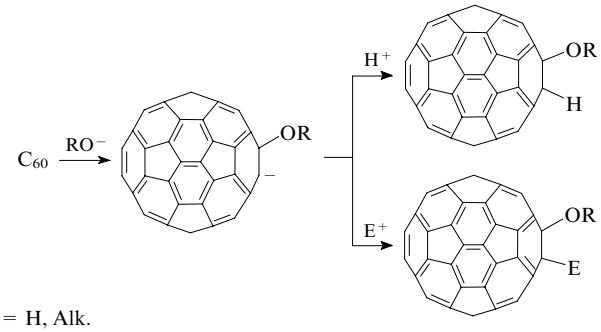
The template approach made it possible to carry out controlled addition of six different cyclopropane fragments (designated by numbers *1*–*6*, substituents are omitted) to the fullerene cage (Scheme 3). Not only malonate derivatives, but electron-deficient fluorenes served also as the reagents.[120, 121]

Table 4 shows several examples of template synthesis as applied to chemistry of fullerenes.

5. Addition of non-carbanionic nucleophiles

Apart from various carbanions, fullerene adds such nucleophiles as hydroxide and alkoxide anions.[128] Although these reactions proceed with ease, no products were hitherto isolated and characterised. One of the reasons for this is the elimination of an alcohol or water molecule from the compounds formed. A possible direction for the further development of this reaction could be the conjugate addition of mentioned nucleophiles with different electrophiles including H^+ (Ref. 128).

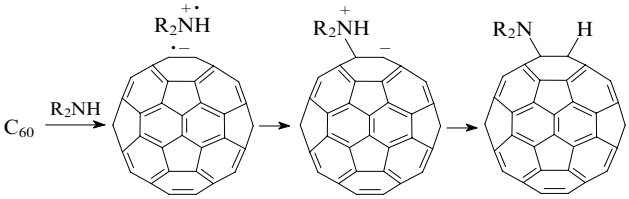
In the beginning of the development of fullerene chemistry, it was shown [129] that C_{60} easily reacts with different primary and secondary amines. For these reactions, the SET mechanism was proposed (SET is single-electron transfer) according



R = H, Alk.

to which the final product is a compound of the $R_2NC_{60}H$ type (Scheme 4).[130]

Scheme 4



However, further studies in this field have revealed that the reaction involves singlet oxygen and affords polyaminofullerenes with the composition $(R_2N)_nC_{60}$ (reactions of fullerene C_{60} with amines are considered in Section VI.2 devoted to radical reactions of fullerenes).

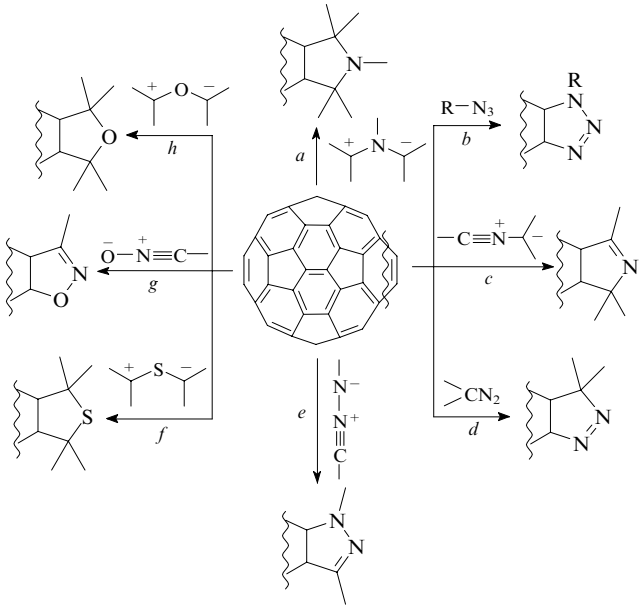
V. Cycloaddition reactions

1. [2 + 1] and [2 + 3] Cycloaddition

a. General description of reactions

Fullerene C_{60} readily undergoes [2 + 3] cycloaddition with different 1,3-dipolar reagents, namely, azomethine ylides (path *a* in Scheme 5), azides (*b*), nitrile ylides (*c*), diazo compounds (*d*), nitrile imines (*e*), thiocarbonyl ylides (*f*), nitrile oxides (*g*) and carbonyl ylides (*h*).[10] However, by no means all of these reactions can be considered as convenient methods of

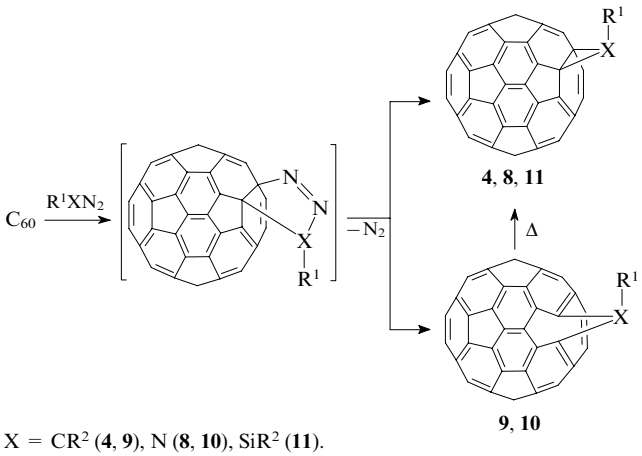
Scheme 5



chemical functionalisation of fullerenes. For example, the reaction of fullerenes with thiocarbonyl ylides (*f*) is so far only theoretically interesting; the generation of such 1,3-dipoles is extremely hindered; hence, these reactions were not used in the fullerene chemistry. On the contrary, [2 + 3] cycloaddition of azomethine ylides has become a very convenient method of fullerene functionalisation.[131]

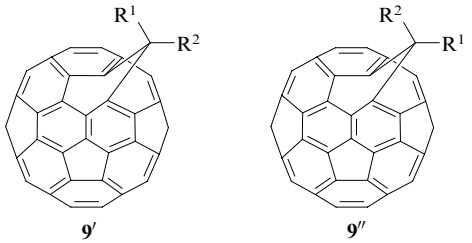
Addition reactions of nitrile ylides (*c*), nitrile oxides (*g*) and nitrile imines (*e*) to fullerenes find limited synthetic application. In fullerene functionalisation, their reactions with azides (*b*) and diazo compounds (*d*) are used rather often, although [2 + 3] cycloaddition of these species to fullerenes afford unstable products: they eliminate a nitrogen molecule to transform into aziridino- (**8**) and methanofullerenes (**4**), respectively (Scheme 6). The reaction is not straightforward and together with the expected 'closed' 1,2-cycloadducts, sometimes affords isomeric fulleroids (**9**) or azafulleroids (**10**) with an open 6 – 5 bond in the cage.[132–134] At high temperatures, (aza)fulleroids **9** and **10** are often (but not always) rearranged into more stable closed 1,2-cycloadducts **4** and **8**.[135] Syntheses conducted in boiling 1,2-dichlorobenzene (DCB) usually afford isomerically pure methanofullerenes **4** and aziridinofullerenes **8**. Hence, these reactions formally pertain to [2 + 1] cycloaddition of carbenes and nitrenes, although they proceed *via* unstable [2 + 3] cycloadducts.

Scheme 6



X = CR^2 (**4**, **9**), N (**8**, **10**), SiR^2 (**11**).

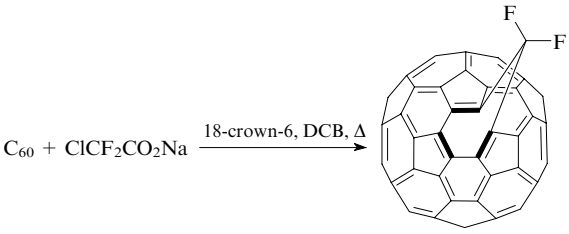
Fulleroids **9** with different substituents exist as two geometrical isomers, namely, group R^1 may be located above the (former) five-membered (**9′**) or six-membered ring (**9″**).



9′ **9″**

The use of certain specific reagents and(or) catalysts makes it possible to generate species R^1X**:** (X = CR^2, N, SiR^2) *in situ*. Indeed, carbenes, nitrenes and silylenes add to fullerene by the mechanism of [2 + 1] cycloaddition to form methanofullerenes (**4**), aziridines (**8**) and silacyclopropanes (**11**), respectively.[21, 136] However, only few examples (Table 5) are known for which it was proved that the reaction follows the [2 + 1] cycloaddition mechanism.

An unusual example of a reaction of fullerene, which presumably involves the [2 + 1] cycloaddition mechanism, was published quite recently.[28] It was shown that the reaction of C_{60} with sodium difluorochloroacetate carried out in dichlorobenzene in the presence of 18-crown-6 affords compound $C_{60}CF_2$ (**12**) with an open 6 – 6 bond in its cage as the major product.



12 (19%)

In compound **12**, three 6 – 5 bonds become multiple (shown in bold), which should destabilise its structure. However, the possibility of existence of such type of adducts was proved using NMR spectroscopy and later confirmed by the X-ray diffraction analysis of the bisadduct $C_{60}(CF_2)_2$.[139]

This result allows one to cast a new look on certain aspects of chemistry of fullerenes. For example, generally known azahomofulleroids (compounds with the composition $C_{60}NR$) are unambiguously identified as open 5,6-annulenes (a 5 – 6 single bond in the cage has been cleaved). However, these compounds may also have the structure of open 6,6-annulenes [as for $C_{60}CF_2$ (**12**)] with the spectral characteristics virtually indistinguishable from those of 5,6-annulenes. Moreover, examples of bisazafulleroids are to date known;[140] they were formed by the addition of two addends to the neighbouring 6 – 6 multiple bonds of the cage. These molecules also have three 6 – 5 double bonds. The elucidation of the exact structure of different monoazafulleroids requires their detailed investigation with the use of the X-ray diffraction method.

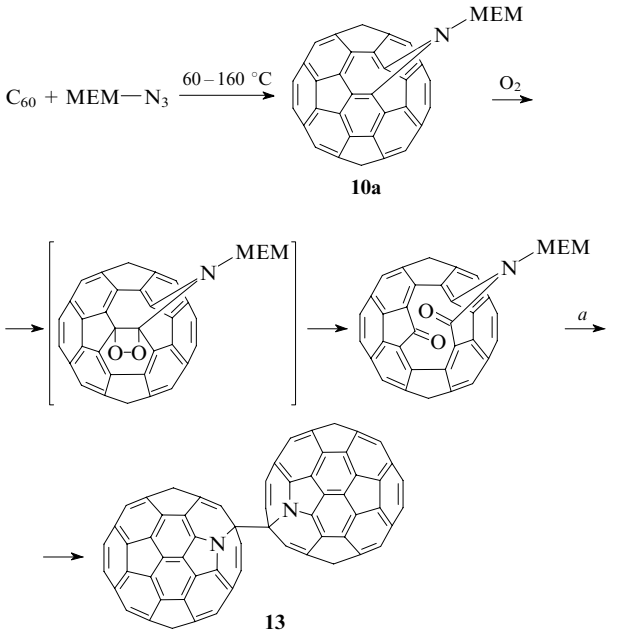
The most important [2 + 3] cycloaddition reactions are considered below in more details.

b. Reactions of fullerenes with azides and diazo compounds

The addition of azides is a rather abundant reaction in chemistry of fullerenes; however, it does not always afford high yields of products. Particularly, this approach was used in the synthesis of a unique dimeric azafullerene $[C_{59}N]_2$ (**13**).[141]

Table 5. Examples of [2 + 1] cycloaddition reactions to fullerene C_{60} (see Scheme 6).

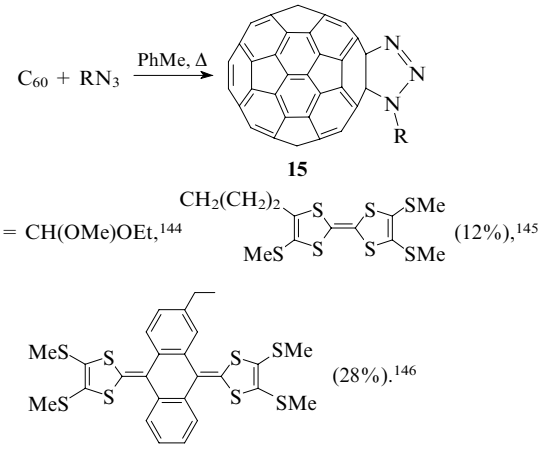
Reagent	Conditions	Product			Ref.
		XR^1	No.	yield (%)	
$PhHgCBr_3$	Δ	CBr_2	**4q**	58	137
N_2CHCO_2Et	$Rh_2(OAc)_4$, 1-methylnaphthalene	$CHCO_2Et$	**4b**	42	138
$(2,6\text{-}Pr^iC_6H_3)_2Si(SiMe_3)_2$	*hv*	$Si(C_6H_3Pr^i\text{-}2,6)_2$	**11**	–	136



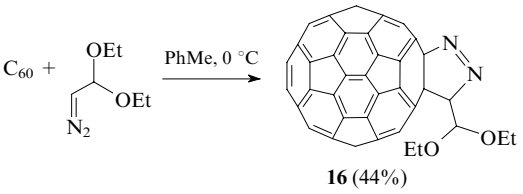
MEM is $MeO(CH_2)_2OCH_2$;
(*a*) TsOH, H_2O, DCB, 180 °C, 10 min

Reactions with azides represent one of the ways of opening the fullerene sphere for the subsequent incorporation of a small molecule. In this manner, compound **14** was synthesised (Scheme 7).[142, 143]

In certain cases, reactions with azides produced fullerene derivatives **15** annulated with a triazole ring.[144–146]

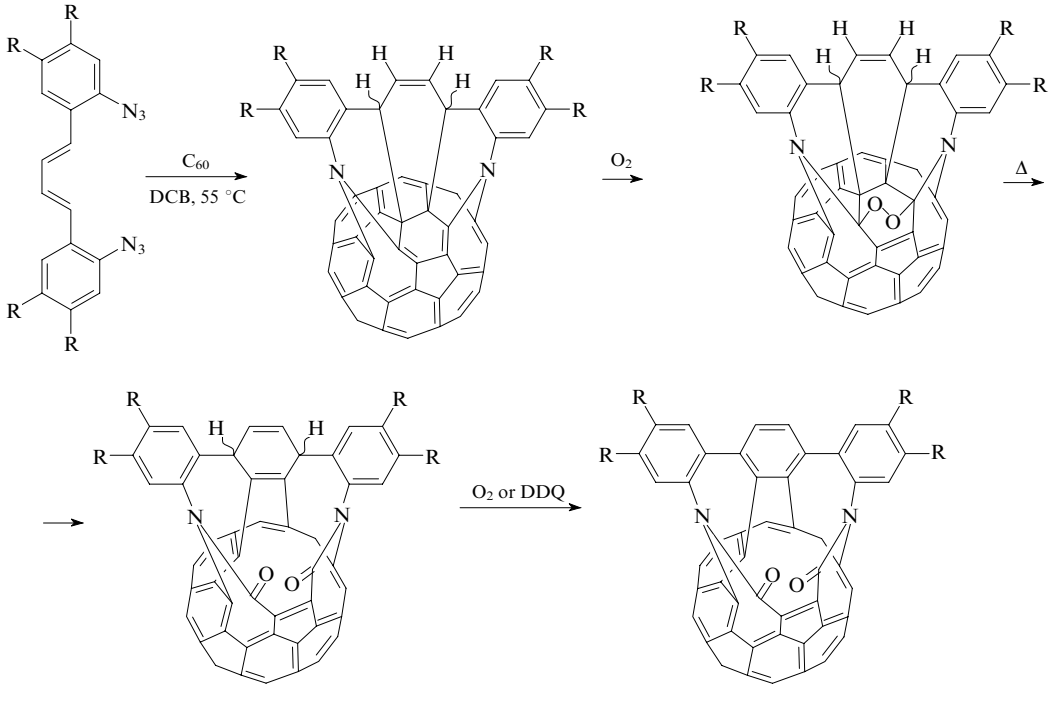


The direct reaction of fullerene with diazo compounds is used rather rarely probably due to the fact that the starting reagents are not always accessible.[10] Yet another example of the preparation of stable pyrazolinofullerene **16** from a diazo acetal under mild conditions is documented.[147]



Diazo compounds are usually generated from stable precursors in the presence of fullerene. It is convenient to

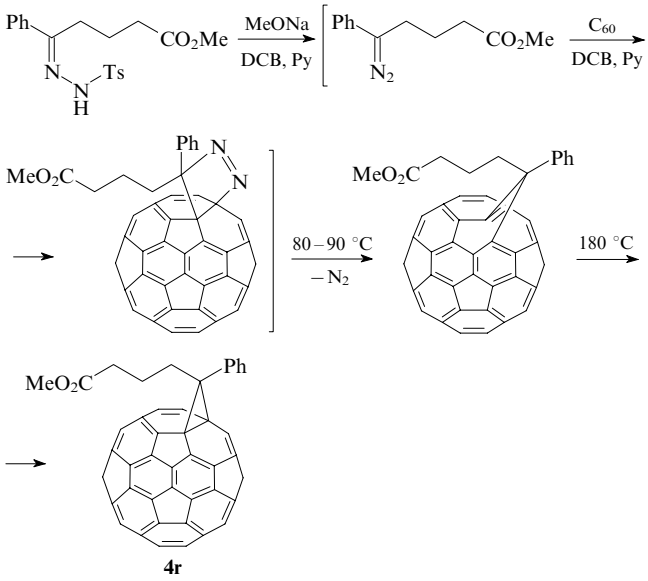
Scheme 7



DDQ is dichlorodicyanoquinone

synthesise diazo compounds *in situ* from tosylhydrazones of aromatic aldehydes or ketones under the action of sodium methoxide. This method was developed by Hummelen and Wudl and successfully used in the synthesis of PCBM (Phenyl-C_{61}-Butyric acid Methyl ester, **4r**), a fullerene derivative widely utilised as the material of plastic organic solar cells (Scheme 8).[148]

Scheme 8



4r

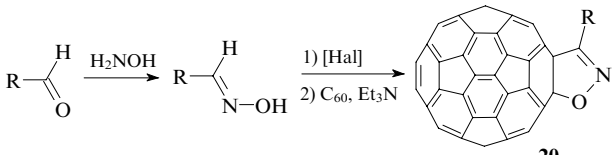
In the first step of the reaction, the diazo compound formed *in situ* adds to fullerene to afford pyrazolinofullerene. Opening of the pyrazoline ring with elimination of a nitrogen molecule occurs at 80–90 °C and is accompanied by the cleavage of a 6–5 single bond in the fullerene cage to afford the corresponding fulleroid; the latter was successfully isolated in the pure form. This fulleroid undergoes quantitative transformation into closed 6–6-methanofullerene **4r** at 180 °C. The Hummelene–Wudl method is the most convenient approach to the synthesis of fulleroids and methanofullerenes that are impossible to synthesise by the Bingel–Hirsch reaction.

Table 6 exemplifies the use of [2+3]-cycloaddition of azides and diazo compounds in functionalisation of fullerene C_{60}.

Among uncommon reaction products, compounds **17**–**19** synthesised by several research groups [163–165] deserve mention (Scheme 9).

c. Addition of nitrile oxides

Various nitrile oxides are generated in halogenation of aldoximes followed by elimination of a hydrogen halide molecule from the hydroximoyl halide formed under the action of triethylamine or sodium carbonate. Most often, *N*-bromo- (NBS) and *N*-chlorosuccinimides (NCS) serve as the halogenation reagents. Cycloaddition of nitrile oxides to C_{60} fullerene yielded oxazolinofullerene **20**.[166–168]

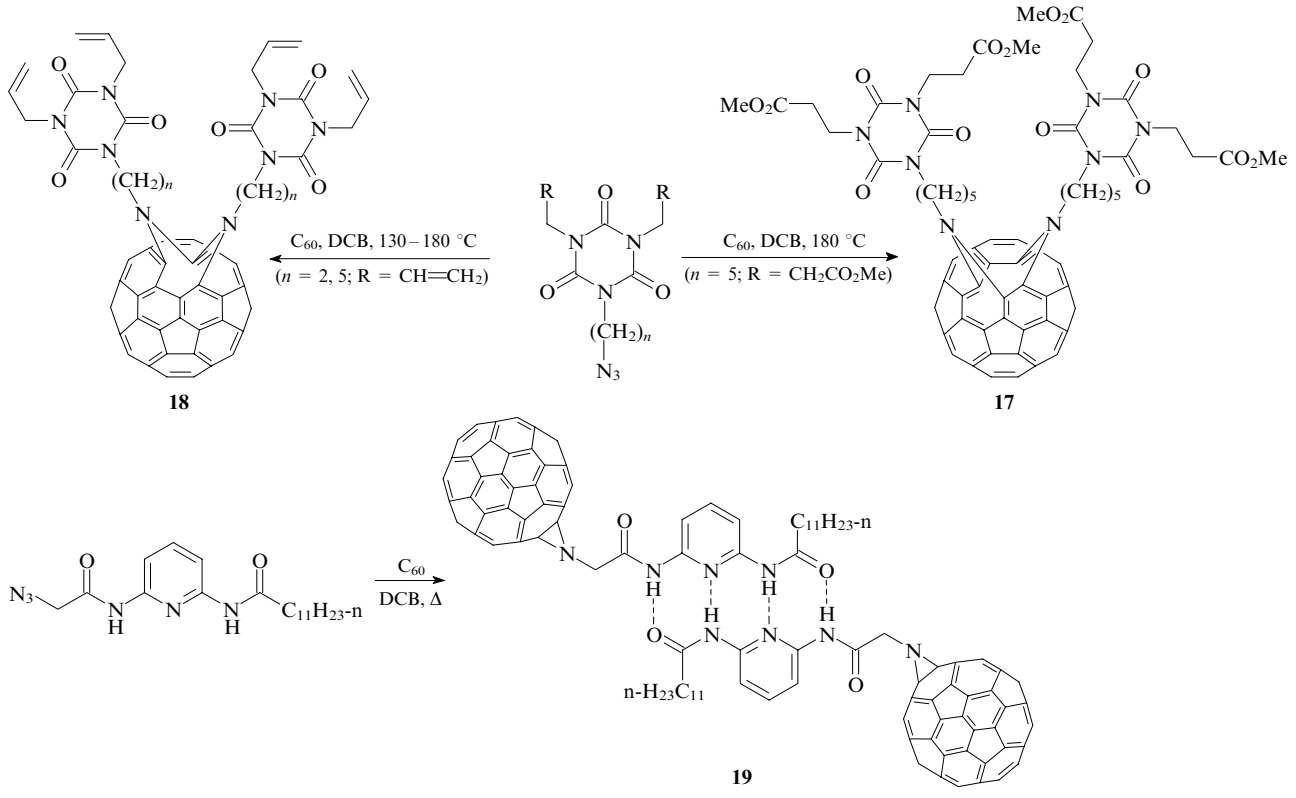


[Hal] is NBS or NCS

20

In place of oximes, their chlorinated derivatives, namely, hydroximoyl chlorides can be introduced into this reaction (Table 7).

Scheme 9



18 **17**

19

Table 6. Reaction of C_{60} with diazo compounds, hydrazones and azides (see Scheme 6).

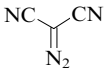
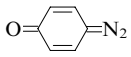
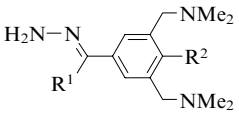
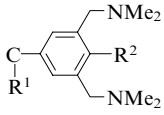
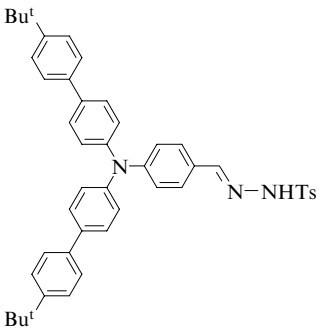
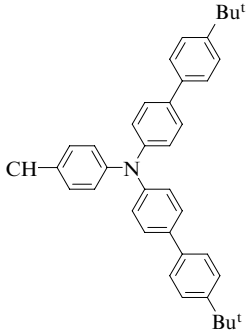
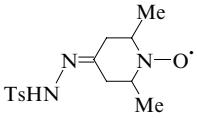
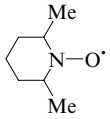
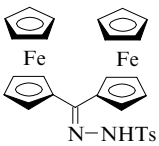
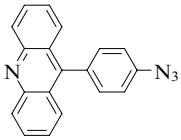
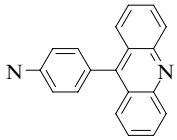
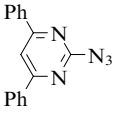
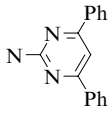
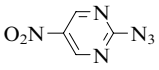
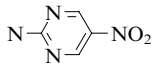
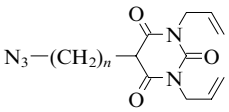
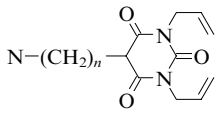
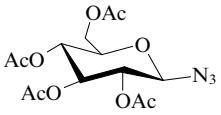
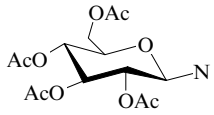
Reagent	Conditions	Product			Ref.
		XR^1	No.	yield (%)	
	*hv*, 45 °C, 10 h	$C(CN)_2$	**4s**	26	105
	*hv*, 10 °C, 1 h		**4t**	47	149
	PhMe, Δ	$CHCO_2Et$	**4b**	5	150
			9′b	20	150
			9″b	10	150
	the same	$CHCONR_2$	**4u**	10	150
			9′u	2	150
			9″u	18	150
(NR_2 = $N(CH_2CH_2)_2O$, NHBz, $NHCH(Bn)CO_2Bn$, $NH(CH_2)_4CH(NH_2)CO_2Et$)					
$(EtO)_2P(O)C(Ph)N_2$		$C(Ph)P(O)(OEt)_2$	**4v**	72	151
 (R^1 = H, Me; R^2 = H, Br)	MnO_2, KOH, EtOH		**4w** + **9w**	35	152
	MeONa		**4x**	25	153
	MeONa		**9a**	7.2	154
	EtONa	$C(Fc)_2$	**4y**	22	155
	DCB, Δ		**10b**	28	156
	DCB, 180 °C		**8c**	12	157
			10c	6	157

Table 6 (continued).

Reagent	Conditions	Product			Ref.
		XR[1]	No.	yield (%)	
	the same		**10d**	–	158
	DCB, 160 °C		**8d**	11	158
	DCB, 100 °C	–	see [b]	10	159
 (n = 2, 4, 6, 10)	DCB, 50–180 °C		**8e**	–	160
			10e	–	160
$(Bu^nO)_2P(O)N_3$	DCB, 180 °C	$NP(O)(OBu^n)_2$	**10f**	20	161
	PhCl, Δ		**10g**	70	162

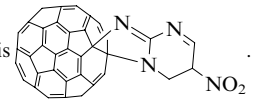
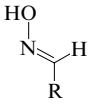
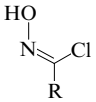
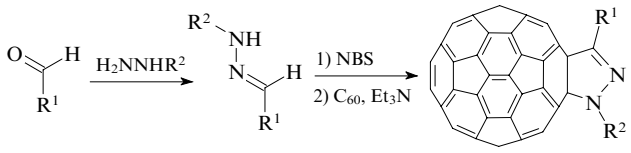
[a] Fc is ferrocenyl; [b] the product is .

Table 7. Addition reactions of nitrile oxides to fullerene C_{60}.

Reagent	R	Conditions	Product		Ref.
			No.	yield (%)	
	C_6F_5	1) NCS, $CHCl_3$ 2) C_{60}, PhMe, Na_2CO_3	**20a**	23	166
	2-$(C_6F_5)C_6H_4$	the same	**20b**	18	166
	4-$(C_6F_5)C_6H_4$		**20c**	2	166
	9-anthryl	C_{60}, PhMe, Na_2CO_3	**20d**	–	167
	$MeO[(CH_2)_2O]_2CH_2$	the same	**20e**	30	168

d. Addition of nitrile imines

Nitrile imines are generated by the analogy with the synthesis of nitrile oxides, where mono-*N*-substituted hydrazine acts as the nitrogen-containing component in the reaction with aldehyde. The synthesis of a large group of disubstituted pyrazolinofullerenes **21** was described.[169] This approach allows one to vary two substituents in the heterocyclic ring of a fullerene, for example,



21a–c

R^1 = 1-phenylpyrazol-4-yl, R^2 = 4-$R^3C_6H_4$ (R^3 = H, OMe, NO_2) (**a**, yields of 35%–55%),[170]

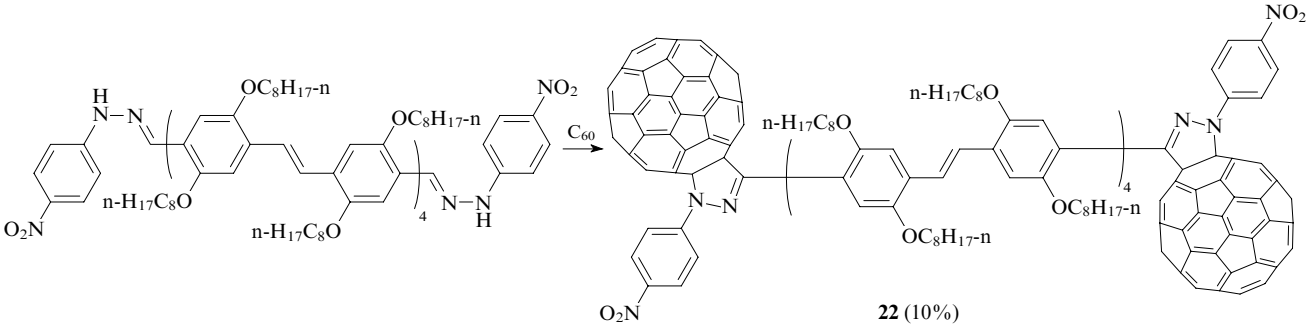
R^2 = Ph; R^1 = 2-pyridyl (**b**), 3-(2-pyridyl)pyridin-2-yl (**c**).[171]

The preparation of bisfullerene derivative **22** in low yield was achieved starting from corresponding bishydrazone (Scheme 10).[172]

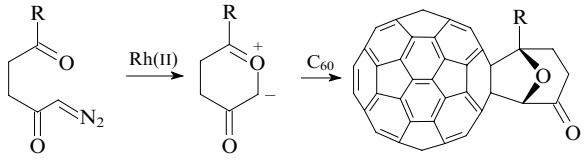
Addition of carbonyl ylides

Reactions of C_{60} fullerene with carbonyl ylides are poorly investigated, which is associated with difficulties in the synthesis of the latter. Relatively recently, the generation of cyclic carbonyl ylides from diazo-1,4-diones, catalysed by bivalent rhodium salts, was studied.[173] Carbonyl ylides synthesised *in situ* smoothly react with [60]fullerene to form the corres-

Scheme 10



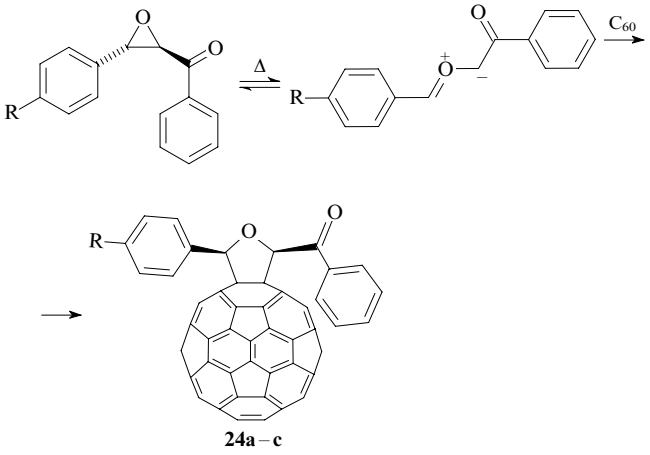
ponding tetrahydrofuran-appended compounds **23a–g**. This reaction has not yet found wide synthetic application due to unaccessibility of the parent diazo-1,4-diones.



23a–g

R = Me (**a**, 40%), Ph (**b**, 45%), 4-MeC_6H_4 (**c**, 48%), 4-$MeOC_6H_4$ (**d**, 31%), 4-ClC_6H_4 (**e**, 39%), 2-HSC_6H_4 (**f**, 53%), Fc (**g**, 40%).

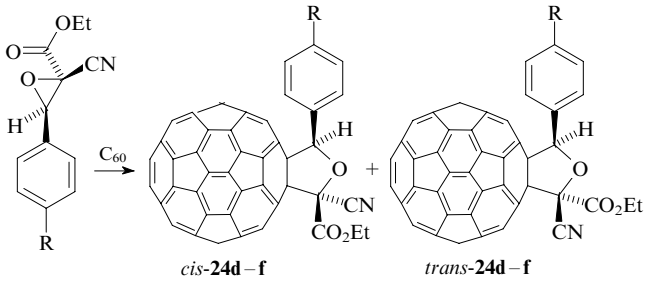
In 2006, a new promising method of carbonyl ylide generation for [2 + 3] cycloaddition to fullerene, based on the thermal tautomerisation of oxiranes, was described.[174] Oxiranes are easily available reagents that can be used in functionalisation of fullerenes.



24a–c

R = H (**a**, 93%), NO_2 (**b**, 42%), OMe (**c**, 35%).

It is important that these reactions are stereoselective, *viz.*, *trans*-2,3-disubstituted oxiranes are converted only in *cis*-2,5-disubstituted tetrahydrofuranofullerenes **24a–c**. Reaction of C_{60} with *cis*-2,3-disubstituted oxiranes was not yet conducted. From 1,1,2-trisubstututed oxiranes, both *cis*- and *trams*-isomers of trisubstituted tetrahydrofuranofullerenes **24d–f** are formed. The major product is an isomer that contains the most bulky groups on one side of the five-membered ring (quasi-*cis*-configuration).



cis-**24d–f** *trans*-**24d–f**

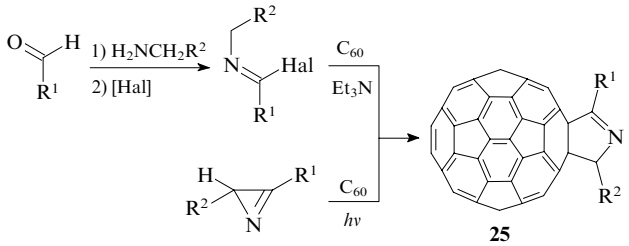
Compound	R	Yield (%)	
		cis	*trans*
24d	H	34	8
24e	NO_2	38	–
24f	OMe	23	20

This a stereochemistry was also observed in [2 + 3] cycloaddition of disubstituted azomethine ylides (see below) to afford *cis*-2,5-disubstituted pyrrolidinofullerene as the major and even the only product. *cis*-Isomers of disubstituted pyrrolidinofullerenes are more stable than *trans*-isomers; hence, in this case, the stereoselectivity is explained by the presence of thermodynamic control in the reaction system. Apparently, *cis*-isomers of disubstituted tetrahydrofuranofullerenes **24** also surpass their *trans*-forms in stability, and their synthesis from C_{60} and oxiranes proceeds under themodynamic control, too.

f. Generation of nitrile ylides and their addition to fullerene C_{60}

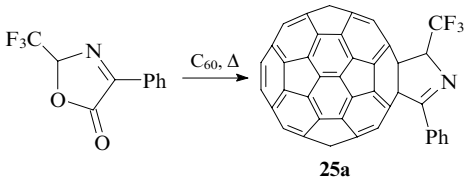
Nitrile ylides can be formed from imidoyl halides by analogy with the generation of nitrile oxides and nitrile amines.[175–177] However, synthesis of the starting imidoyl halides is often a non-trivial task; hence, this approach was not widely used.

An alternative approach to the synthesis of pyrrolinofullerenes **25** is the photochemical ring opening of mono- or disubstituted azirines in the presence of fullerene C_{60}.[178, 179] However, the accessibility of azirines is also very limited, and this reaction is scarcely used.



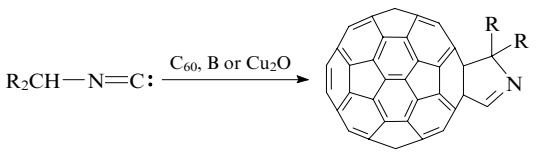
25

Disubstituted pyrrolinofullerenes, for instance, compound **25a**, can be synthesised by thermal decomposition of certain heterocyclic compounds that easily eliminate a CO_2 or SO_2 molecule.[180] The main problem with the practical use of this reaction is also unaccessibility of the starting heretocycles containing different substituents.



25a

Pyrrolinofullerenes **25b** *gem*-disubstituted in position 5 of the heterocycle were synthesised by addition of different isocyanides to the fullerene cage.[181] This reaction was catalysed by bases or copper(I) monoxide, the yields of products depended on the nature of reagents, varying from 10% to 90%. However, this method, too, has not received wide utilisation.

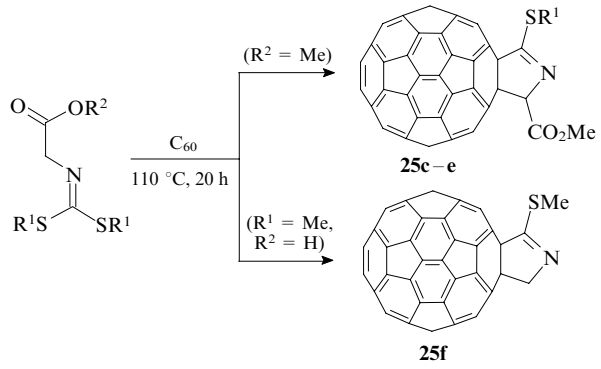


25b

B is a base

Recently, it was shown[182] that thermal elimination of a thioalkyl residue from activated imidodithioates may also serve as the method of generating nitrile ylides which afford derivatives **25c–e** in the reactions with fullerene C_{60}. If a

compound containing an α-carboxyl group was used as a reagent, the reaction was accompanied by decarboxylation to form monoalkylthiosubstituted pyrrolinofullerene **25f**.

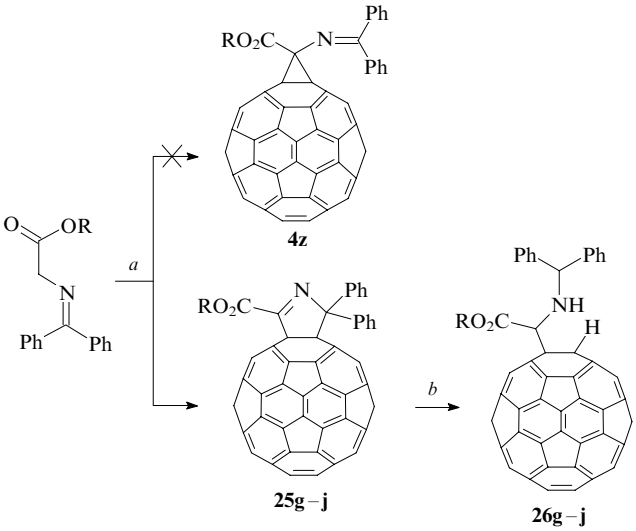


25c–e

25f

R^1 = Me (**c**), Et (**d**), Pr^i (**e**); R^2 = H, Me.

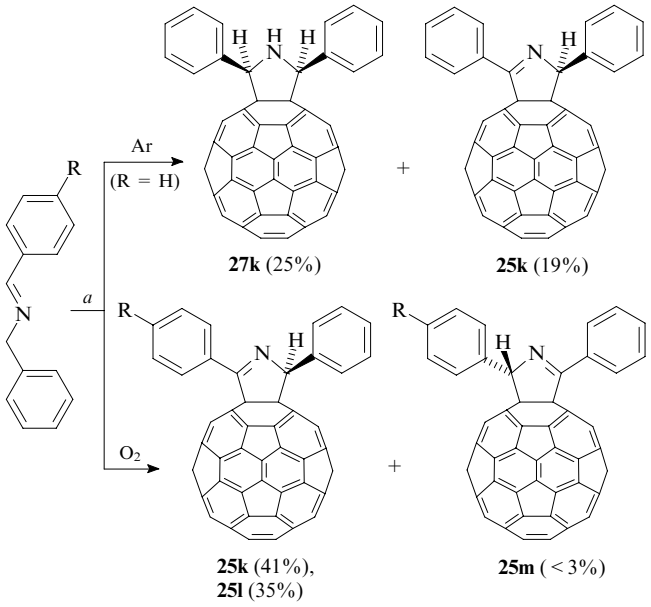
The most promising approach to the synthesis of pyrrolinofullerenes employs imines of glycine esters as the reagents. Initially, it was assumed [183–186] that the action of CBr_4 and DBU on benzophenone imines derived from glycine esters in the presence of C_{60} affords methanofullerenes **4z** by analogy with the Bingel–Hirsch reaction; however, seven years later, it was found [187] that it is pyrrolinofullerenes **25g–j** that are the reaction products. Taking into account the accessibility of the starting ketones and glycine esters, the reaction can find wide use in the synthesis of various pyrrolinofullerenes.



(*a*) C_{60}, CBr_4, DBU, PhCl; (*b*) $NaBH_3CN$, $BF_3 \cdot Et_2O$;
R = Et (**g**, 76%), Bu^t (**h**, 46%), CH_2CO_2Et (**i**, 46%), 1-menthyl (**j**, 31%).

Pyrrolinofullerenes **25g–j** are reduced with sodium borocyanohydride is the presence of boron trifluoride etherate with opening of a single C–N bond and the addition of a hydrogen atom to the double C=N bond to form compounds **26g–j**.

Yet another approach to the synthesis of pyrrolinofullerenes is the oxidative addition of benzylamine-derived imines to fullerene C_{60}. In air, this reaction afforded pyrrolinofullerenes **25k–m** as the only products, whereas in the argon atmosphere, pyrrolidinofullerene **27k** was also formed.[188] The availability of the parent amines makes this method very attractive for the synthesis of pyrrolinofullerenes.

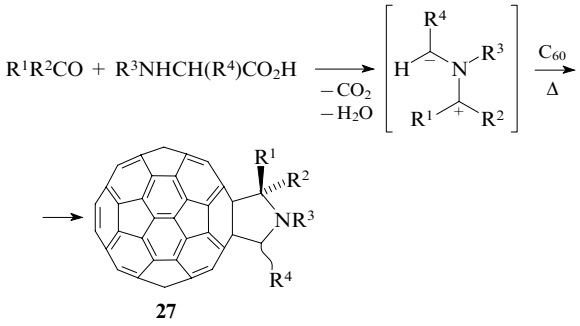


(*a*) C_{60}, Pr^nCO_2H, DCB, 180 °C; R = H (**k**), NMe_2 (**l**, **m**).

g. Addition of azomethine ylides to fullerenes to afford pyrrolidinofullerenes

The addition of azomethine ylides to the fullerene cage is one of the most important reactions in the chemistry of fullerenes. Back in 1993, it was found [189] that the reaction of *N*-substituted α-amino acids with carbonyl compounds and C_{60} affords the corresponding pyrrolidinofullerenes (the sarcosine method of Prato, Scheme 11). Later, modified versions of [2+3] cycloaddition of azomethine ylides to the fullerene cage were found, which are also often referred to as the Prato reaction.

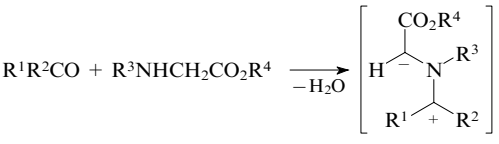
Scheme 11



27

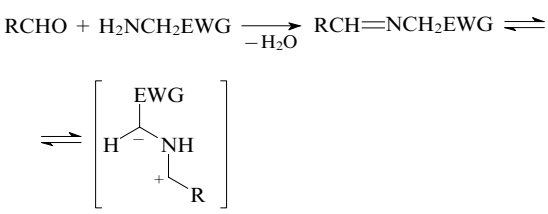
R^1, R^2 = H, Alk, Ar; $R^3 \neq H$, R^4 = H; R^3 = H, $R^4 \neq H$.

For example, azomethine ylides can be synthesised from esters of α-amino acids and carbonyl compounds [reaction (1)],[190] by tautomerisation of imines containing an activated methylene group (2),[191] photochemical cleavage of certain aziridines (3),[190, 192, 193] and elimination of small molecules from the corresponding heterocyclic derivatives (4).[194]



(1)

R^1, R^2 = H, Alk, Ar; R^3, $R^4 \neq H$.

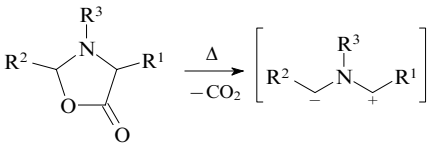


(2)

R = H, Ph; EWG = CO_2Me, $C(O)NHCH_2CO_2Me$, $P(O)OMe_2$.

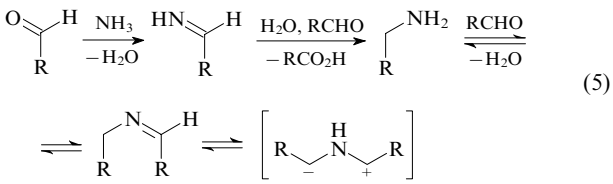


(3)



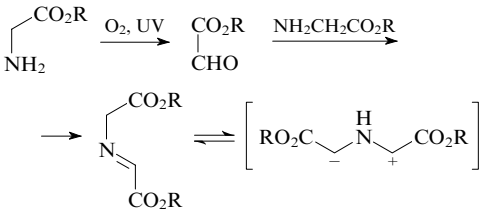
(4)

The reaction of aldehydes with aqueous ammonia seems also to proceed *via* azomethine ylides (5).[195] In this case, aldehyde taken in excess acts as a reducing agent to transform the intermediate aldimine into an amine; the reaction of the latter with the original aldimine affords an imine, which is tautomerised into the azomethine ylide.



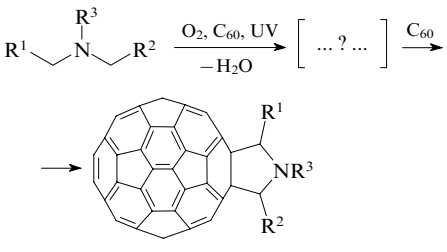
(5)

Oxidative photochemical addition of esters of α-amino acids and tertiary amines to fullerenes affords pyrrolidinofullerenes; however, the mechanisms of these two reactions substantially differ. An imine that contains an activated methylene group was formed as an intermediate when esters of α-amino acids were irradiated in air [reaction (6)]. The reaction mechanism involves partial oxidation of the amino acid ester to aldehyde followed by further tautomerisation of the imine formed.[196, 197]



(6)

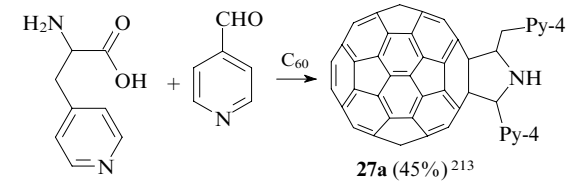
The mechanism of photochemical oxidative addition of aliphatic tertiary amines (7) to [60]fullerene is still unclear; presumably, it involves the intermediate formation of biradicals.[198–200]



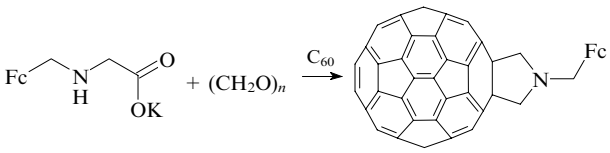
(7)

27

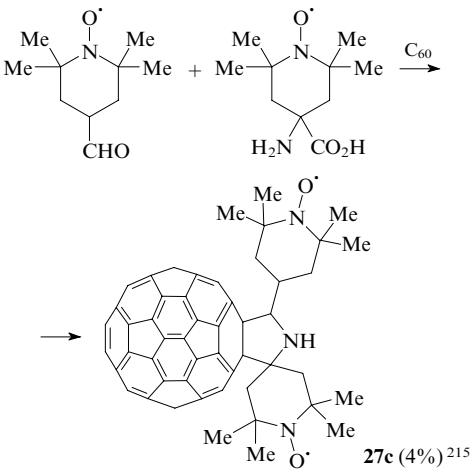
Among all considered methods of azomethine ylide generation, only the route shown in Scheme 11 was widely used in the synthesis of different fullerene derivatives. Thus based on sarcosine and different aldehydes, a number of *N*-methylpyrrolidino[60]fullerenes **27** ($R^1 = R^2 = H$, $R^3 = Me$) substituted in position 2 of the heterocycle were obtained (Scheme 12). The synthesis of compounds **27a–c** can be assigned to this type of reaction.



27a (45%)[213]

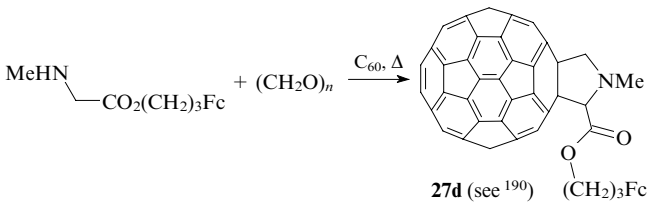


27b (58%)[214]

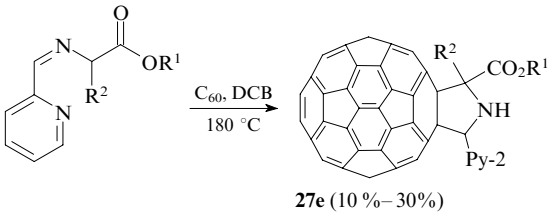


27c (4%)[215]

Certain examples of synthesis of pyrrolidinofullerenes **27d–g** are known in which azomethine ylides were obtained in reactions (1)–(4), respectively.[190, 192, 216]



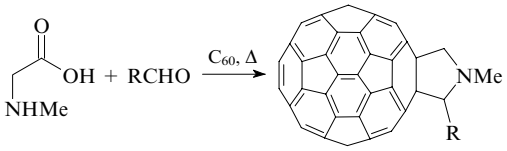
27d (see [190])



27e (10%–30%)

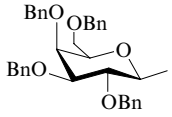
R^1 = Me, Et; R^2 = Me, Bn, 4-$HOC_6H_4CH_2$.[216]

Scheme 12

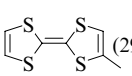


27

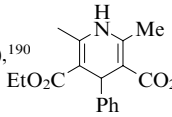
R = H (41%),[189] 4-$O_2NC_6H_4$ (60%),[201] Fc (57%), 4-Py (44%),[190] 4-$(ClCH_2CH_2)_2NC_6H_4$ (36%),[202] 3,5-Bu^t_2-4-HOC_6H_2 (42%),[203]



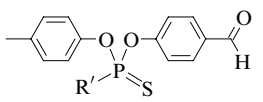
(14%),[204]



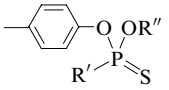
(29%),[190]



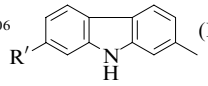
(see [205]),



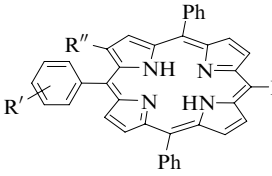
(R′ = Me, Ph; 14%–35%),[206]



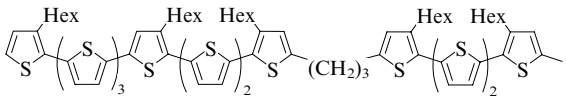
(R′ = Et, R″ = Pr^n; R′ = EtO, R″ = Et; 31%–40%),[206]



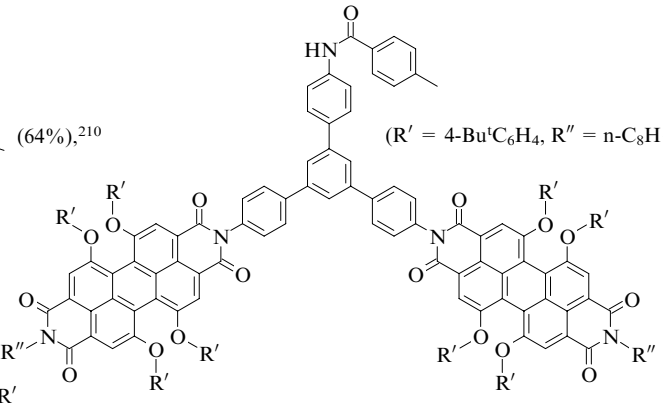
(R′ = H, CHO; 40%–56%),[207]



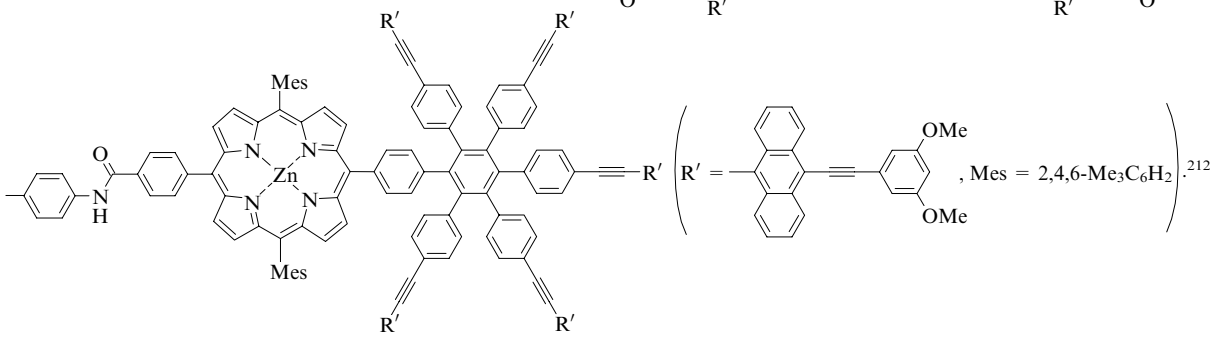
[R′ = 4-$C_6H_4O(CH_2)_2O$, R″ = H (20%–30%);[208] R′ = H, R″ is a bond (40%)[209],



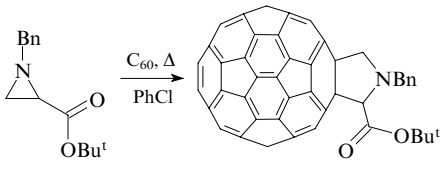
(64%),[210]



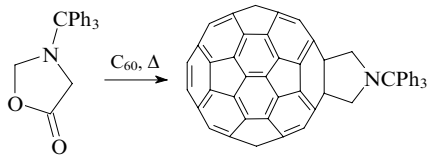
(R′ = 4-$Bu^tC_6H_4$, R″ = n-C_8H_{17}; 37%),[211]



, Mes = 2,4,6-$Me_3C_6H_2$).[212]



27f (38%)[192]

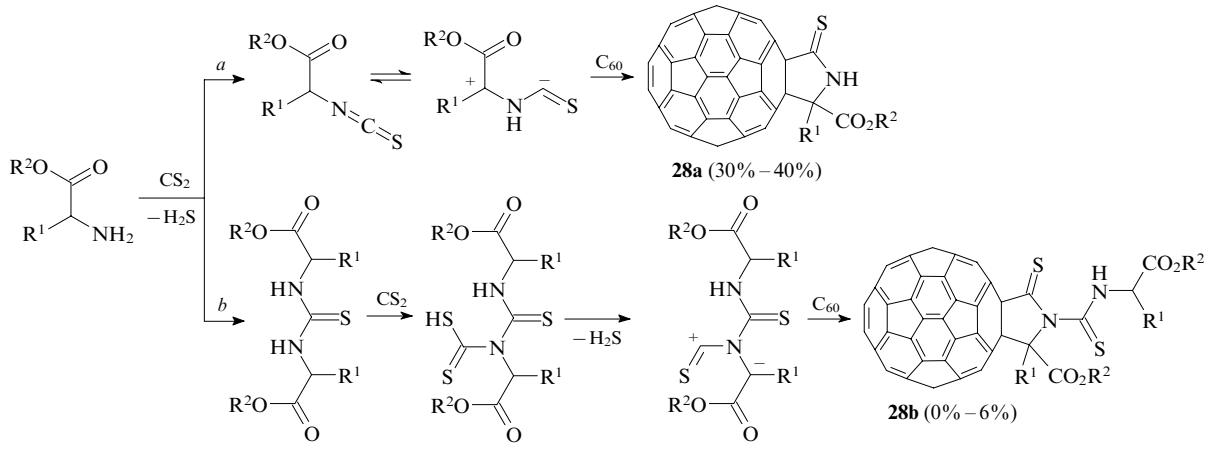


27g (39%)[190]

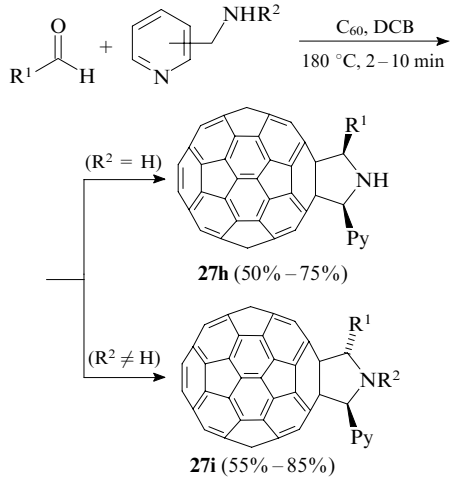
An unusual method of synthesis of pyrrolidinethiones **28a**,**b** is a reaction of C_{60} with amino acid esters and carbon disulfide in the presence of triethylamine.[217] It was assumed that this reaction follows a stepwise mechanism with the nucleophilic addition of a $R^2O_2CC^-(R^1)N{=}C{=}S$ anion to the fullerene cage as the key stage. However, we believe that the formation of azomethine ylide by reaction (2) where carbon disulfide acts as a carbonyl component [*i.e.*, the reaction of C_{60} with CS_2 and amino acid esters follows path *a* (Scheme 13)] is more probable. A side reaction product **28b** is formed by a mechanism (path *b* in Scheme 13) similar to that of reagent generation according to Eqn (1).

A very promising new route for synthesising pyrrolidinofullerenes **27h**,**i**, which is based on the use of picolylamines and aldehydes, has been proposed recently.[218] Non-substituted picolylamines react with aldehydes in the presence of a fullerene according to Eqn (2), where the pyridine ring acts as an electron-withdrawing group. The reaction of *N*-substituted picolylamines with aldehydes proceeds by the same mechanism as reaction (1) and the pyridine ring acts as a substitute for the activating $COOR^4$ group.

Scheme 13



R^1 = H, Me; R^2 = Me, Et, n-C_8H_{17}.



R^1 = Ph, 2-Py, 3-Py, 4-Py, 4-(imidazol-1-yl)phenyl;
R^2 = H, Bn, 2-PyCH_2, 3-PyCH_2; Py is 2-, 3- and 4-isomers.

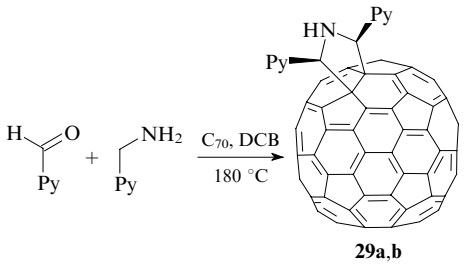
In contrast to the classical sarcosine method of Prato and its versions described above, the picolylamine method has certain important advantages.

1. The process is completed in several minutes, whereas the Prato reaction requires heating of reactants for many hours.

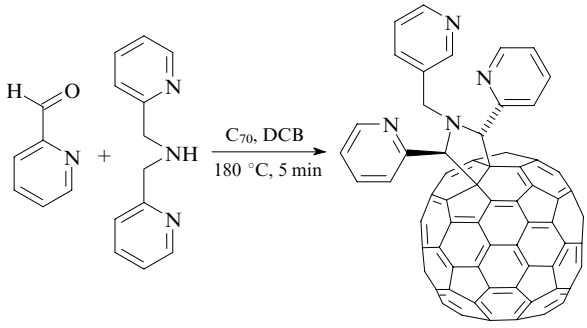
2. Yields of products vary from 50% to 85%, which exceeds twofold the yields of the cycloaddition by the Prato reaction. This is explained by the fact that, in contrast to amino acids, picolylamines are well soluble in organic solvents (*e.g.*, in 1,2-dichlorobenzene) and the reaction proceeds in a homogeneous system. The heterogenous nature of the Prato system apparently leads to the formation of a larger number of side products.

3. The picolylamine method allows one to produce *cis*-2,5-disubstituted and *trans*-1,2,5-trisubstituted pyrrolidinofullerenes. The surprisingly high stereoselectivity of addition is apparently explained by the establishment of a thermodynamic control, which determines the exclusive formation of the most stable stereoisomers.

4. As applied to fullerene C_{70}, the picolylamine method results in highly regioselective addition, namely, only 1,2-cycloadducts [219] were formed, whereas the standard Prato reaction afforded a mixture of the following three regioisomers: 1,2-, 5,6- and 19,20-adducts (see Fig. 3). Moreover, the picolylamine approach allows one to control the reaction stereoselectivity, *viz.*, 2,5-disubstituted pyrrolidino[70]fullerenes **29a**,**b** are formed exclusively as *cis*-isomers and 1,2,5-trisulstituted product **29c** is in its *trans*-form. Complete regio- and stereoselectivity of azomethine ylide addition to C_{70} is also explained by the thermodynamic control over reactions.



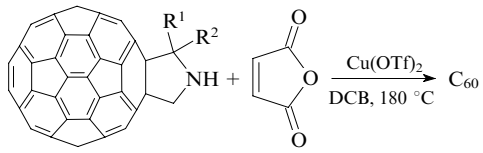
Py is 2-pyridyl (**a**, 38%), 3-pyridyl (**b**, 43%)



Apparently, the picolylamine synthesis is now the most effective way of organic fullerene functionalisation. Apart from its aforementioned merits, it deserves mention that scaling of the synthesis to gramme amounts of fullerene affords the same yields of products as with milligrammes. This is untypical of the Prato and many other reactions of fullerenes; hence, the picolylamine synthesis is very promising for synthesising organic compounds of fullerenes in amounts dictated by their practical use.

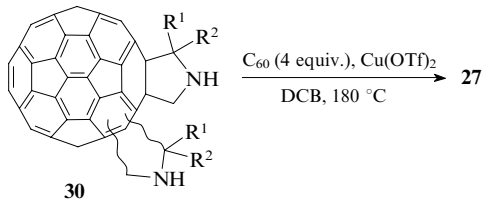
Recently, it has been found [220] that the [2 + 3] cycloaddition reaction of azomethine ylides to a fullerene may be reversible under certain conditions. Thus the reaction of pyrrolinofullerenes **27** (R^3 = R^4 = H) with other active dipolarophiles (*e.g.*, maleic anhydride) in the presence of copper triflate as the

catalyst produced unmodified fullerene in virtually quantitative yield.



27

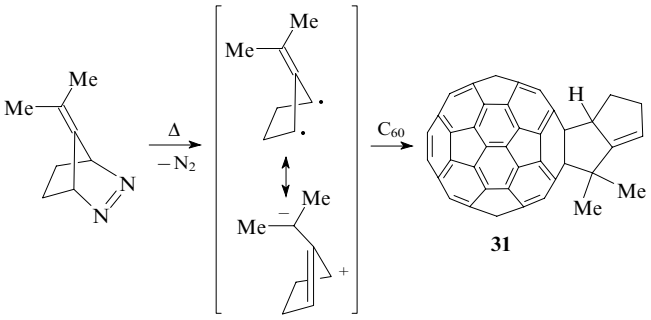
This reaction is equally applicable to pyrrolidine derivatives of fullerenes C_{60} and C_{70}. The reaction of excessive fullerene with a mixture of isomers of bisadduct **30** that contains two pyrrolidine rings attached to the fullerene cage afforded monoaddition product **27** in almost quantitative yield. The latter reaction can find practical use.



30

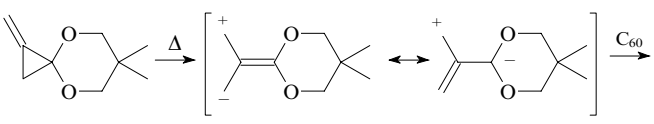
h. Annulated cyclopentane and cyclopentene derivatives of fullerenes

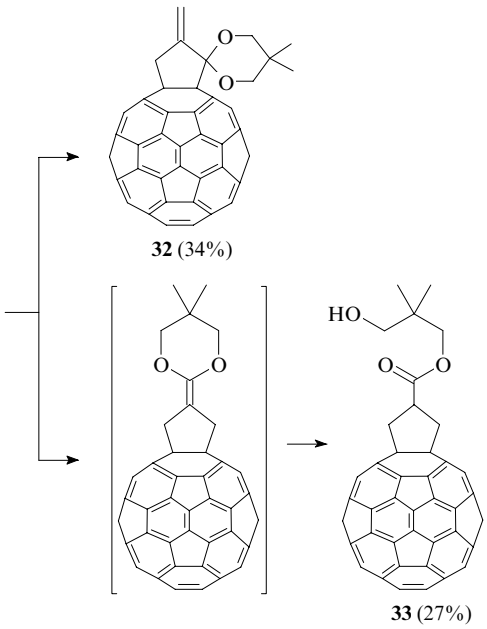
Several addition reactions of carbocyclic fragments to fullerene were described. At present, these transformations are of no synthetic significance, albeit interesting from the theoretical viewpoint, providing direct information on the mechanisms of reactions involving fullerenes. For example, a fullerene reaction with a bicyclic azo compound is known to produce adduct **31**.[221] Presumably, the bicycle decomposes to form a biradical intermediate; however, the probability that the reaction follows the [2 + 3] cycloaddition mechanism cannot be ruled out.



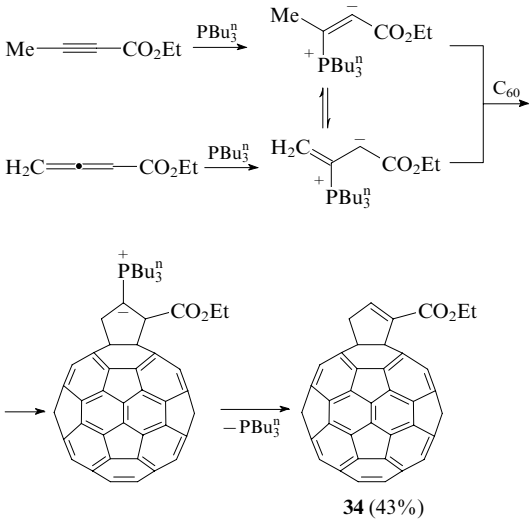
31

Cyclopentanofullerenes **32** and **33** were obtained in the reaction of C_{60} with methylenecyclopropane ketal.[221] It was assumed that the mechanism of this reaction corresponds to the dipolar [2 + 3] cycloaddition.





Synthesis of cyclopentenofullerene **34** is based on the addition of esters of but-2-ynoic or butadienoic acids in the presence of a catalytic amount of tributylphosphine.[222, 223]

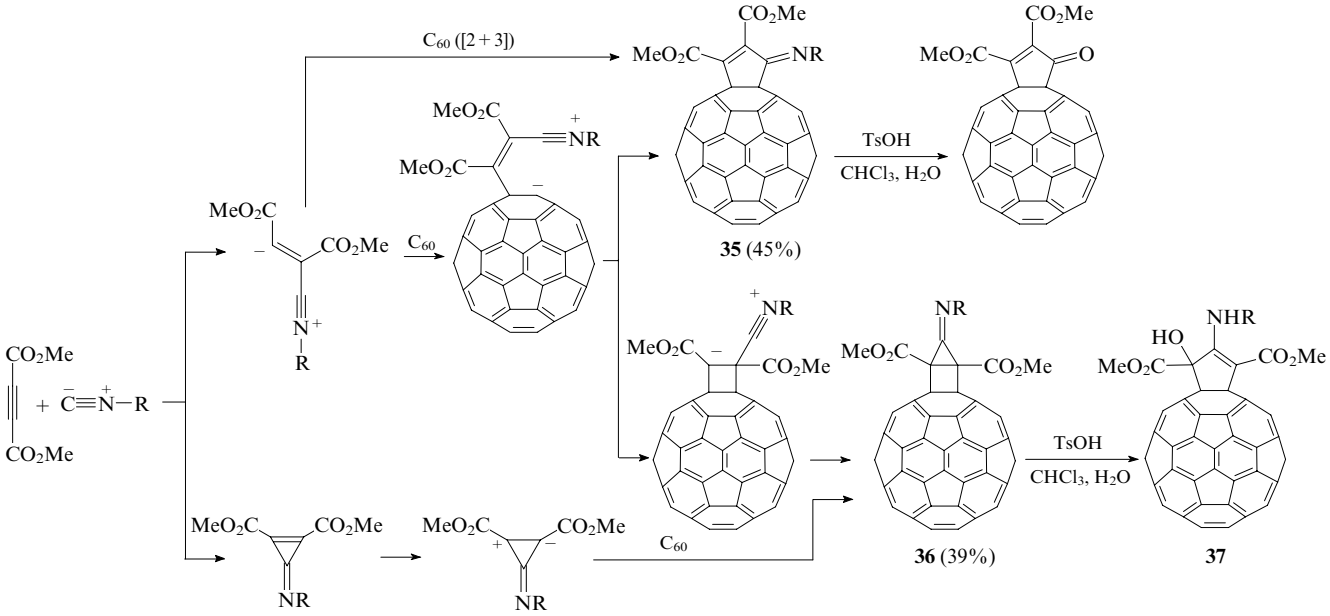


Recently, it has been found [224] that the reaction of acetylenedicarboxylates with isocyanides and C_{60} affords cyclopentenofullerene (**35**) and unusual bicyclopentane (housane, from English word 'house') derivative of fullerene (**36**). The putative mechanisms for the formation of these compounds are depicted in (Scheme 14).

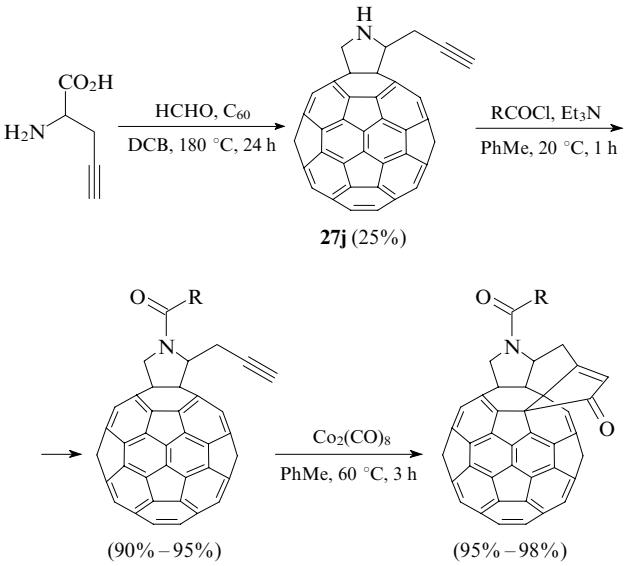
Compounds **35** and **36** undergo hydrolysis in the presence of *p*-toluenesulfonic acid. In the latter case, the nucleophilic opening of cyclopropane takes place to afford product **37**, which represents cyclopentenofullerene (see Scheme14).

An interesting approach to the synthesis of complex cyclopentenone derivatives of fullerenes is the intramolecular Pauson–Khand reaction, where pyrrolidinofullerene **27j** containing a propargyl group serves as the substrate.[225]

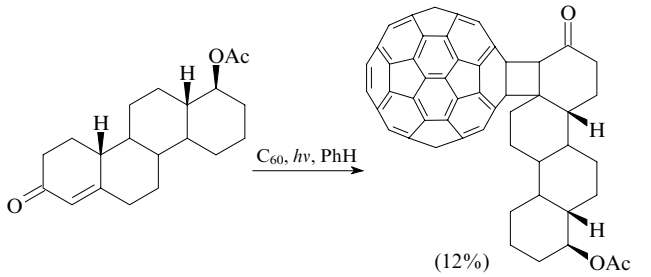
Scheme 14



R = Bu^t, cyclo-C_6H_{11}, 4-$MeOC_6H_4$.

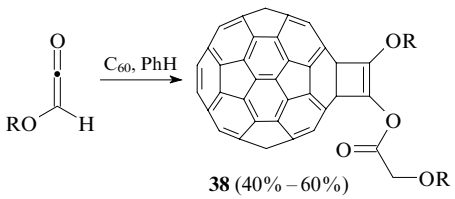


R = Ph, Bn.



The rate constants for the reaction of C_{60} with acyclic ketones are very small; hence, the mentioned reagents should be taken in a large excess.[229] In addition to α,β-unsaturated ketones, various alkenes may be used in such reactions;[230–233] in this case, the substituents at the alkene multiple bond did not retain their configuration.[230] The addition of alkynes and dehydrobenzene to C_{60} also deserves attention.[234, 235]

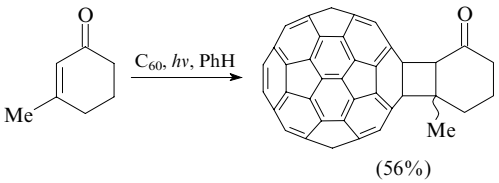
Reaction of [60]fullerene with alkoxy- and aryloxyketenes leads to ketones, which under the reaction conditions, undergo enolisation and acylation by an excess of ketene to afford the corresponding esters **38**.[236]



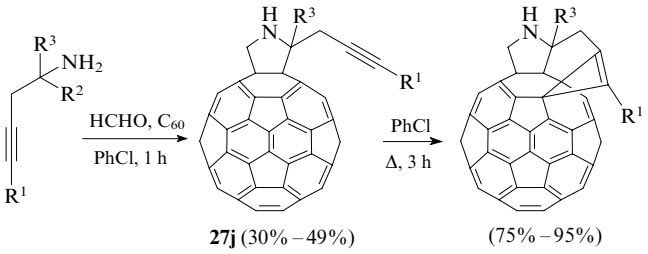
R = Me, Et, Bn, Ph, 4-ClC_6H_4.

2. [2 + 2] Cycloaddition

Cycloaddition to fullerenes by the [2 + 2] mechanism is largely of theoretical interest. It was shown[226–228] that under illumination, fullerene C_{60} adds α,β-unsaturated ketones. This reaction is reversible and proceeds smoothly with cyclic substrates, for example, 3-methylcyclohex-2-enone and a steroid ketone.

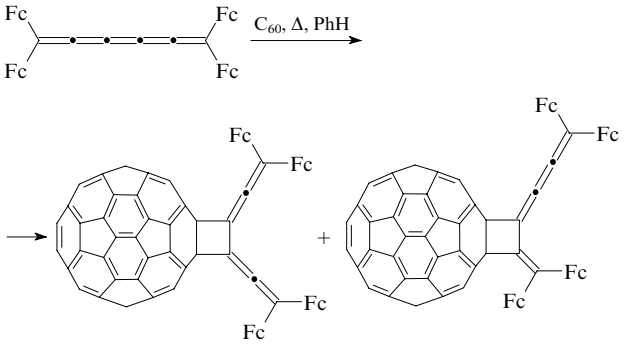


Moreover, an intramolecular version of [2 + 2] cycloaddition to the fullerene derivative **27j** containing propargyl substituent in the pyrrolidine ring is known.[237] An unexpected point is that this reaction is initiated thermally rather than photochemically.

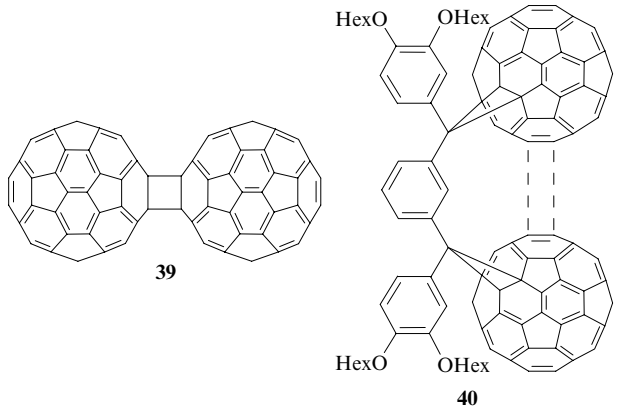


$R^1 = R^2 = H$: $R^3 = H, CO_2Et$; $R^1 = H$, $R^2 = CO_2H$, $R^3 = Me$; $R^1 = Me_3Si$, $R^2 = H$, $R^3 = CO_2Et$.

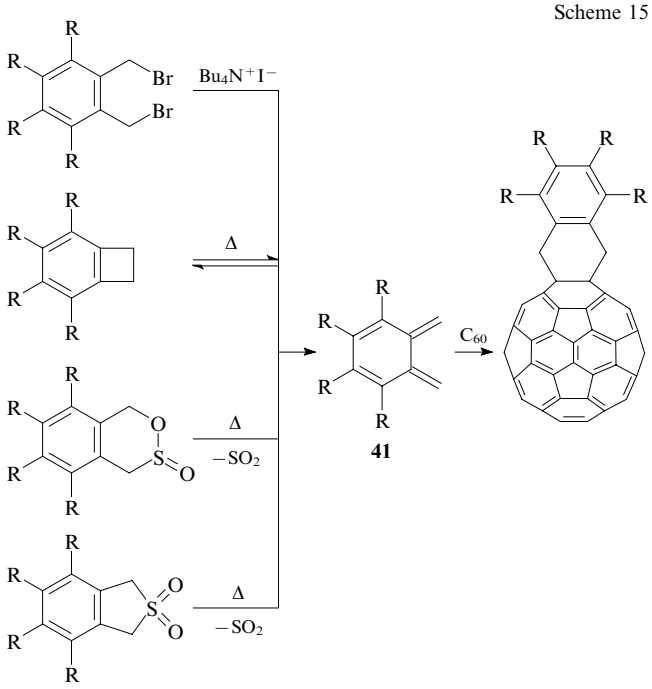
Under conditions of thermal initiation 1,1,6,6-tetraferrocenylhexapentaene adds to C_{60}.[238] Unfortunately, no yields or ratios of products were reported.



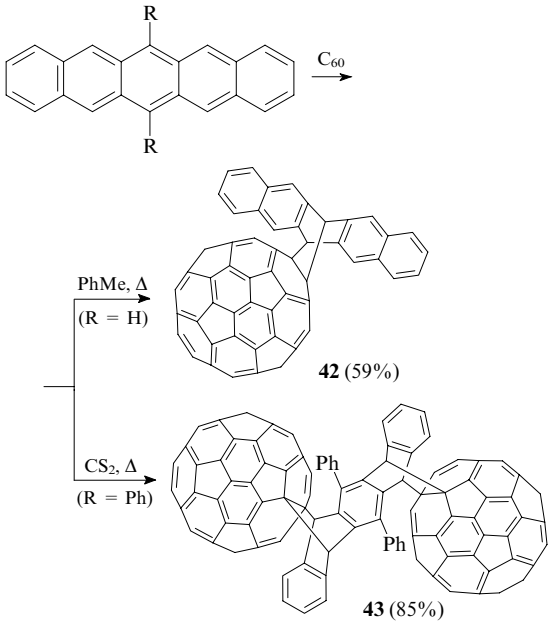
Dimer **39** was isolated in 70% yield as a result of grinding of [60]fullerene in a high-speed jar mill in the presence of KCN or K_2CO_3.[239] A similar cyclobutane derivative was synthesised upon irradiation of bisfullerene **40** (17 °C, yield 84%).[240]



Scheme 15



As the examples of more complex Diels–Alder reaction products involving C_{60}, compounds **42** (Ref. 241) and **43** (Ref. 242) can be shown.

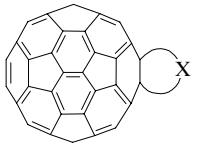


3. [2 + 4] Cycloaddition

In [2 + 4] cycloaddition reactions, fullerene acts as an active dienophile. To date, no examples of the involvement of multiple bonds of the C_{60} cage as the diene component are known. The Diels–Alder reaction in its conventional version is reversible and the case of [60]fullerene is no exception. On the one hand, this fact severely complicates the procedure of adduct isolation and, on the other hand, the thermodynamic control provides high regioselectivity of polycycloaddition.[23]

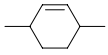
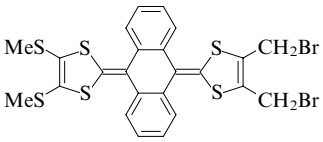
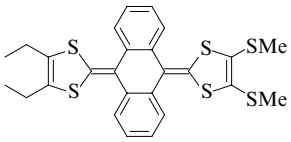
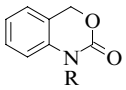
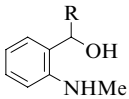
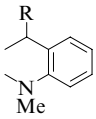
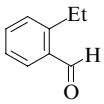
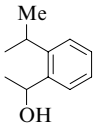
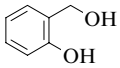
o-Quinodimethanes **41** were used most often as the dienes in the reactions with C_{60}. These compounds are readily generated *in situ* from various precursors, their addition to [60]fullerene proceeds virtually irreversibly with high yields of products (Scheme 15).

In addition to *o*-quinodimethanes, their heterocyclic analogues are widely employed in this reaction. This have put [2 + 4]-cycloaddition among the most important synthetic methods in chemistry of fullerenes.[10] However, at present such syntheses are totally displaced by more convenient Bingel–Hirsch and Prato reactions. Table 8 exemplifies the [2 + 4] cycloaddition reactions which lead to fullerene C_{60} derivatives, namely, compounds **44a–g**.



44a–g

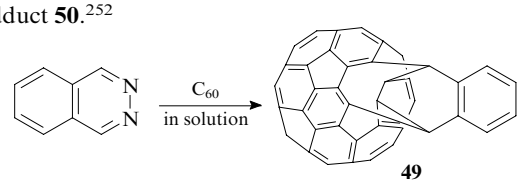
Table 8. [2 + 4] Cycloaddition reactions to [60]fullerene.

Reagent	Conditions	Product			Ref.
		X	No.	yield (%)	
	PhH, 20 °C		**44a**	30	243
	PhMe, NaI, 18-crown-6, Δ		**44b**	25	244, 245
	DCB, Δ		**44c**	–	246
 (R = Me, Ts, CO_2Et)	1,2,4-$Cl_3C_6H_3$, Δ		**44d**	46 – 80	247
 (R = Ph, 4-$MeOC_6H_4$)	DCB, Δ		**44e**	25 – 30	248
	*hv*, PhH		**44f**	85	249
	Δ		**44g**	70	249

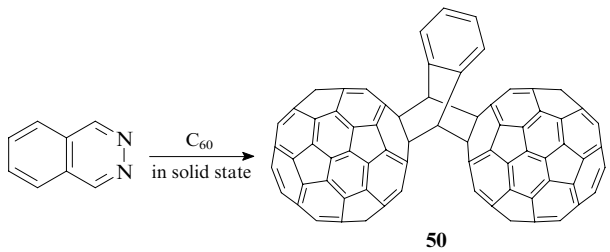
The mechanism of [2 + 4] cycloaddition was also invoked in the synthesis of porphyrin **45** containing four fullerene fragments (Scheme 16).[250]

Isomers **46** and **47** were formed in the reaction of [60]fullerene with iron complex **48** in the presence of *N*-methylmorpholine *N*-oxide (NMMO) [251] (see Scheme 16).

Unexpected results were obtained when phthalazines and 1,2,4,5-tetrazines were used as the diene components in reactions with fullerenes. Thus a reaction of C_{60} with phthalazine in solution afforded bisfulleroid **49** with two open bonds in the fullerene cage; the solid-phase reaction of the same components (grinding in a high-speed mill) afforded bisfullerene adduct **50**.[252]

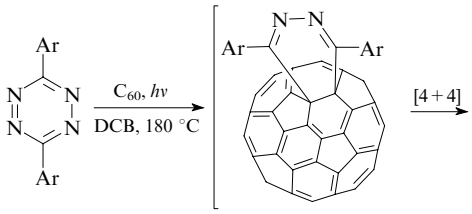


49

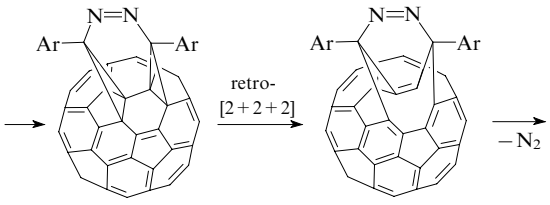


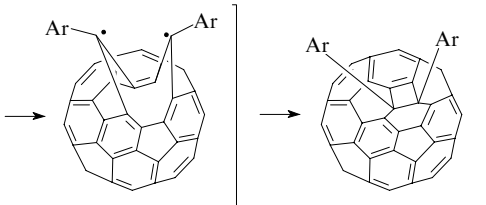
50

Reaction of fullerene C_{60} with 3,6-diaryl-1,2,4,5-tetrazines under intense illumination (1 kW mercury lamp) produced reasonable yields of derivatives (**51**) of a new fullerene C_{62}, which contains a four-membered ring in its carbon cage.[253] This transformation is of great theoretical interest for the studies of reaction mechanisms involving fullerenes.



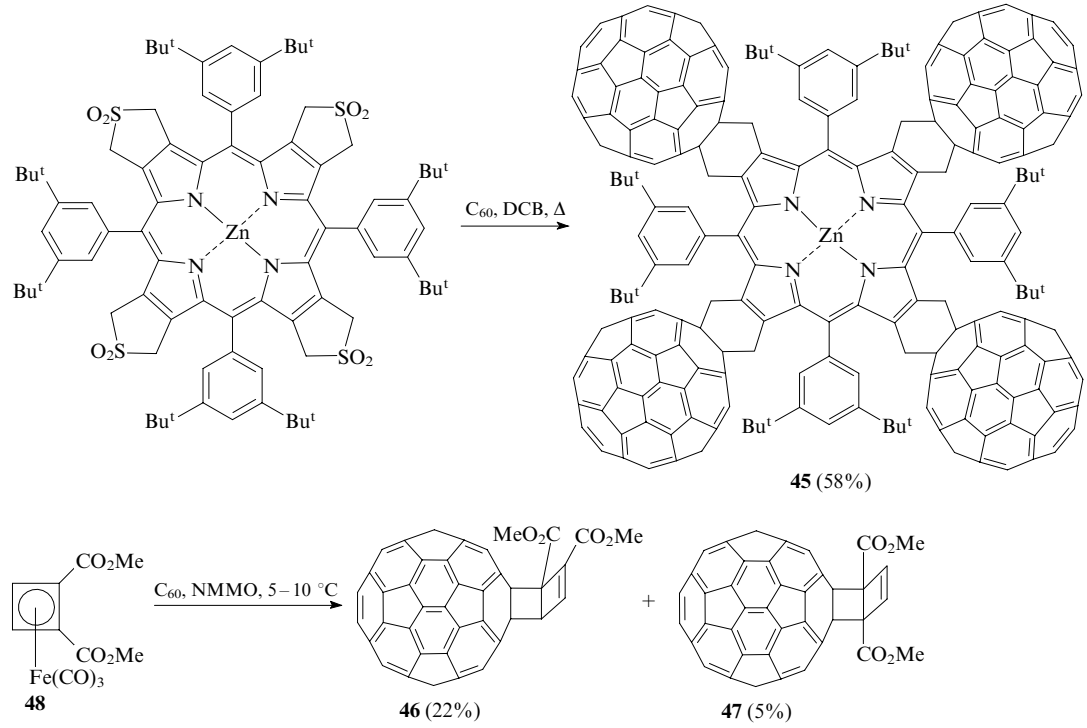
52



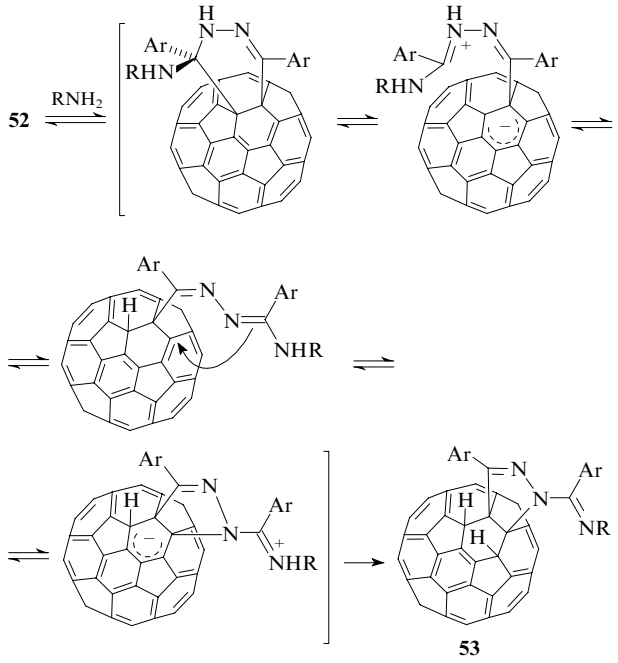


51 (25 % – 30%)

Scheme 16



Note that the thermally induced reaction of C_{60} with 3,6-diaryl-1,2,4,5-tetrazines stopped after formation of pyridazinofullerenes **52**, which proved to be very reactive compounds with respect to different diprotic nucleophiles such as XH_2 (X = RN, O). Thus the addition of an amine brings about a rearrangement with the transfer of protons to the fullerene cage to form pyrazolinofullerene **53**.[254, 255]



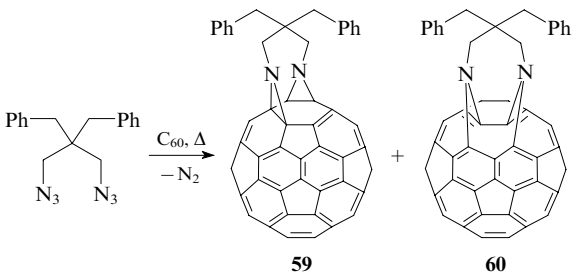
An attractive feature of compound **53** is that this formally is an adduct with the pyrazoline ring fused to a 6–5 bond of the carbon cage. Apparently, this is the only fullerene cycloadduct with an addend in such an unusual position, which was proved by the X-ray diffraction analysis.

Reaction of C_{60} with 1,3,4-triazines was studied.[256] The photochemically or thermally induced reaction of C_{60} with 1,3,4-triazines afforded bisfulleroid **54** in high yield (Scheme 17). Upon irradiation in air, compound **54** was oxidised to form three oxygen-containing derivatives **55**–**57** in which a substantial part of fullerene-cage bonds were broken.

Small molecules, *e.g.*, hydrogen or helium, can be easily incorporated into cages of compounds **55**–**57**. Moreover, the 'hole' in the cage of compound **56** was successfully 'mended' to produce endohedral complex $C_{60}@H_2$ in a rather high yield (**58**, Scheme 18).[257]

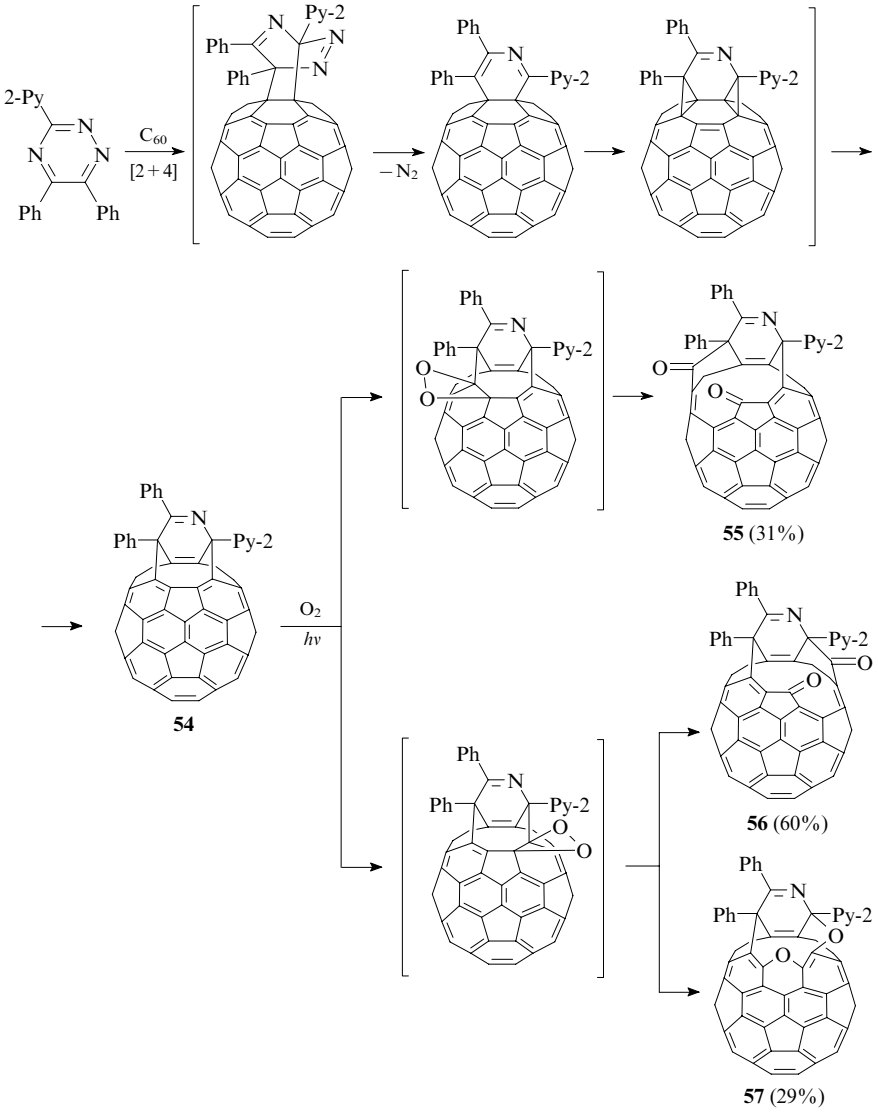
4. Polycycloaddition reactions

On the whole, polycycloaddition reactions exhibit the same features as those described in the Section devoted to nucleophilic polycyclopropanation of fullerene C_{60} (see Section IV.4) with the exception of azide addition. Studies of regiochemistry of reactions of C_{60} with diazides have shown[140] that *cis*-1-isomer often dominates among the isomeric bisadducts. *cis*-1-Adducts (for example, compound **59**) were formed most readily if two or three azide groups were linked through a short bridge.[258–260]

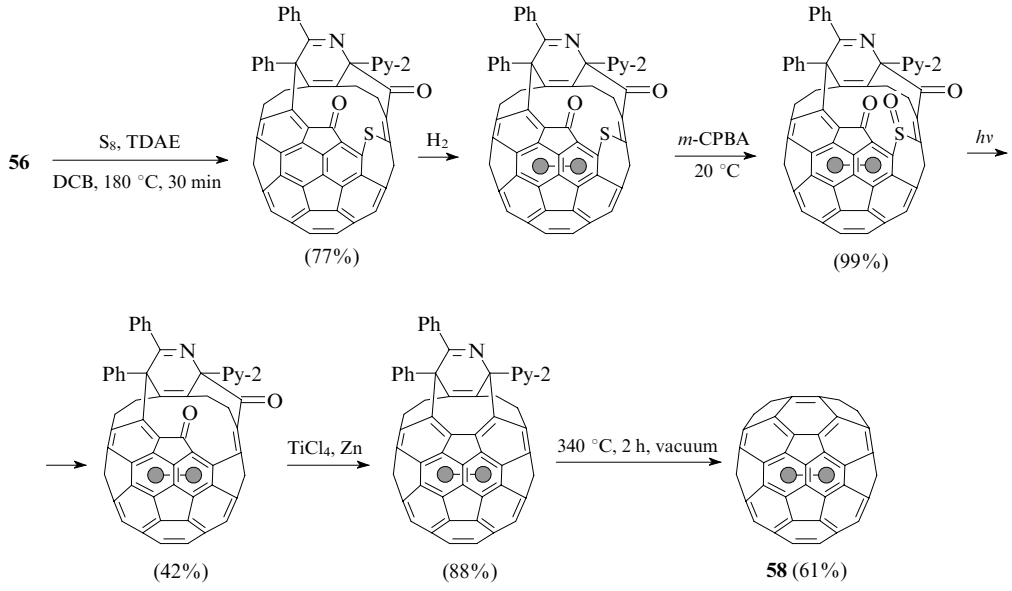


The addition of organic polyazides can serve as a powerful tool for opening of a fullerene sphere. Thus together with the addition product **59** the above reaction affords fulleroid **60**.

Scheme 17

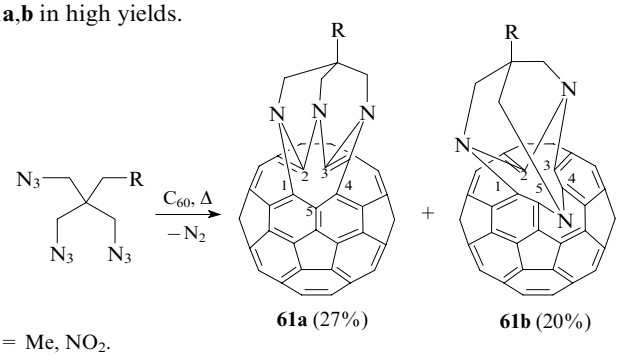


Scheme 18



TDAE is tetrakis(dimethylamino)ethylene, *m*-CPBA is *m*-chloroperoxybenzoic acid, ● is H atom.

A recent publication [261] showed an example of an analogous reaction with a triazide to afford two isomeric triazafulleroids **61a**,**b** in high yields.

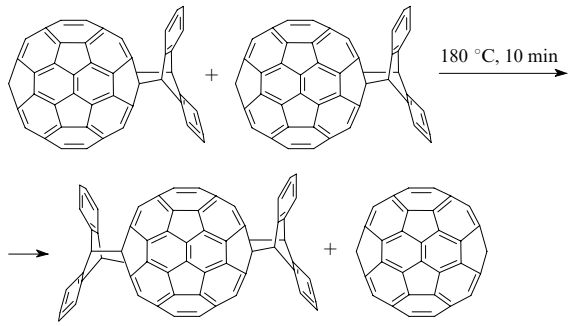


61a (27%) **61b** (20%)

R = Me, NO_2.

Products **61a**,**b** result from incorporation of the nitrogen atoms into 6—5 bonds of the same five-membered ring of the fullerene cage differing only in the addition modes, *viz*., the cleaved bonds were C(1)—C(2), C(2)—C(3) and C(3)—C(4) in the former case and C(1)—C(2), C(2)—C(3) and C(4)—C(5) in the latter case.

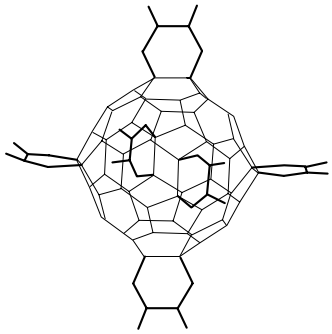
The lattice of a fullerene derivative can serve as a template that fixes reagent molecules in the necessary position. Thus heating of a crystalline adduct of [60]fullerene with anthracene afforded *trans*-1-bisadduct **6** and fullerene in virtually quantitative yields.[262] Such an unexpected mechanism was associated with the packing of molecules in the crystal according to the 'head-to-tail' type.



6

The resulting bisadduct **6** finds wide application in the synthesis of certain unusual fullerene compounds. For example, on its basis, a two-step synthesis according to the Bingel—Hirsch reaction produced compound **7** with four malonate addends located in equatorial positions on the fullerene cage (see Section IV.4).[119] Tetraadduct **7** was introduced into the Prato reaction, which allowed the sequential addition of two different pyrrolidine rings at the remaining equatorial positions of the fullerene cage.[263] Then, four malonate addends were removed by the electrochemical retro-Bingel reaction. This produced *trans*-1-bis(pyrrolidino)fullerene **62** with different substituents (Scheme 19). Thus, the proposed reaction sequence made it possible to control the regiochemistry of the double [2 + 3] cycloaddition of azomethine ylides to the fullerene cage.

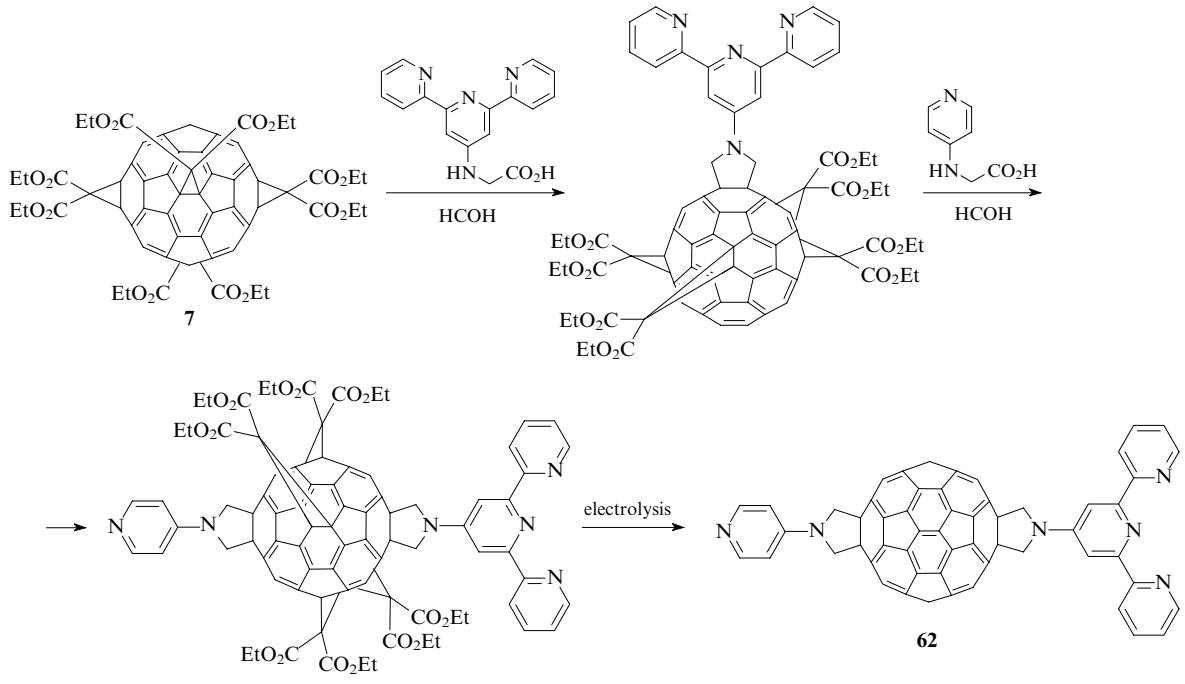
Reactions of fullerenes with a large excess of azomethine ylides or dienes led to the formation of symmetrical hexakisadducts with a typical 'pseudooctahedral' mode of addend arrangement. For the reversible Diels—Alder reactions, the process was controlled by thermodynamics; this is why the hexakisadduct was as a rule the only product. For example, six molecules of 2,3-dimethylbuta-1,3-diene were successfully added [76] to fullerene C_{60} to afford product **63a**.



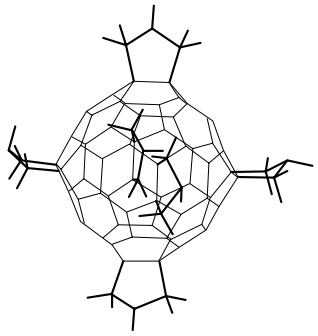
63a

The Prato method exhibited lower selectivity, the target products were formed in low yields due to numerous minor products. For example, the reaction of [60]fullerene with

Scheme 19



2-aminoisobutyric acid and acetone (heating in chlorobenzene for 4–5 days) produced hexaadduct **63b** in low yield; the major product was a D_3-symmetrical trisadduct with the *trans*-3-arrangement of addends.[75]



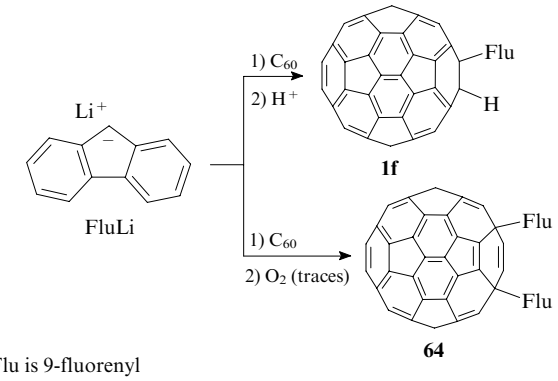
63b (12%)

VI. Radical addition reactions

The reaction mechanisms in chemistry of fullerenes are hitherto insufficiently clear. The radical nature of many processes is either merely postulated or hypothesised based on indirect data (the solvent effect or the addition mode). In this review, the reactions of fullerenes C_{60} and C_{70} are assigned to radical processes in accordance with the generally accepted assumptions.

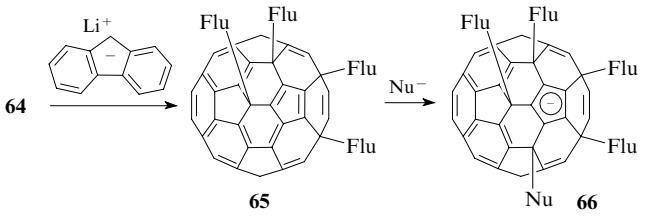
1. Reactions of C_{60} with organometallic compounds

Above, we considered the nucleophilic addition of organometallic substrates to the [60]fullerene cage to afford different 1,2-adducts (see Table 1). However, in the presence of small amounts of oxygen, the reaction changed its direction,[264] *viz.*, anionic species were oxidised to generate the corresponding radicals, which later added to positions 1 and 4 in the C_{60} molecule to form product **64**. The competition of nucleophilic and radical addition mechanisms is well illustrated by the reaction of C_{60} with fluorenyllithium under aerobic and anaerobic conditions.

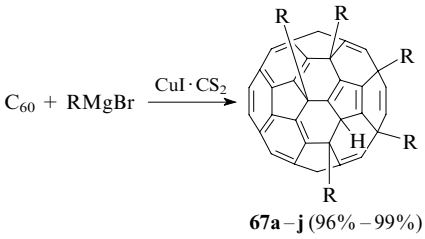


Flu is 9-fluorenyl

It is noteworthy that further addition of radicals to 1,4-difluorenyl[60]fullerene (**64**) proceeds regiospecifically to afford tetraadduct **65** with C_s-symmetry the structure of which corresponds to the cyclopentadiene addition mode. The reaction of obtained tetrafluorenyl[60]fullerene (**65**) with anionic nucleophiles can generate stable cyclopentadiene anion **66** on the basis of the fullerene cage.[264]



A reaction of fullerene C_{60} with organocopper reagents discovered by Nakamura and co-workers [265, 266] proceeds by a similar mechanism to afford hexaadducts **67a–j** isostructural to polyhalofullerenes $C_{60}Cl_6$ and $C_{60}Br_6$ (see above) in nearly quantitative yields.



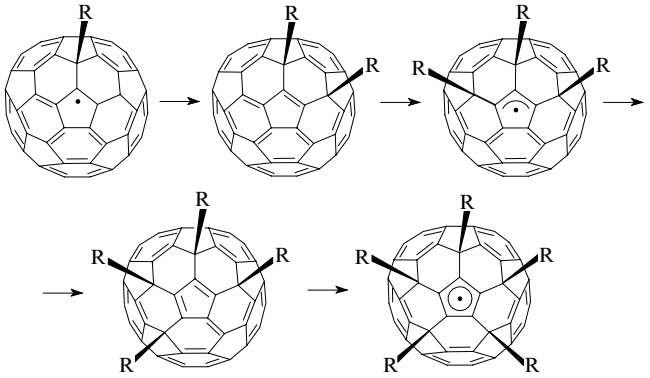
67a–j (96%–99%)

R = Me (**a**), *cis*-CH=CHMe (**b**), *trans*-CH=CHMe (**c**), *trans*-CH=CHPh (**d**), C_6H_4X-4 [X = H (**e**), Cl (**f**), Bu^n (**g**), CF_3 (**h**), Ph (**i**)], 1-naphthyl (**j**).

The mentioned reaction was recently used in the synthesis of dimers $[C_{60}Ar_5]_2$ and derivatives of [60]fullerene containing 7 and 8 aryl addends.[45]

Despite being known for more than 10 years, this reaction has not yet found wide application in chemistry of fullerenes because could successfully be reproduced exclusively by the Nakamura group.

The formation of products of the cyclopentadiene type is a general feature of fullerene reactions. The use of EPR spectroscopy made it possible to elucidate the sequence of stages for the addition of five labelled benzyl radicals to the C_{60} cage.[267]



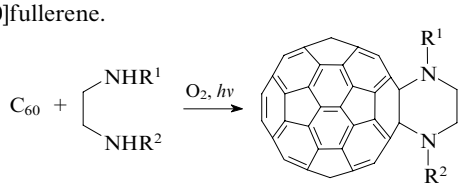
R = $^{13}CH_2Ph$.

2. Reactions of C_{60} with amines

In the very beginning of the development of chemistry of fullerenes, it was found [129] that fullerene readily adds secondary amines R_2NH. It was assumed that the reaction products are compounds of the $R_2N-C_{60}-H$ type in which a hydrogen atom migrates over the fullerene cage surface (see Scheme 4). Somewhat later, the fallibility of this assumption was demonstrated and the reaction was proved to proceed by a radical mechanism, which involved photochemically generated singlet oxygen.[268] The products of these transformations were aminofullerenes

$(R_2N)_nC_{60}$ and water. The reaction of C_{60} with substituted ethylenediamines was studied most thoroughly.[269, 270]

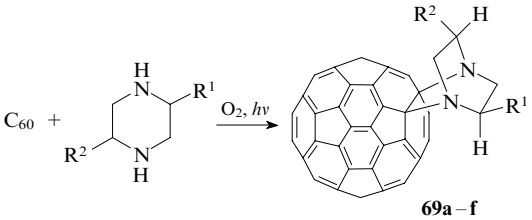
The presence of a short dimethylene bridge in ethylenediamines determines the exclusive formation of 1,2-adducts, namely, piperazinofullerenes **68a–d**, in their reactions with [60]fullerene.



68a–d

Compound **68**	R^1	R^2	Reaction conditions	Yield (%)	Ref.
a	H	H	PhMe, 20 °C, 20 days or 80 °C, 8 days	6–13	269
b	H	Me	PhMe, 65 °C, 48 h	20–60	269
c	Me	Me	PhMe, 70 °C, 3 days	15–46	269, 270
			Xe-lamp, 1 h	32	271
d	Et	Et	PhMe, 70 °C, 3 days	1.2–3.5	269

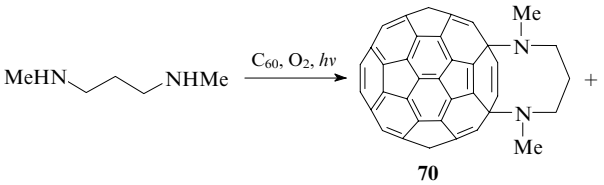
1,2-Addition products **69a–f** were synthesised in a reaction of C_{60} with piperazines unsubstituted at the nitrogen atoms.



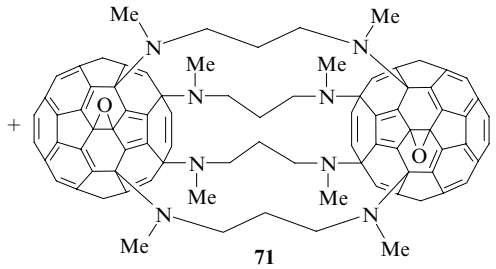
69a–f

Compound **69**	R^1	R^2	Reaction conditions	Yield (%)	Ref.
a	H	H	PhMe, 85 °C, 6 days	43–67	269
			Xe-lamp, 1 h	55	271
b	Me	H	*hv*, PhMe, 64 h	41	272
c	CH_2Hex	H	the same	10	272
d	$CONH_2$	H	"	6	272
e	$CONHPr^n$	H	"	27	272
f	CH_2OH	H	"	43	272
g	Me	Me	"	20	272

Reactions with secondary diamines in which amino groups were separated by three methylene groups afforded both cyclic 1,4-diaminofullerenes **70** and oxygen-containing bisfullerenes **71**.[273, 274]

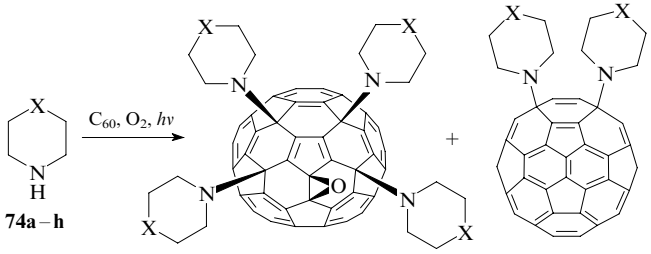


70



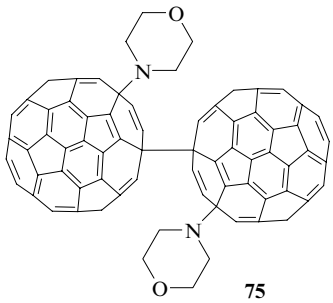
71

It has been claimed earlier [275] that the reaction of fullerene C_{60} with different secondary amines proceeds with high selectivity to afford epoxy derivatives of tetraaminofullerenes **72** in yields reaching 98%.



74a–h **72a–h** **73a–h**

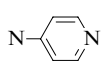
However, the above publication provided no spectral data to confirm the composition and structure of products. A more detailed study of the photochemical addition of *N*-substituted piperazines to fullerene has shown [276] that in the majority of reactions, tetraaminofullerenes are formed together with many other compounds. Thus the reaction of morpholine with C_{60} afforded compound **72a** in a yield as low as 9.1%, while substituted bifullerene **75** was the major product (yield 50%).[41]



75

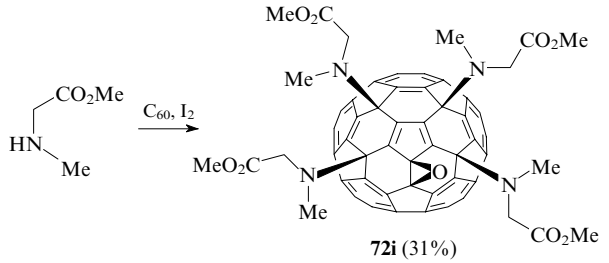
The most selective reactions led to the formation of a mixture of 1,4-diaminofullerenes **73** and epoxy derivatives of tetraaminofullerenes **72**. Table 9 shows the composition and yields of amino derivatives of fullerene C_{60} synthesised from cyclic secondary amines **74a–h**.

Table 9. Reactions of fullerene C_{60} with secondary amines.

Amine		Reaction conditions	Yield (%)		Ref.
No.	X		**72**	**73**	
74a	O	Δ	9.1	8.5	41
74b	NMe	*hv*, PhCl, 20–30 h	98	0	275
		the same	see [a]		276
74c		*hv*, DCB, 20–30 h	72	5	276
74d		the same	80	–	276
74e			23	6	276
74f	$CHNHCO_2Bu^t$	DCB, DMSO, O_2	88	–	277
74g	$CHCH_2OH$	the same	84	–	277
74h	$CHCH_2CH_2OH$		78	–	277

[a] A mixture of products was formed, yields were not shown.

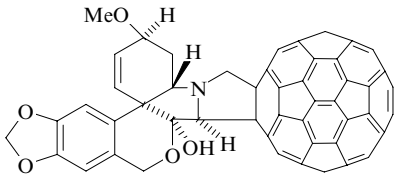
It was found [43] that molecular iodine acts as the oxidant in reactions of C_{60} with amino acid esters to afford tetraaminofullerenes, *e.g.*, compound **72i**.

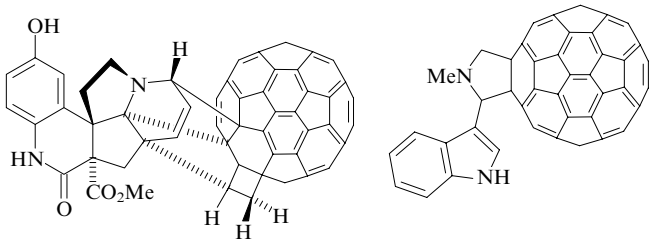


72i (31%)

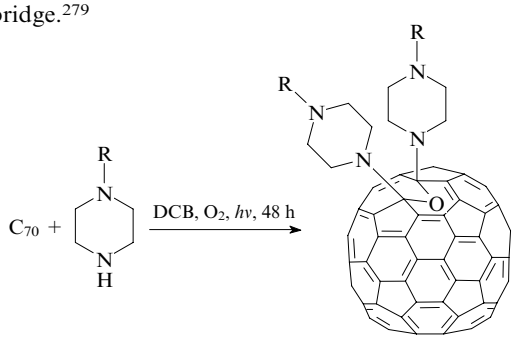
Reactions of oxidative addition of tertiary amines to C_{60} are also documented. In the simplest case, substituted pyrrolidinofullerenes were formed.[198] By the example of dimethylaminoarenes, it was demonstrated that different products are formed (Scheme 20).[278]

The products were almost always obtained in low yields and a large amount of [60]fullerene remained non-consumed; this is why this reaction has not found wide synthetic application. However, its use is justified in some cases. For instance, this method allowed a one-step synthesis of alkaloid adducts to fullerenes.[200]





Unusual products were formed in reactions of fullerene C_{70} with amines. In diamino derivatives **76a**,**b**, the oxygen atom is incorporated into the fullerene cage structure as a C–O–C bridge.[279]

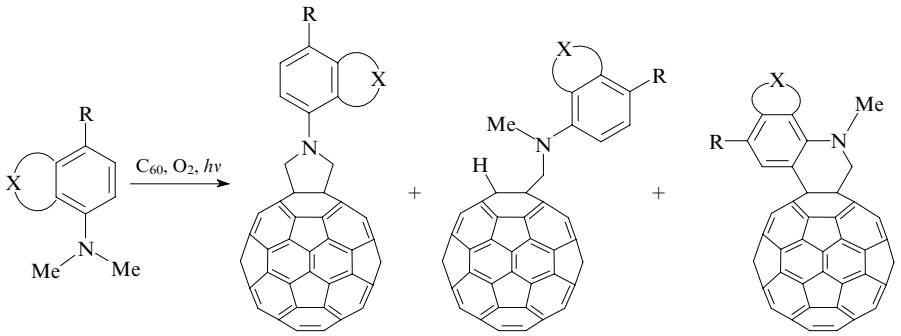


76a,**b** (25% – 30%)

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

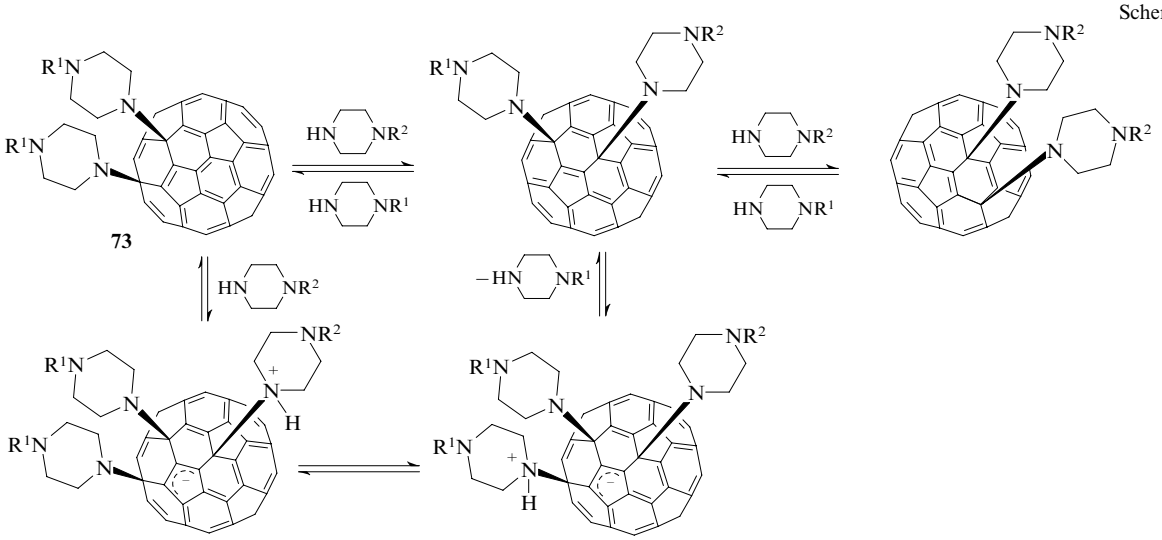
It was shown [280] that 1,4-diamino derivatives **73** (X = NAlk) can reversibly substitute amino groups on the fullerene sphere (Scheme 21). A reaction of 1,4-diaminofullerne with an excess of another amine proceeded smoothly even

Scheme 20



X	R	Yield (%)			
		A	**B**	**C**	C_{60}
2 H	H	3	5	8	84
	OMe	0	9	11	45
	Br	0	0	0	90
Benzo	H	1	22	0	30

Scheme 21

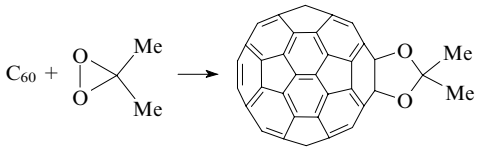


at room temperature and did not require involvement of any initiators (the presence of oxygen or illumination). It is noteworthy that none of other amino derivatives enter into this reaction; hence, the reactivity of compounds **73** (X = NAlk) should be associated with the peculiarities of their structures. Based on the obtained results, a mechanism of this extraordinary reaction was proposed (see Scheme 21).[281]

This mechanism implies the addition of one more amine molecule to 1,4-diaminofullerene **73** into the *para*-position with respect to the neighbouring six-membered ring of the fullerene cage, which corresponds to the cyclopentadiene mode of addition. In the resulting zwitter ion, the negative charge was resonance-stabilised to form an allylic anion. It was proved [267] that 1,4-$C_{60}Bn_2$ was transformed into the radical $[C_{60}Bn_3]^{\bullet}$ (see Section VI.1) with the structure similar to that of the hypothetical zwitter-ionic intermediate in the interconversions of 1,4-diaminofullerenes. All reaction steps were reversible, and the equilibrium could be shifted in the required direction by adding an excess amount of one or another amine.

3. Addition of peroxides and hydroperoxides

One of the first reactions of this kind was the reaction of C_{60} with a cyclic peroxide, namely, dimethyldioxirane, to afford the corresponding 1,3-dioxolanofullerene **77**.



77

The reaction of fullerene with *tert*-butyl hydroperoxide in the presence of diacetoxyiodosobenzene as the oxidant was studied in detail and can well illustrate the regiochemistry of radical addition to the C_{60} and C_{70} cages.

For fullerene C_{60}, the major product was the compound $C_{60}(OOBu^t)_4O$ formed according to the cyclopentadiene addition mode (Fig. 12 *a*).[41] Several fullerene derivatives were isolated as minor products. Two isomers of $C_{60}(OOBu^t)_2$ and epoxide $C_{60}(OOBu^t)_2O$, were formed upon 1,2- and 1,4-addition (Fig. 12 *b*–*d*). In $C_{60}(OOBu^t)_4$ (see Fig. 12 *e*), the *tert*-butoxyperoxy groups surround one five-membered ring in such a way that the attachment of the next two addends affords a single isomer $C_{60}(OOBu^t)_6$, which contains an isolated cyclopentadienyl fragment (see Fig. 12 *f*). Such a structure is also typical of epoxy derivatives $C_{60}(OOBu^t)_4O$, $C_{60}(OOBu^t)_4O_2$ and $C_{60}(OOBu^t)_2O_3$. In the structures of the latter, one can distinguish an isolated cyclopentenyl fragment that was formed from the cyclopentadienyl moiety as a result of addition of an oxygen atom to a multiple bond (see Fig. 12 *g*–*i*).

The reaction of fullerene C_{70} with *tert*-butyl hydroperoxide produced a decakisadduct $C_{70}(OOBu^t)_{10}$ with the equatorial addition mode as the major product.[35] Due to the detailed analysis of the reaction products, the whole series of $C_{70}(OOBu^t)_n$ derivatives, where $n = 2, 4, 6, 8, 10$, was obtained for the first time. This series illustrates the order of radical addition of addends to fullerene C_{70} according to the equatorial mode (Fig. 13 *a*–*e*). It was found that for fullerene C_{70}, the cyclopentadiene mode of addition could also be realised, as proved by isolating the corresponding adducts $C_{70}(OOBu^t)_n$ where $n = 2, 4, 6$ (see Fig. 13 *f*–*h*). Apart from mentioned compounds, the reaction mixture contained two isomers of $C_{70}(OOBu^t)_2$ with peroxide groups in positions that could be assigned to neither cyclopentadiene nor equatorial addition modes (see Fig. 13 *i*, *j*).

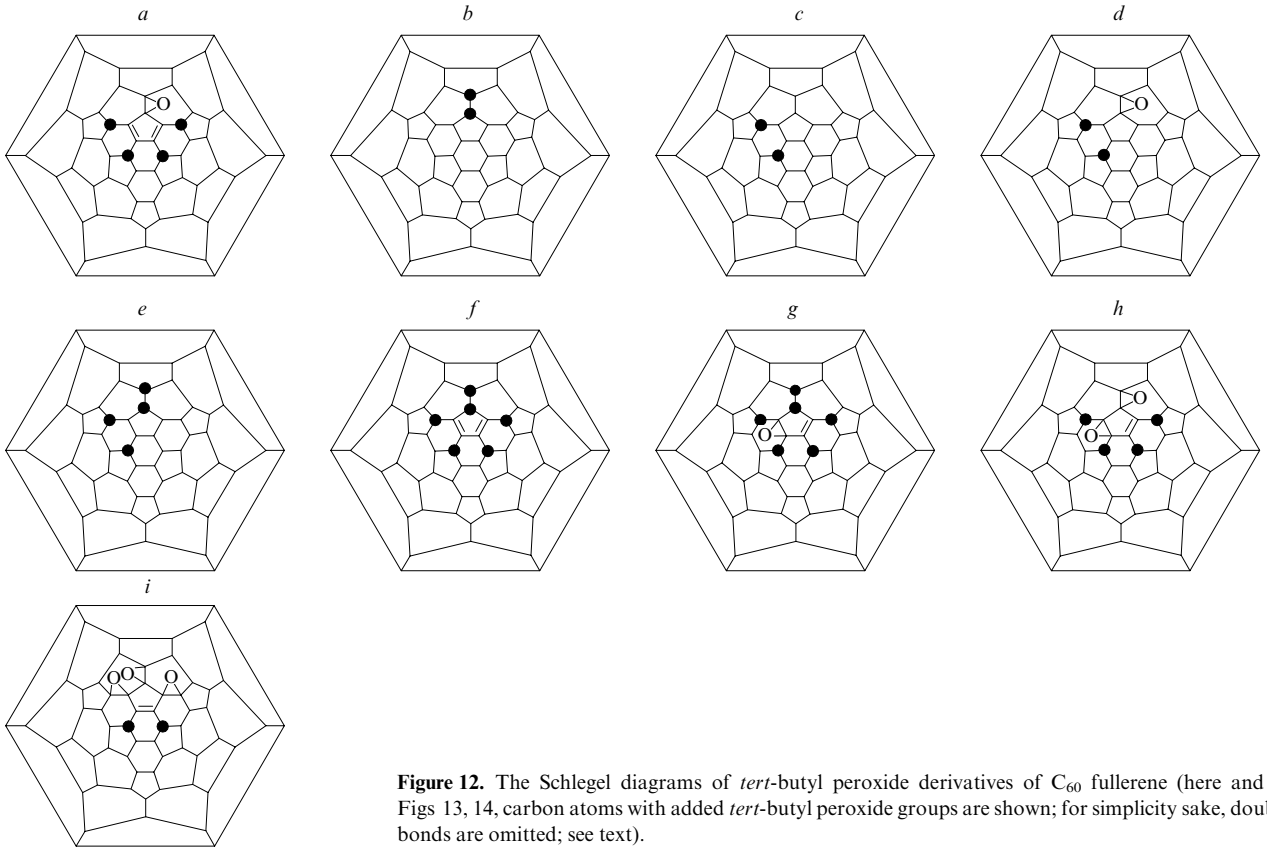


Figure 12. The Schlegel diagrams of *tert*-butyl peroxide derivatives of C_{60} fullerene (here and in Figs 13, 14, carbon atoms with added *tert*-butyl peroxide groups are shown; for simplicity sake, double bonds are omitted; see text).

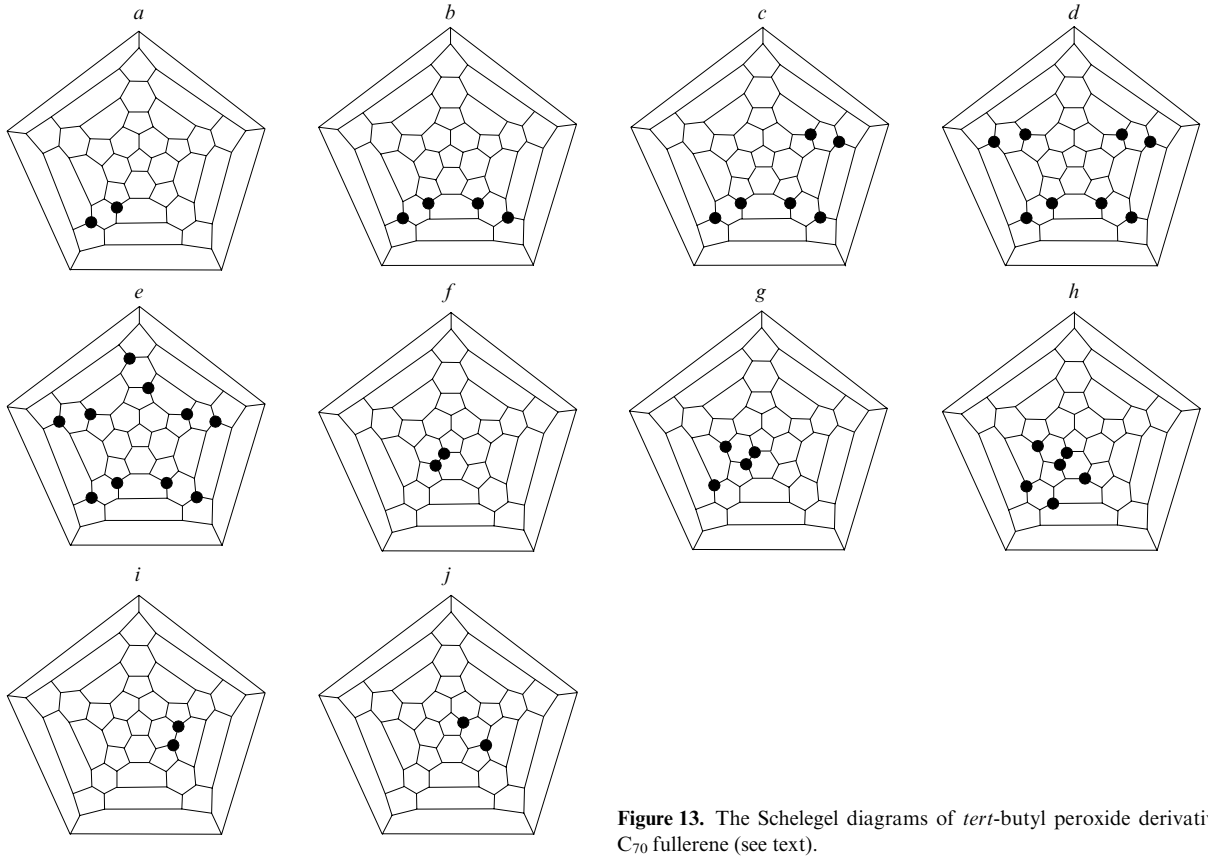
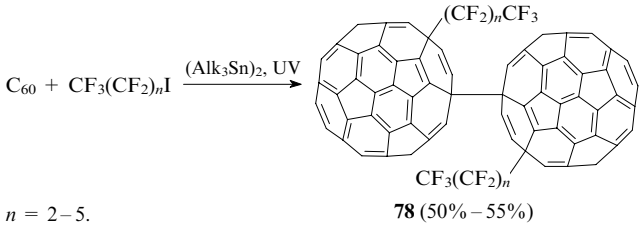


Figure 13. The Schelegel diagrams of *tert*-butyl peroxide derivatives of C_{70} fullerene (see text).

The chemical properties of synthesised peroxide derivatives of fullerene C_{60} were studied.[282] These proved to be extremely reactive with respect to nucleophilic species such as the methoxide anion, which allowed a large series of unusual compounds to be synthesised (Fig. 14 *a*–*e*). The reaction of *tert*-butyl peroxide derivatives of [60]fullerene with organic, inorganic and Lewis acids afforded products containing halogen atoms and a nitro group (see Fig. 14 *f*–*i*). A 1,3-dioxolane fragment was introduced into a C_{60} molecule as a result of the addition of a molecule of trifluoroacetic acid to epoxyfullerene (see Fig. 14 *j*).

4. Perfluoroalkylation of fullerenes

Photochemical addition of perfluoroalkyl radicals to fullerene afforded dimers **78** with fullerene cages bonded by a single C–C bond. Such compounds undergo dissociation at high temperatures.[93, 283]



$n = 2–5$. **78** (50%–55%)

In recent years, appreciable success was achieved in the synthesis and isolation of trifluoromethyl derivatives of fullerenes.[57, 284] The following two methods were employed in generating trifluoromethyl radicals: thermal decomposition of trifluoroacetates of heavy metals (silver, mercury)[36, 285–287] and pyrolysis of trifluoromethyl iodide.[284] The latter method is much more selective than the former; however, in all cases, the authors faced the problem of formation of mixtures of products, which might point to the insufficient thermodynamic control over this system.

To date, dozens of trifluoromethyl derivatives of fullerenes have been isolated, including one isomer of $C_{70}(CF_3)_2$ one isomer of $C_{70}(CF_3)_4$,[288] three isomers of $C_{70}(CF_3)_6$,[288, 289] two isomers of $C_{70}(CF_3)_8$,[56, 288] one isomer of $C_{70}(CF_3)_{10}$,[57] two isomers of $C_{70}(CF_3)_{12}$,[290] five isomers of $C_{70}(CF_3)_{14}$,[291] two isomers of $C_{60}(CF_3)_6$,[44, 285] three isomers of $C_{60}(CF_3)_8$,[292, 293] three isomers of $C_{60}(CF_3)_{10}$,[284] two isomers of $C_{60}(CF_3)_{12}$ and one isomer of $C_{60}(CF_3)_{14}$,[48, 294] one isomer of $C_{60}(CF_3)_4O$ (Ref. 44) and several others. The high-temperature reaction of fullerene C_{60} with C_2F_5I made it possible to prepare and characterise adducts $C_{60}(C_2F_5)_4O$,[44] $C_{60}(C_2F_5)_6$ and $C_{60}(C_2F_5)_8$.[295] Moreover, seven isomers of $C_{70}(C_2F_5)_{10}$ were described.[296] This list of perfluoroalkylated fullerenes is being replenished.[297, 298] Thus trifluoromethyl derivatives of higher fullerenes, namely, C_{74}, C_{76} and C_{78}, have been synthesised quite recently.[299, 300]

From our viewpoint, the structure of trifluoromethyl derivative S_6-$C_{60}(CF_3)_{12}$ (**79**), which contains two triphenylene fragments (painted grey in Fig. 15 *a*), is of special interest. A crystal of compound **79** contains short contacts (3.3 Å) between conjugated triphenylene systems of neighbouring molecules (see Fig. 15 *b*).[301]

Moreover, note that compounds $C_{60}(CF_3)_4O$ and $C_{60}(C_2F_5)_4O$ pertain to the cyclopentadiene addition mode and are isostructural to the corresponding tetraamino and tetra(*tert*-butylperoxy) derivatives of C_{60} (see Fig. 5, type **D**).[44] In one of $C_{60}(CF_3)_{12}$ isomers, the cyclopentadiene addition

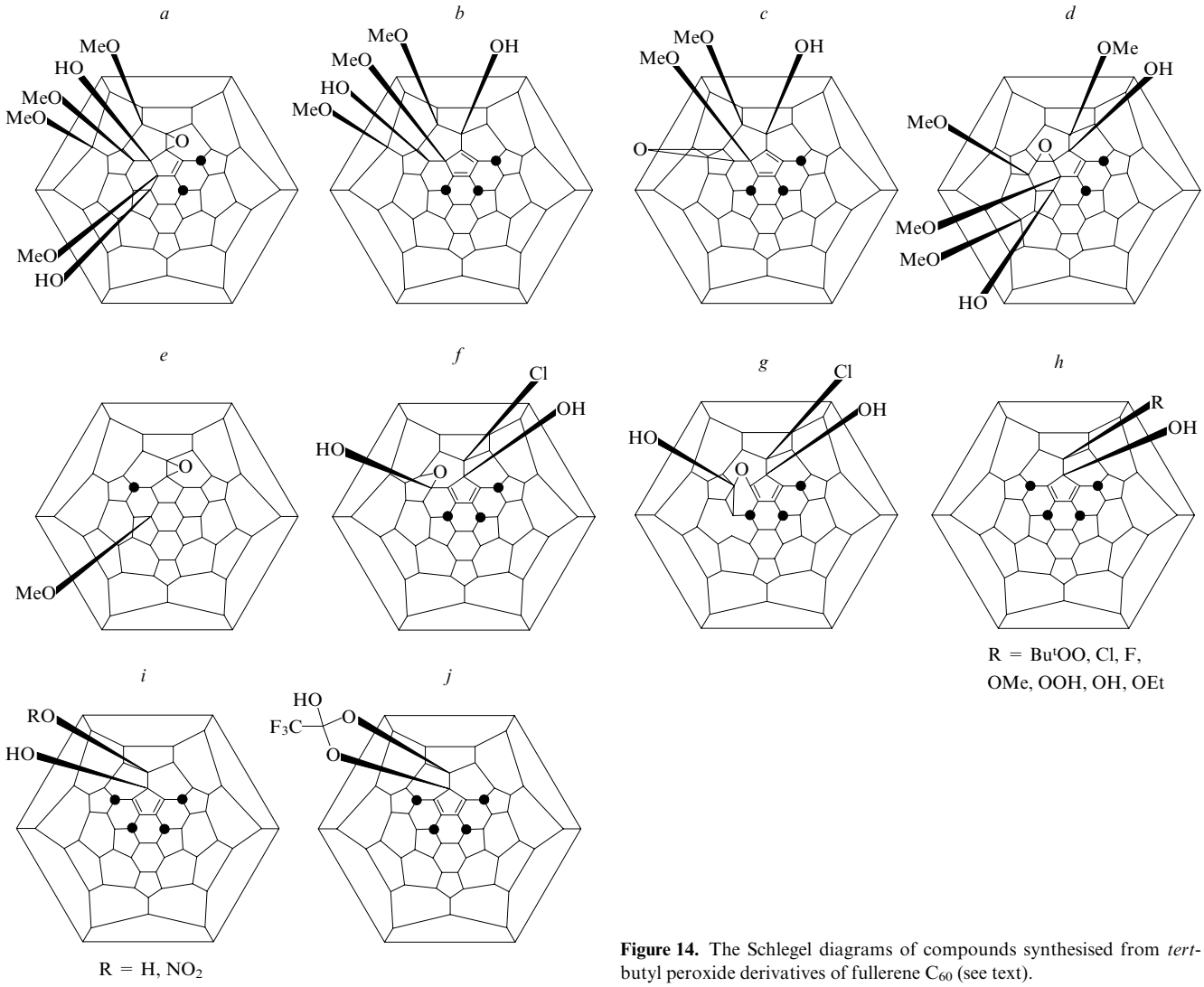


Figure 14. The Schlegel diagrams of compounds synthesised from *tert*-butyl peroxide derivatives of fullerene C_{60} (see text).

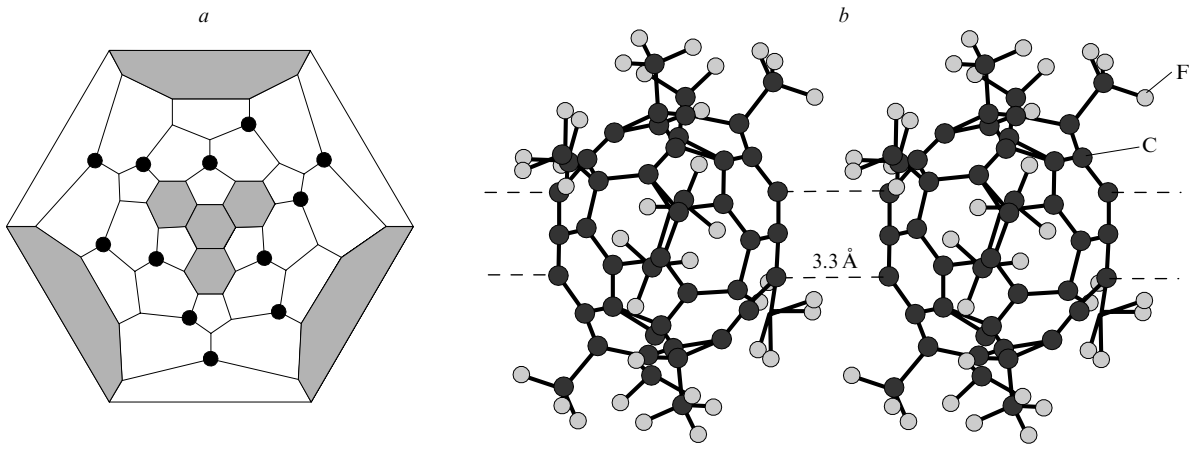


Figure 15. The Schelegel diagram (*a*) and crystal structure of S_6-$C_{60}(CF_3)_{12}$ (**79**) (*b*).
Short contacts between conjugated triphenylene fragments of neighbouring molecules **79** are shown.[301]

mode was realised twice (see Fig. 5, type **E**).[48] At the same time, the derivatives $C_{70}(CF_3)_8$ and $C_{70}(CF_3)_{10}$ exemplify compounds with equatorial mode of addition to fullerene C_{70} (see Fig. 5, structures **B** and **C**).

Reactions of fullerenes C_{60} and C_{70} with terminal diiodoperfluoroalkanes $I(CF_2)_nI$ afforded a series of derivatives with annulated tetrafluoroethylene ($n = 2$) and octafluorobutylene ($n = 4$) fragments. Particularly, two isomers of $C_{60}[(CF_2)_4]_2$ and one isomer of $C_{60}[(CF_2)_4]_6$ and $C_{70}[(CF_2)_2]_2$ each were isolated and their structures were determined by X-ray diffraction analysis. In $C_{60}[(CF_2)_4]_6$, four addends added to 6–6 multiple bonds of the fullerene cage and two more biradicals

$^{\bullet}CF_2CF_2CF_2CF_2^{\bullet}$ added to 1,4-positions of the neighbouring six-membered rings to afford two annelated octafluorocycloheptane fragments (Fig. 16).[302]

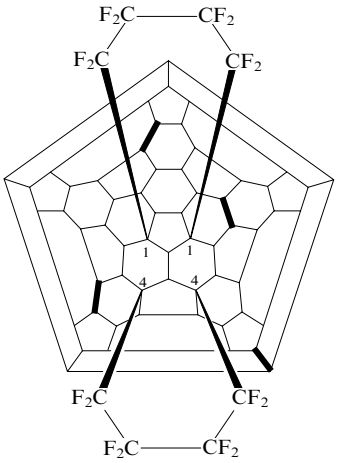


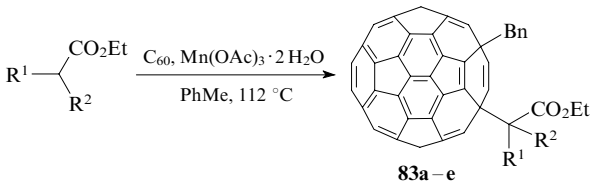
Figure 16. The Schlegel diagram of compound $C_{60}[(CF_2)_4]_6$ (only two perfluorobutylene fragments that are added to positions 1, 4 are shown; addition sites of the rest four addends are shown by heavy lines).

In the recent literature, a possibility is discussed of using perfluoroalkylated fullerenes as the air-resistant electron-withdrawing materials for manufacturing solar cells, organic transistors, *etc*. The mobility of electrons in such a material should not be below 10^{-3} cm^2 V^{-1} s^{-1}. This value is reached in, *e.g.*, PCBM films (see Scheme 8) and in certain other simple fullerene derivatives.[303] Addition of one bulky or several small organic molecules to a fullerene cage reduces the mobility by 1–3 orders of magnitude and results in the critical loss of characteristics of electronic devices.[304, 305] In our opinion, it is quite likely that perfluoroalkylated fullerene derivatives exhibit mobilities of no less than 10^{-5} cm^2 V^{-1} s^{-1}, which prevents their use as stable organic n-type semiconductors. Probably, certain compounds containing a large number of addends can find application as dielectrics for organic transistors.

5. Reactions of fullerenes induced by manganese(III) acetate

Acetate of trivalent manganese can abstract a hydrogen atom from an activated methylene group ($X-CH_2-EWG$). This affords radicals $EWG(X)CH^{\bullet}$ the reactions of which with fullerene C_{60} lead to monomeric (**80**, **81**) and dimeric (**82**) 1,4-adducts (Scheme 22).[306] The latter represent mixtures of stereoisomers.

This reaction carried out in toluene is accompanied by competitive generation of benzyl radicals from the solvent; these radicals also react with C_{60}. As a result, non-symmetrical products **83a**–**e** were obtained.[306]

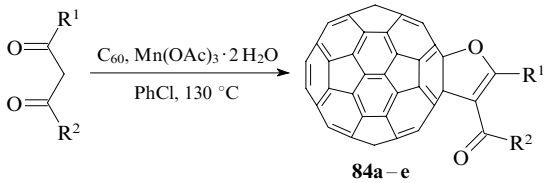


83a–**e**

$R^2 = CO_2Et$: R^1 = Me (**a**, 62%), Et (**b**, 62%), Br (**c**, 56%), CO_2Et (**d**, 31%); R^1 = H, R^2 = CN (**e**, 19%).

It should be noted that the reaction of C_{60} with malononitrile in the presence of $Mn(OAc)_3$ afforded methanofullerene **4s** (yield 36%) rather than 1,4-adducts of dicyanomethyl radical. Ethyl cyanoacetate reacted with C_{60} in the similar way (yield 51%).[306]

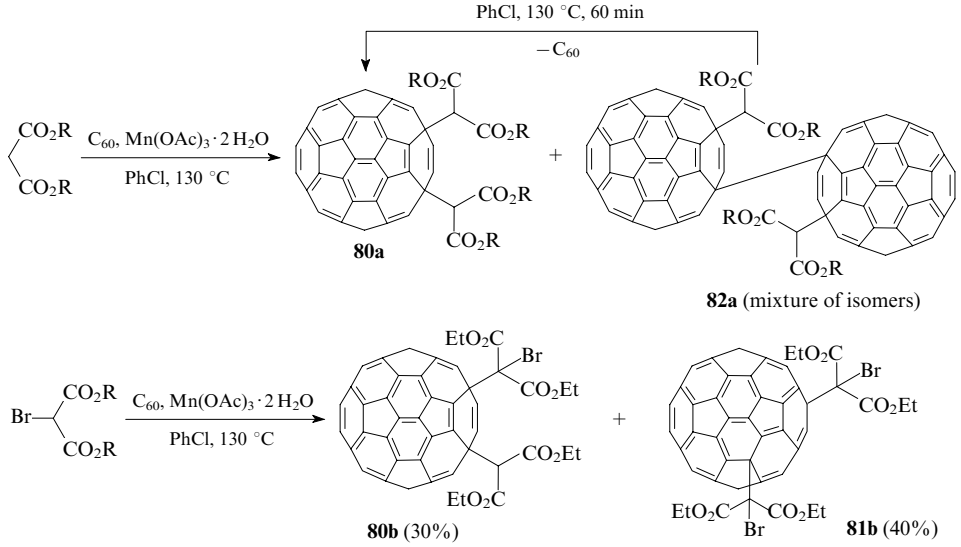
The reaction of β-keto esters and β-diketones with [60]fullerene results in dihydrofuran derivatives **84a**–**e**.[307]



84a–**e**

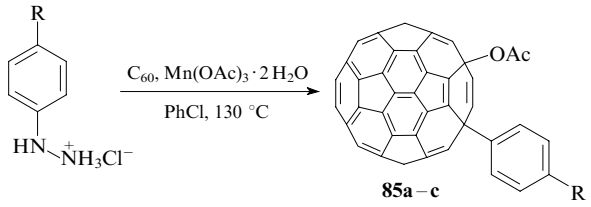
$R^1-R^2 = CH_2CMe_2CH_2$ (**a**, 52%), CH_2CH_2 (**b**, traces);
R^1 = Me: R^2 = Me (**c**, 34%), OMe (**d**, 48%);
R^1 = Ph, R^2 = OEt (**e**, 44%).

Scheme 22



Reaction time	Yield (%)	
	80a	**82a**
20 min	0	65–70
1 h	36–45	< 1

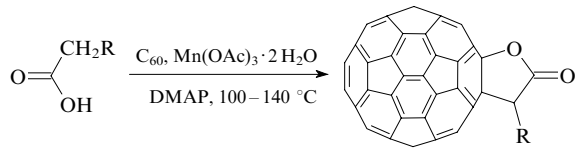
Arylhydrazine hydrochlorides reacted with [60]fullerene to form 1,4-acetoxy(aryl)fullerenes **85a–c**.[308]



85a–c

R = H (**a**, 72%), Me (**b**, 61%), Cl (**c**, 73%).

The reaction of carboxylic acids and their anhydrides with fullerenes in the presence of manganese triacetate afforded lactones **86**.[309]

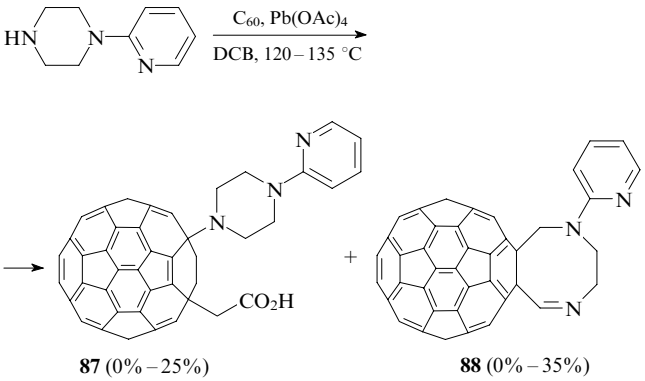


86 (20%–40%)

R = Me (27%), Ph (34%); DMAP is 4-dimethylaminopyridine

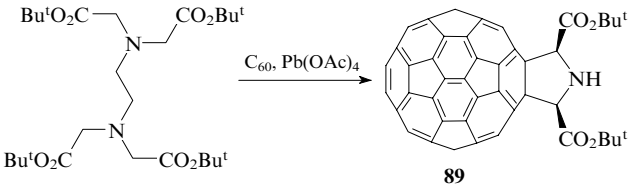
6. Fullerene reactions induced by lead tetraacetate

Lead tetraacetate can serve as a reagent that ensures the oxidative reaction of organic compounds with fullerenes. For example, in the presence of $Pb(OAc)_4$, the reaction of fullerene with *N*-(2-pyridyl)piperazine led to either a mixture of products **87** and **88** or one of them, depending on the temperature and the heating time.[310] Compound **87** was formed as a result of 1,4-addition of an *N*-centred piperazinyl radical and $^{\bullet}CH_2COOH$ to the fullerene cage. The latter radical is the oxidation product of acetic acid formed upon reduction of $Pb(OAc)_4$. Compound **88** contains a diazacyclooctene fragment and is the first representative of this class of compounds. Apparently, the key step in the formation of derivative **88** is the scission of a single C–C bond in the piperazine ring followed by the biradical addition to the fullerene cage.

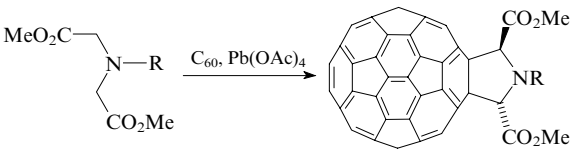


87 (0%–25%) **88** (0%–35%)

The other compounds that reacted with fullerenes in the presence of lead tetraacetate were esters of amino acids. Depending on the parent ester structure, the reaction produced isomerically pure *cis*-2′,5′-disubstituted (**89**) and *trans*-1′,2′,5′-trisubstituted (**90a–c**) pyrrolidinofullerenes.



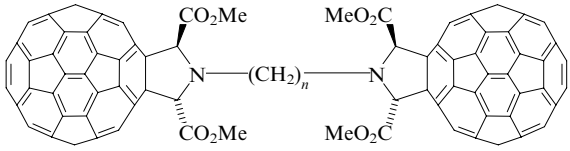
89



90a–c

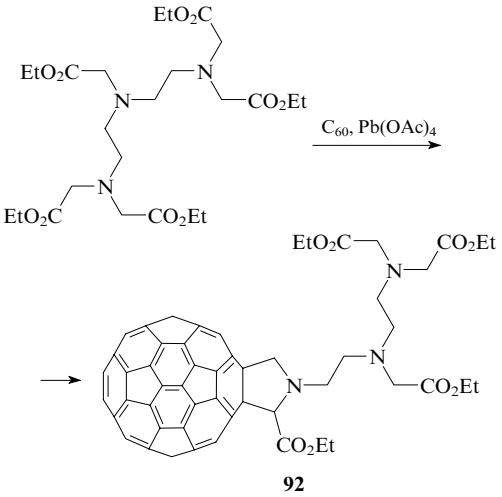
R = CH_2CO_2Me (**a**), $(CH_2)_nN(CH_2CO_2Me)_2$ [n = 2 (**b**), 6 (**c**)].

In addition to derivatives **90b**,**c**, reactions of C_{60} with $(MeO_2CCH_2)_2N(CH_2)_nN(CH_2CO_2Me)_2$ afforded compounds **91b**,**c** with two fullerene fragments.



91b,**c**

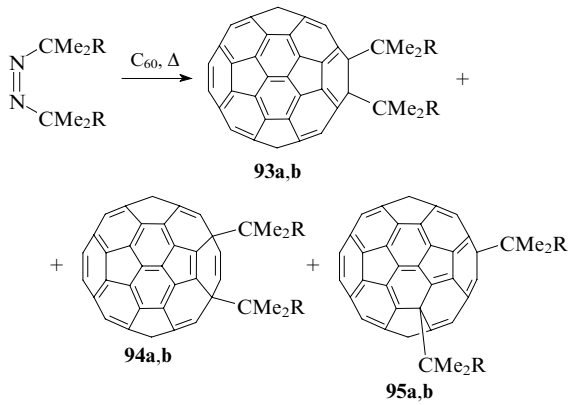
The outcome of reactions is not totally predictable, although the products were always synthesised in high yields (40%–60%). The mechanism of oxidative addition is not yet entirely clear. In the majority of shown examples, two protons were eliminated from an amino acid ester to afford a pyrrolidine ring. However, in certain cases, *e.g.*, for sterically hindered substrates, the starting amino acid ester underwent fragmentation with the cleavage of C–C or C–N bonds. This was confirmed by the formation of pyrrolidinofullerenes **89** and **92**.



92

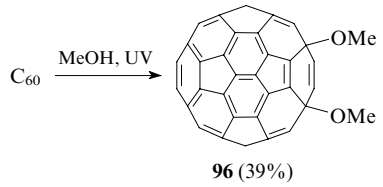
7. Miscellaneous radical reactions of fullerenes

The reaction of [60]fullerene with azobis(isobutyronitrile) or azobis(methyl butyrate) is one of few reactions that afford 1,2-(**93a**,**b**), 1,4-(**94a**,**b**) and 1,16-adducts (**95a**,**b**).[311, 312] The reason for such regiochemistry lies in the large volume of radicals formed.

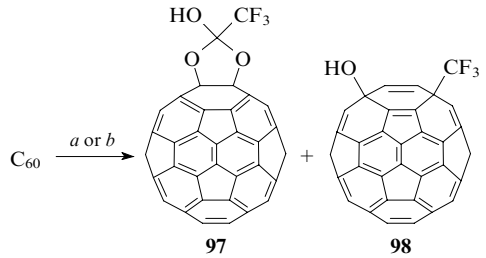


Compound	R	Yield (%)		
		93	**94**	**95**
a	CN	2	12	4
b	CO_2Me	0	21	27

Certain reactions of radical addition to fullerenes were carried out under illumination. In this case, fullerene served as an effective sensitiser that promoted the generation of singlet oxygen; the latter 'triggered' a series of radical processes. Apparently, it is by this mechanism that the formation of 1,4-dimethoxy[60]fullerene **96** occurred.[313]



Recently, it has been shown[314] that fullerene C_{60} readily reacts with trifluoroacetyl hypohalides to afford 1,3-dioxolanofullerene **97** and a small amount of 1,4-$C_{60}CF_3(OH)$ (**98**). The same products were obtained earlier in the decomposition of bis(trifluoroacetyl) peroxides in the presence of fullerene.[315]



(*a*) CF_3CO_2Ag, I_2 or Br_2; (*b*) $(CF_3C(O)O)_2$, Δ.

VII. Practical application of fullerene derivatives

Many of fullerene derivatives have valuable properties and may find application in various fields of science and technology. Thus alkali metal fulleroids were discovered to exhibit high-temperature superconductivity,[316] fullerene-containing donor-acceptor complexes exhibited ferromagnetic properties;[317] the quest among fullerene derivatives produced materials with non-linear optical properties,[318, 319] stationary phases for chromatography,[320] proton conductors,[321] *etc.*[322] Attention is focused on water-soluble fullerene derivatives[323] and also various systems with a fullerene core with one or several organic electron donors bound.[324–327]

Interest of scientists in water-soluble fullerene compounds is directly related to their biological activity. It was shown[328] that certain soluble derivatives are HIV inhibitors, among which dendrimer **4p** containing 18 carboxyl groups is the most efficient today. The synthesis and the use of this compound in medicine were patented in the USA (C-sixty Corporation); at present, this drug undergoes clinical trials as a promising medication for treatment of AIDS.[329] Fullerene derivatives can be used in the photodynamic cancer therapy,[330] as antibacterial agents,[331, 332] medications of neuroprotective action.[333–335]

Unusual physical properties were revealed in studies of covalently bound and coordination fullerene dyads with different electron donors (metallocenes, porphyrins, phthalocyanines, tetrathiafulvalenes, *etc.*). Under irradiation with visible light, charge-separated states are generated in them in high quantum yields and with lifetimes of approximately 3 orders of magnitude larger than the known analogues. This effect is associated with the low reorganisation energy of fullerene molecules in their transition from the neutral to radical anionic state.[326] The studies of covalently and non-covalently bound systems of the fullerene–organic donor type are still theoretical; however, it cannot be ruled out that such compounds may be used in converters of solar energy into electrical or chemical energy.[324]

Dyads of fullerenes with metalloporphyrins are interesting objects that mimic the properties of natural photosynthetic antennas. Studying these models may help to gain insight into the processes that occur in initial stages of photosynthesis. In the future, such compounds might allow one to simulate the photosynthesis. Coordination-bound systems that consist of pyridyl or imidazolyl derivatives of fullerenes as the electron-withdrawing component and metalloporphyrins as the donor component most closely resemble the natural ensembles (Fig. 17). This type of compounds have attracted keen attention in the recent years.[327, 336]

A very important field the successful development of which is totally due to the fullerene-based materials is organic photovoltaics.[337] Different working models of organic solar cells in which fullerene C_{60} or its organic derivatives served as the acceptor are already being elaborated. The efficiency of solar light conversion in fullerene-based units exceeds 5%, which is higher much than in other organic solar cells.

Although the efficiency of conventional silicon solar cells exceeds 20%, *i.e.*, 4–5 times higher than that of the best organic cells, there are several reasons for the developments and modernisation of the latter devices. First, the cost of production of organic light-converting devices compared to the corresponding inorganic analogues is lower by more than two orders of magnitude. This is largely due to the possibility of applying active layers of organic cells from solutions. An analogue of a common jet printer is loaded with cartridges filled with the corresponding 'ink' that represents a solution containing a mixture of the donor (polyconjugated polymer) and acceptor (well soluble fullerene derivative) components. Next, both the electrodes and the photoactive cell components are printed on a common polymeric film. The printing method allows manufacturing several hundred metres of a photoconverting plastic per hour on a single production setup.

Second, an important merit of organic solar cells is their flexibility. They can be rolled up, cut, spread over any surfaces. Particularly, such a plastic can be used for covering both the inner and outer walls of buildings; cells of any colour and texture can be manufactured (Konarka Technologies, http://www.konarkatech.com/). Commercially available

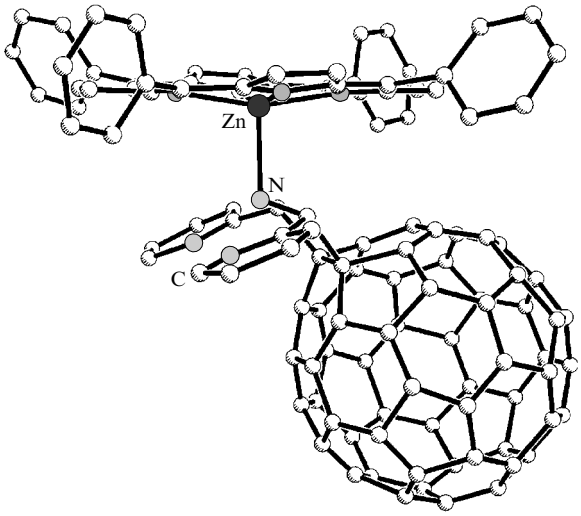


Figure 17. Structure of a coordination-bound dyad formed by pyridyl-substituted pyrrolydinofullerene **27h** (R^1 = 2-Py) and ZnTPP.

examples of suits with integrated solar cells are manufactured. Thus walking in a warm and sunny day may help to charge the cellular phone batteries. American military departments actively support projects associated with organic solar cells, because these materials demonstrate high capabilities to be used in new armaments and attendant systems (power supply for night vision equipment, thermosuits, *etc*.).

Great expectations are also associated with the use of organic cells in the advertising and packaging business. This involves autonomous luminous banners, large liquid-crystal line displays, packing for foodstuff and other articles with built in microchips containing information on serviceableness, use-by date, storage conditions and the other, *e.g*., advertising data.

Organic solar cells are intended to successfully supplement the conventional inorganic cells rather than substitute them. Thanks to its properties, light-conversion plastic will be used in those fields in which it is impossible or pointless to employ silicon cells. On the contrary, due to the low stability of organic materials, cells on their basis will never approach their inorganic analogues in the service life.

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