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Fullerenes: functionalisation and prospects for the use of derivatives

E N Karaulova, E I Bagrii

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Abstract. Published data on the functionalisation of fullerenes (mainly, C_{60}) including those using addition reactions (cyclo addition, hydrogenation, oxidation, *etc*.) are surveyed. The participation of fullerenes in catalysis and fullerene-containing polymers are considered and the prospects for the practical use of fullerene derivatives are discussed. The bibliography includes 191 references.

I. Introduction

Synthesis of polyhedral carbon clusters, fullerenes C_{60}, C_{70} and so on,[1] from hot carbon plasma has initiated and triggered vigorous development of a new line of research in the chemistry of cage compounds, namely, study of the reactivity of fullerenes. In 1996, Kroto, Curl and Smalley were awarded the Nobel Prize in chemistry for the discovery of fullerenes, a new allotropic modification of carbon. In this respect, it is pertinent to consider the essence of this discovery, the history of which is presented in detail in the Nobel lectures of the authors.[2–4]

A necessary condition of the success was the original apparatus designed by Smalley for the preparation and investigation of clusters formed on heating of high-melting compounds. This was a supersonic source of cluster beams with laser vaporisation. In this setup, a slowly rotating graphite disc was exposed to the radiation of a pulsed laser. The carbon vapour was treated with a helium flow in the supersonic flash regime and cooled to a temperature of several Kelvins by adiabatic expansion. The cluster beams were directed into a time-of-flight mass spectrometer with photoionisation of the molecular beam.

By varying the conditions of clustering and the time of cooling, the researchers attained the predominance of the stable C_{60} cluster in the mixture. The researchers[2–4] proposed and substantiated the structure of C_{60} fullerene as a spherical hollow molecule shaped like a truncated icosahedron (Fig. 1). To verify the presence of a cavity inside the C_{60} spheroid, the graphite disc of the setup was impregnated with an aqueous solution of lanthanum chloride; in this case, laser vaporisation gave a stable complex with the metal located inside the fullerene cage.

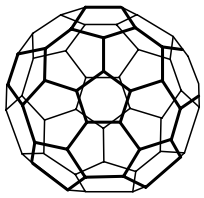


Figure 1. C_{60} fullerene (see Ref. 3).

Calculations for the C_{60} molecule, which gave rise to the suggestion that this molecule should be stable, had been performed[5,6] fifteen years ahead of the experiments of Smalley *et al*.[1] (according to Kroto's assertion,[3] they were not acquainted with these data).

Vigorous development of the physics and chemistry of fullerene became possible only when Krätschmer, Lamb, Fostiropoulos and Huffman[7] had developed a method for the preparation of macroscopic quantities of fullerenes. The fact that fullerenes are formed during vaporisation of graphite electrodes in an electric arc in a helium atmosphere, discovered by these investigators, served as the basis for this method. The researchers[7] prepared and studied crystals of the C_{60} cluster.

The development of the preparative-scale method for the synthesis of fullerenes brought about an avalanche-like increase in the number of publications devoted to this topic. Osawa, who had predicted the stability of icosahedral fullerenes in 1970,[5] composed a computer database (fullerene literature data base, FLDB), based on reprinting from *Current Contents*.[8]

The journal *Fullerene Science and Technology* was founded in 1993, the to-be Nobel Prize winners being among its editors.

Reviews on fullerenes are published routinely (see, for example Refs 9 – 17). A widely cited monograph by Hirsch[18] on fullerene chemistry appeared in Germany in 1994 (a year later it was re-edited in the USA).

In the present review, we cover the most important recent achievements in the functionalisation of fullerenes, mainly C_{60}

E N Karaulova, E I Bagrii A V Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prosp. 29, 117912 Moscow, Russian Federation.
Fax (7-095) 230 22 24. Tel. (7-095) 955 41 25. E-mail: tips@tips.aha.ru

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fullerene, and new prospects for the use of fullerenes including participation in polymerisation and in catalysis.

II. General aspects, synthesis and separation

Fullerenes constitute a subclass of polyhedranes, closed cage structures consisting of tricoordinated carbon atoms and having 12 pentagonal and $n/2-10$ hexagonal faces ($n \geqslant 20$), each pentagon adjoining only hexagons.

The nomenclature and atom numbering in fullerene systems were proposed in 1993 by Taylor.[19] In 1995 Diederich *et al.*[20] introduced a system of numbering for chiral fullerene derivatives. The chemical and electronic structures of fullerene have been considered comprehensively in the report by Sokolov and Stankevich.[9] An algorithm for the bond designation based on the spiral pattern of numbering generally accepted for fullerene derivatives [9] has been proposed;[21] it permits unambiguous assignment of the [6-6] and [5-6] bonds in addition products (compatible with the rules proposed in another publication [20]). In 1997, the Commission on Nomenclature of the IUPAC, having Taylor as a member, accepted a terminology and a tentative nomenclature of fullerenes (see Refs 22 and 23 and the Atlas of Fullerenes [24]).

A system of numbering for fullerenes based on the Schlegel diagrams [9] (Fig. 2) is described in detail in a special appendix to a study by Wudl *et al.*[22] In this review, we mainly adhere to the nomenclature used in the publications cited.

Carbon clusters, *i.e.* chains of carbon atoms, were discovered by astrophysicists in the spectra of some extraterrestrial objects (carbon stars, comet tails and interstellar dust),[25] but the hypothesis that these include C_{60}, C_{70} or C_{60}^{+} clusters has not been confirmed.[2] Corannulene $C_{20}H_{10}$, a possible hydrocarbon precursor of C_{60}, which could be formed upon condensation of corannulene with carbon vapour, has been detected in meteorites.[26]

Natural fullerenes have been found in some minerals. The $C_{70}:C_{60}$ ratio in them varies from 0.21 to 0.36.[25] Fullerenes are assumed to favour migration and accumulation of some elements, in particular, they presumably influence the formation of diamond deposits.[25] Kinetic measurements and mathematical simulation of the fullerene synthesis in an arc reactor led researchers to the conclusion [27,28] that the $C_{60}:C_{70}$ ratio remains invariant over a broad range of the arc process parameters and amounts to $\sim 85:15$.

One of the preparative methods for the synthesis of higher fullerenes (up to C_{108}) is combustion of benzene in a mixture of oxygen and argon.[29] To increase the yield of higher fullerenes in the arc synthesis, carbon electrodes are doped with hafnium, zirconium or titanium.[30] The lower limit of the temperature of fullerene formation is 1200–1500 °C. Recently, a pyrogenetic process for the production of fullerene soot has been developed.[31] According to this method, a hot mixture of H_2 and a carbon-containing compound is fed through a nozzle into a water-cooled spherical reactor; the best results are attained with C_2Cl_4 as the carbon precursor. At the outlet of the nozzle, plasma is formed. The yield is 0.2 g of fullerenes per kV, which corresponds to the conversion of 2.1% of the carbon from the C_2Cl_4 introduced. The $C_{60}:C_{70}$ ratio depends on the cooling conditions.

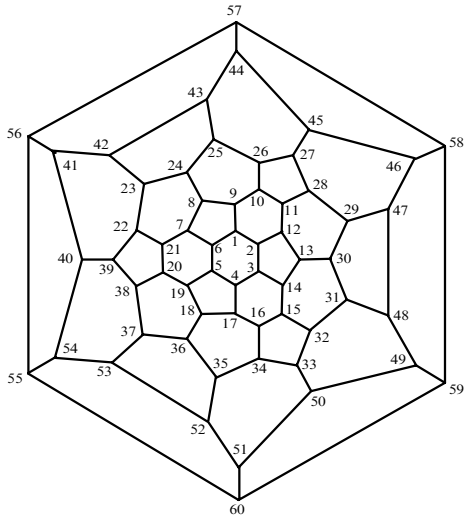


Figure 2. Numbering of carbon atoms in C_{60} fullerene (Schlegel diagram).[19]

Several mechanisms have been proposed for the formation of fullerenes from the precursor nuclei. Thus it has been assumed [32] that the first stage of this process is a gas–liquid transition in the expanding flow of supersaturated carbon vapour and this is followed by the formation of small clusters with a dendrite [32] or corannulene (curled sheet) structure.[33] It has been found [34] that on heating, pure C_{60} crystals are transformed into amorphous carbon. Based on this finding, the researchers conclude that the C_{60} liquid phase, described previously, does not actually exist.

Mixtures of C_{60} with 5%–15% of C_{70} are often used for the functionalisation of C_{60} because C_{70} usually does not enter into reactions. However, in some cases, especially in the measurements of physical characteristics of processes, it is required that C_{60} should have a purity of $\geqslant 99\%$. Nowadays, C_{60} and C_{70} are normally separated by HPLC, which sharply increases the cost of the product; therefore, the interest in the optimisation of methods for fullerene isolation does not abate. The sorbents currently used for this purpose consist of polyaromatic compounds, π-acids, porphyrins and phthalocyanines immobilised on silica gel.[35] The commercially available Buckyclutcher, which is 3,3,3-tris(dinitrobenzene)propyl silica gel, is commonly used. The use of tetraphenylporphyrin immobilised on silica gel ensures the preparation of C_{60} with 98.5% purity and C_{70} with a >99% purity for a 5-mg batch.[36] Preparative quantities of C_{60} and C_{70} have been successfully separated using the chromotropic acid tetramer with formaldehyde bound to γ-aminopropyl silica gel as the sorbent.[35] A sorbent based on Al(X) tetraphenylporphyrin fixed on hydroxydimethylsilyl silica gel has been proposed for the separation of large amounts of fullerenes.[37]

Recently it has been found [38] that the solubility of C_{60} exhibits an abnormal temperature dependence: the maximum of the fullerene solubility in toluene and carbon disulfide falls down to 0 °C, and that in *o*-xylene is observed at 30 °C. In the case of C_{70}, the temperature variation of the solubility follows a standard pattern. This fact might prove useful for the separation of mixtures of C_{60} and C_{70}.

The main distinctive features of the C_{60} fullerene molecule permitting its functionalisation are the 'pseudo-aromaticity',[9] which governs the reactions with nucleophiles, carbenes and free-radical species to give various adducts, and the presence of the spherical cavity within the cage.[2]

III. Complexes and inclusion compounds

A unique chemical feature of fullerenes is the formation of metallofullerenes, endohedral complexes, in which one or several metal atoms reside inside the carbon cage.† A metal atom occurring as a cation cannot be extracted from the fullerene polyhedron without complete destruction of the cage, which can take place, for example, in the presence of oxygen.

Fullerenes are capable of forming charge transfer complexes (CTC).[39] Strictly speaking, the formation of CTC and endometallofullerenes cannot be regarded as functionalisation of fullerenes; nevertheless, we present here some novel data concern-

† Endohedral complexes of fullerenes are designated using the character @. The metal atoms occurring inside the cage are written to the left of this character, *e.g.*, La@C_{82}.

ing this type of reaction in order to characterise the properties of fullerenes more fully and because these compounds are highly promising.

Even a weak nucleophile such as iodine forms a CTC with fullerene of the composition $C_{60} \cdot I_2$. This complex is unstable, its stability constant is < 0.1 litre mol^{-1} (see Ref. 40). In an earlier study,[9] it was reported that this complex was not formed.

A new method for the synthesis of CTC of fullerenes, in particular the complex with iodine, has been proposed;[41] the method involves doping with iodine of other CTC prepared beforehand (for example, complexes with substituted tetrathiafulvalenes).

In the syntheses of potential precursors of new superconductors, special attention is paid to CTC of C_{60} fullerene having layered structures. For example, a complex of this type with tetramethyltetraselenofulvalene has been synthesised.[42] Doping of the octamethylenetetrathiafulvalene $\cdot C_{60} \cdot$ benzene complex with potassium resulted in the detection of superconductivity with $T_c = 17-18.8$ K, while doping with rubidium produced superconductivity with $T_c = 23-26$ K.[43]

A new type of superconductor has been obtained by the inclusion of potassium into non-superconducting Ba_3C_{60}.[44] The compound KBa_3C_{60}, which possesses block superconductivity at 5.6 K, is synthesised by heating a mixture of K and Ba_3C_{60} powders in a sealed glass tube for three days in a high vacuum at 260 °C.

Endohedral fullerene complexes $M@C_n$ are usually prepared in an arc discharge with a metal–graphite composite as the positive electrode. These complexes were isolated in a pure state only in 1994,[45] and since 1996 they have been studied successfully using scanning tunnelling microscopy.[45]

The C_{82} fullerene forms complexes with Sc, La, Y, Ce, Pr and Gd; they are most stable in air. The data obtained by electron paramagnetic resonance showed the occurrence of 'intrafullerene' transfer of electrons from the endohedral atom to the carbon cage. According to X-ray diffraction data,[45] the metal atom does not reside in the centre of the cage but, perhaps, wanders inside the spheroid; strong metal–cage interaction takes place in this system. Endohedral complexes are mixtures of isomers with different arrangements of five- and six-membered rings in the cage with respect to the metal.[45] The cages of some higher fullerenes can accommodate two or three metal atoms.[46] For instance, the complexes $Sc_2@C_{84}$, $Sc_3@C_{82}$ and $La_2@C_{80}$ have been isolated. It was established for the latter complex that the La atoms execute a circular motion inside the spheroid.[45]

The data from high-energy spectroscopy provided the basis for the conclusion that the lanthanide ion in $Tm@C_{82}$ is in the divalent state.[47] The synthesis, isolation, and, what is the most important, purification of the compound $Dy@C_{82}$ have been described in detail.[48]

Endometallofullerenes with calcium were synthesised for the first time by evaporation of a graphite anode filled with calcium carbide particles in an arc discharge.[49] Extraction with carbon disulfide gave a reaction product in which the majority of $C_{58}-C_{100}$ fullerenes contained one calcium atom but some held two calcium atoms inside the cage.

Endohedral complexes of fullerenes find use in studies of cells in molecular biology.[45] The variation of the EPR spectra of solutions of the endohedral metallofullerenes $La@C_{82}$ and $Y@C_{82}$ (their preparative synthesis has been reported[50]) as functions of the oxygen concentration can be employed for the monitoring of oxygen in biological, physical and chemical processes.[51,52]

IV. Addition reactions

The most important line in functionalisation of C_{60} is exohedral addition to the fullerene cage. The exohedral covalent attachment to the fullerene cage is possible for many classes of compounds. From 1990 to 1995, cycloaddition, radical and nucleophilic addition, hydrogenation, oxidation and halogenation as well as complex formation with transition metals had been studied. The features of the fullerene reactivity have been considered in detail in reviews by Diederich and Thilgen[12,17] and Hirsch,[13] which cover publications up to the end of 1995.

The C_{60} molecule is constructed of 12 five-membered rings, each being surrounded by six-membered rings (20 altogether). It has thirty bonds between six-membered rings ([6-6] bonds) and sixty bonds between six- and five-membered rings ([6-5] bonds). The fact that [6-6] bonds are shorter (1.38 Å) than the [6-5] bonds (1.45 Å) influences the chemical behaviour of C_{60}.

The conjugated π-system in C_{60} is not completely delocalised, the reactivity of this cluster being similar to that of an electron-deficient polyolefin. The electrophilic double [6-6] bonds readily add nucleophiles and radicals. The addition of 34 methyl radicals to C_{60} has been detected by mass spectrometry.[10] Therefore, C_{60} fullerene is referred to as a 'radical sponge'.

In the adducts, some of the carbon atoms in the functionalised fullerene cage have changed the hybridisation from sp^2 to sp^3. Nucleophilic and carbene attacks, cycloaddition and hydrogenation usually occur as 1,2-addition, while radical reactions, for example, halogenation, follow the 1,4-addition pattern. However, the latter type of addition is also possible for nucleophilic reactions if they involve bulky fragments. Thus adducts **A** and **B** have been described[12] (Fig. 3).

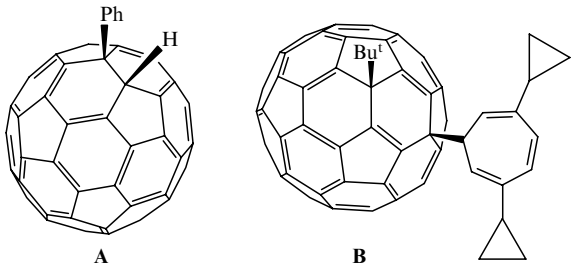


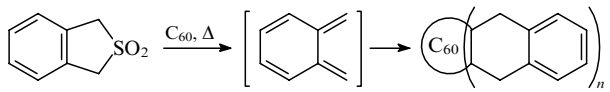
Figure 3. Addition to the C_{60} molecule. **A** is 1,2-adduct, **B** is 1,4-adduct.

When porphyrins or phthalocyanines contain fullerene fragments, the photoinitiated electrical conductivity of their solutions increases. In this case, photoinitiated electron transfer with participation of C_{60}^* and C_{70}^* takes place to give $C_{60}^{-\bullet}/C_{70}^{-\bullet}$ (see Ref. 53). The unpaired electron in the $RC_{60}^{\bullet}$ radicals is mainly delocalised over the atoms of the two six-membered rings adjacent to the C−CR bond.[10] The molecule of C_{70}, unlike C_{60}, contains five types of nonequivalent atoms; therefore, free-radical addition to C_{70} can yield five isomeric $RC_{70}^{\bullet}$ radicals.[10]

1. Cycloaddition reactions

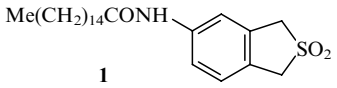
Cycloaddition to fullerenes gives mainly products of monoaddition, commonly, 1,2-addition to a [6-6] bond, which is energetically more favourable than addition to a [6-5] bond.[13] The reaction products are used as the initial compounds for further functionalisation. The $[m+2]$ cycloaddition reactions with C_{60} ($m = 1-4$) have found wide use, because they are facilitated by the low LUMO energy; [4+2] cycloaddition and, in particular, Diels–Alder reactions, proceed especially easily; [6-6] bond is always dienophilic. The addition of various alkenes has been considered in a review.[13]

In recent years, quinodimethanes are successfully used as dienes in reactions with fullerenes. These compounds are either synthesised beforehand or formed *in situ* upon thermally induced elimination of SO_2 from heterocyclic sulfones or sultines



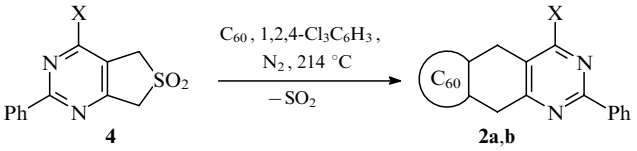
$n \geqslant 1$.

This reaction underlies the so-called 'reactive extraction' method, which permits recovery of higher fullerenes from fullerene soot.[54] The soot is first extracted with toluene and 1,2,4-trichlorobenzene and the residue is heated with quinodimethane precursor **1**.



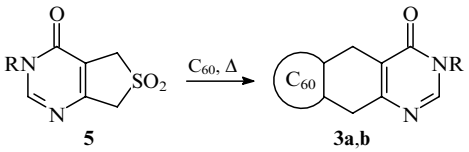
1

This gives rise to a product soluble in conventional solvents and containing $C_{60}-C_{400}$ clusters including multisubstituted ones. The ordinary extraction from commercial soot recovers 8.4% of fullerenes, whereas reactive extraction gives additionally 11.8%. Derivatives **2a**,**b** and **3a**,**b** result from reactions of C_{60} with sulfones **4**, **5**, which act as precursors of pyrimidine- and pyrimidonequinodimethanes.[55]



4 **2a**,**b**

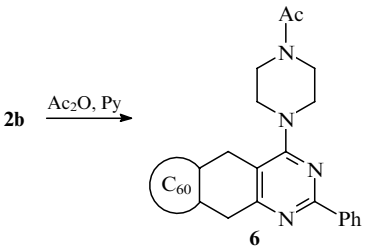
X = OMe (**a**, 77%),  (**b**, 95%).



5 **3a**,**b**

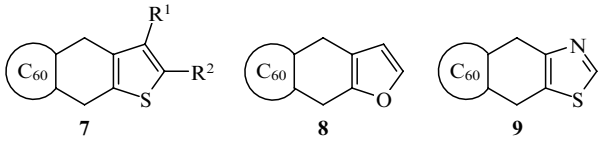
R = H (**a**, 82%), Me (**b**, 52%).

The biological activities of these derivatives can be assayed, if they have been transformed into water-soluble products, for example, into acetyl derivatives **6**.[55]



6

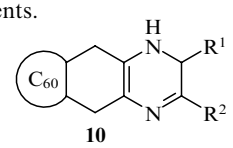
Fullerene derivatives **7**–**9** have been prepared by [4+2] cycloaddition to C_{60} of six-membered heterocyclic analogues of *o*-quinodimethane generated *in situ* from the corresponding thiophenes, furans and thiazoles.[56]



7 **8** **9**

$R^1 = R^2 = H$; $R^1 = H$, $R^2 = CO_2Me$; $R^1-R^2 = (CH=CH)_2$.

When the reactants are exposed to microwave radiation, the reaction time becomes shorter and the product yields increase. Thus microwave irradiation was used to synthesise compound **10** by the reaction of C_{60} with quinodimethanes prepared *in situ* from the corresponding *o*-bis(bromomethylated) quinoxaline and pyridine derivatives on treatment with NaI in the presence of a crown ether.[56] The use of microwave radiation for other Diels–Alder reactions and for 1,3-dipolar cycloaddition to C_{60} has also been proposed .[57] The reaction time decreases to several minutes, which makes it possible to avoid decomposition to the initial components.

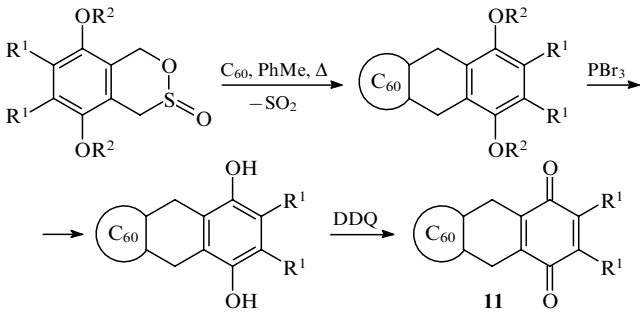


10

$R^1-R^2 = (CH=CH)_2$,  ; $R^1 = R^2 = CN$.

The redox potentials for all newly synthesised organofullerenes were determined by voltammetry in solution.[56] The first reduction potentials for these compounds were found to undergo slight cathodic shifts with respect to that for C_{60}.

In another study, [58] sultines (prepared from commercially available rongalite) were used as the precursors of quinodimethanes. On heating in toluene in the presence of C_{60}, sultines eliminate SO_2; the resulting adducts are converted into quinones **11** on further modification.

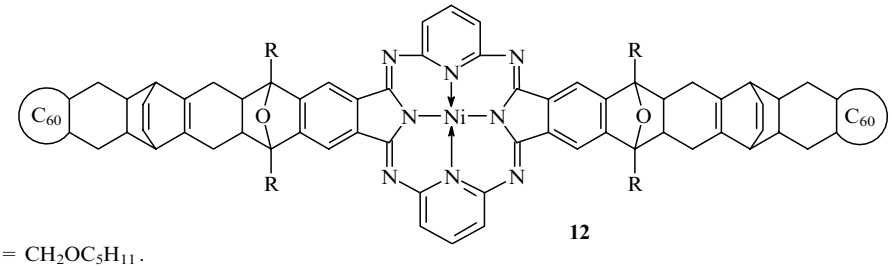


11

R^1 = H, $R^2 = C_6H_{13}$, Me; R^1 = Br, R^2 = Me; $R^1-R^1 = (CH=CH)_2$, R^2 = Me; DDQ is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Quinodimethanes have also been used to prepare adducts of C_{60} with phthalocyanines and hemiporphyrazine; electrochemical characteristics of these compounds have been determined.[59] In particular, triad **12**, containing two fullerene fragments was synthesised for the first time in the 1-chloronaphthalene medium (Scheme 1).

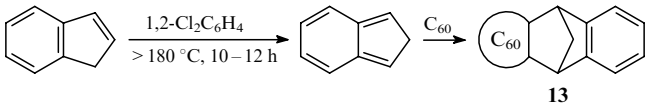
Scheme 1



12

R = $CH_2OC_5H_{11}$.

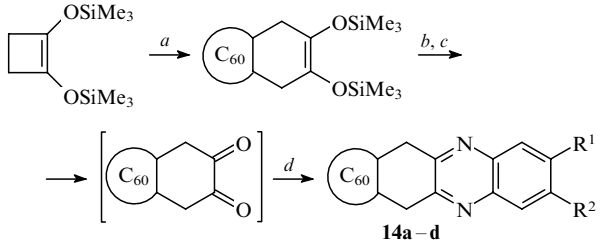
Yet another example of functionalisation of C_{60} *via* [4+2] cycloaddition is its reaction with indene, which isomerises into isoindene under the reaction conditions. The yield of the reaction product **13** was 30%, while about 35% of the C_{60} recovered unchanged. The electron-withdrawing capacity of the adduct was somewhat lower than that of C_{60} (see Ref. 60).



13

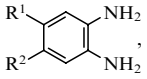
The researchers cited [60] believe that the indene adducts might be useful for the development of new materials for optics and electronics.

The new method for the synthesis of 1,3-diazines fused to fullerene, described by Torres-Garcia *et al.*,[61] can be extended to a large number of diamines. It should be noted that the last stage is carried out in an acid medium in order to prevent nucleophilic addition to fullerenes.

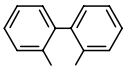


14a–d

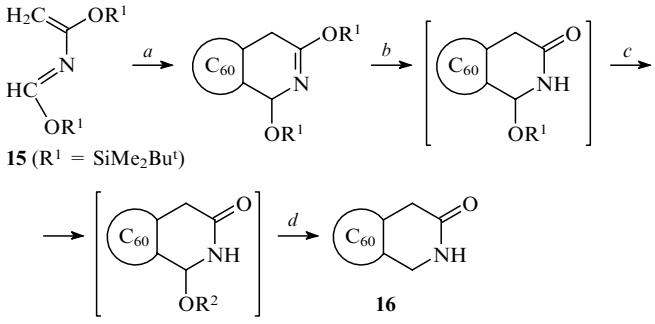
(*a*) C_{60}, 1,2-$Cl_2C_6H_4$, 180 °C, > 50%; (*b*) Br_2, −77 °C; (*c*) $Et_3N \cdot 3HF$;

(*d*) , 1,2-$Cl_2C_6H_4$, AcOH;

$R^1 = R^2 =$ H (**a**, 37%); $R^1 =$ H; $R^2 =$ OMe (**b**, 29%);

$R^1 - R^2 = (CH=CH)_2$ (**c**, 32%),  (**d**, 10%).

1,3-Bis(*tert*-butyldimethylsilyloxy)-2-azabuta-1,3-diene (**15**) adds to C_{60} fullerene at room temperature.[62] Hydrolysis, replacement of the silyloxy group by an alkoxy group (in order to avoid the retro-reaction) and dealkoxylation yield a fullerene derivative of δ-valerolactam **16**, which is a very interesting starting compound for the synthesis of amino acids and polyamides containing a fullerene fragment. These derivatives can be prepared after opening the six-membered ring.

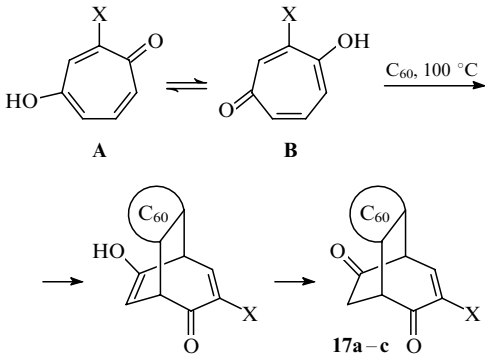


15 ($R^1 = SiMe_2Bu^t$)

16

(*a*) C_{60}, PhH, 20 °C, Ar, 4 h; (*b*) 10% HCl (77%);
(*c*) conc. HCl, R^2OH, $CHCl_3$, Δ, 12 h: $R^2 =$ Et (100%), $(CH_2)_3OH$ (62%); (*d*) Et_3SiH, CF_3CO_2H, $CHCl_3$, Δ, 12 h (88%).

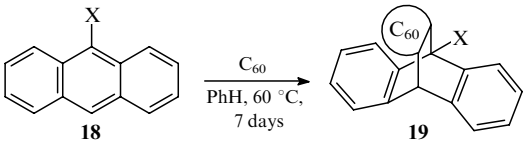
On prolonged heating, C_{60} adds 7-substituted 4-hydroxytropone.[63] The tropone moiety exists as two tautomeric forms, **A** and **B**. Since the reactivity of the sterically more hindered form **B** increases at elevated pressures, in most cases, the yields of reaction products **17a–c** increase when the reaction is carried out under a pressure of 300 MPa.



A **B** **17a–c**

X = H (**a**), OMe (**b**), Cl (**c**).

γ-(9-Anthryl)-7-oxaoctanoic acid **18** adds to C_{60} in a similar way.[64] Adduct **19** forms true Langmuir films on an aqueous phase; they can be transferred as monolayer and multilayer films onto substrates, quartz, Si[111] or calcium fluoride plates.[64]

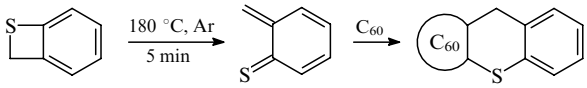


18 **19**

X = $CH_2O(CH_2)_5CO_2H$.

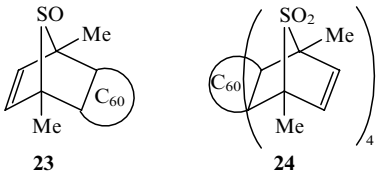
At 160–180 °C, fullerene C_{60} reacts with norbornadiene and its 7-spirocyclopropane derivatives (a 200- to 300-fold excess of the diene is used in the reaction) to give, depending on the substituent in the cyclopropane ring, [1+3]-, [1+4]- or [2+2]-type adducts, including polyaddition products.[65]

The fullerene analogue of thiochroman **20** was obtained by the hetero-Diels–Alder reaction with thioquinonemethide (**21**),[66] formed *in situ* from benzothietane (**22**).



22 **21** **20**

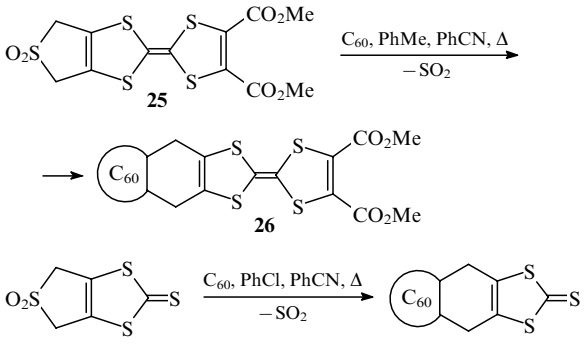
The bulky fullerene fragment does not prevent oxidation of compound **20** at the sulfur atom by *m*-chloroperbenzoic acid. This reaction at 20 °C gave a sulfoxide (yield 89%) and sulfone (yield 45%). At room temperature, C_{60} readily reacts with 2,5-dimethylthiophene *S*-oxide and with 2,5-dimethylthiophene *S*,*S*-dioxide; the reaction with the sulfoxide affords monoadduct **23**, and the reaction with the sulfone gives tetraadduct **24**.[67]



23 **24**

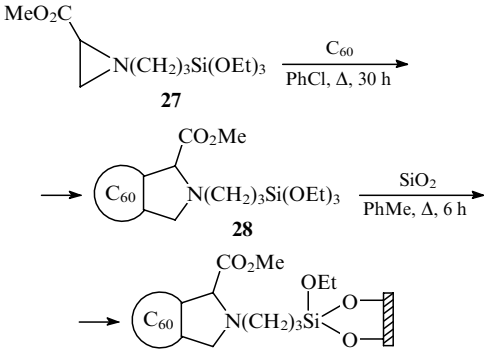
The goals of the synthesis of the adducts **23** and **24** were firstly, to carry out further functionalisation at the SO and SO_2 groups and, secondly, to study their biological activities, because cycloadducts with thiophene oxide fragments are used as biologically important reactive metabolites.

Llacay *et al.* [68] were the first to synthesise the fullerene adducts with organosulfur compounds containing a sulfonyl group capable of being eliminated, for example, with tetrathiofulvalene **25**.



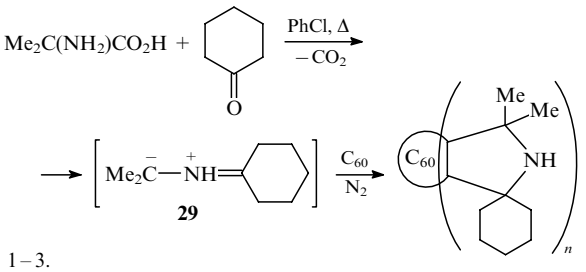
Thione **26** was isolated in 41% yield as a highly stable clathrate including 0.5 molecules of CS_2.

Fulleropyrrolidines, which are fairly promising compounds for the preparation of stationary phases for liquid chromatography of biological objects, have been synthesised by stereospecific thermal 1,3-dipolar cycloaddition of C_{60} to *cis*- and *trans*-*N*-benzyl-1,2-diphenylaziridines.[69,70] Thermally induced cleavage of the aziridine ring in *N*-[3-(triethoxysilyl)propyl]-2-methoxycarbonylaziridine (**27**) in the presence of C_{60} gives rise to fulleropyrrolidine **28**, which can be attached by a covalent bond to silica gel used for HPLC.



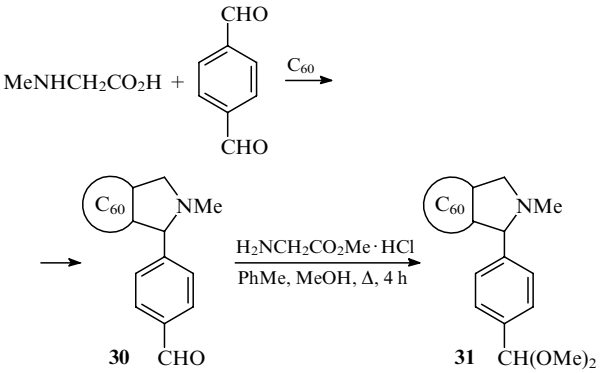
This new adsorbent with the immobilised fullerene-containing group displays an exceptionally high separating capacity with respect to cyclic oligomeric compounds, calixarenes or cyclodextrins in both organic and mixed aqueous-organic media.[70] Optically pure fulleropyrrolidines have also been synthesised.[71] Stationary phases modified with chiral fullerenes can be used for separation of enantiomers.

When a mixture of α-amino acid, a carbonyl compound and C_{60} fullerene is heated in chlorobenzene, fullerene undergoes a [2 + 3]-type cycloaddition to the intermediate azomethine ylide **29**, giving rise to oligoadducts containing one to three pyrrolidine fragments, depending on the reaction conditions.[72–77]



n = 1–3.

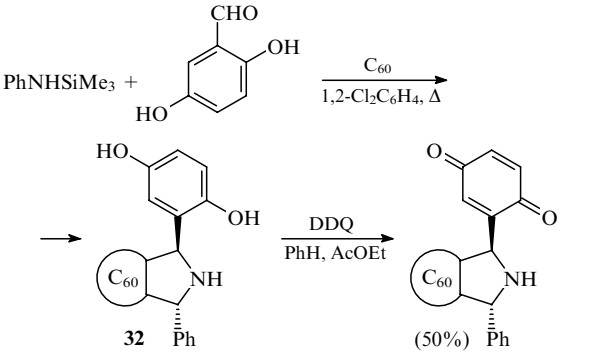
The reaction with methyl nonyl ketone follows a similar route.[72] Heating of sarcosine, terephthalic aldehyde and C_{60} in toluene (in this case, the intermediate ylide is stabilised by the phenyl group) gave compound **30**, which was converted into the amphiphilic 1-methyl-2-(4-dimethoxymethylphenyl)fullereno-[C_{60}][*c*]pyrrolidine (**31**).[74]



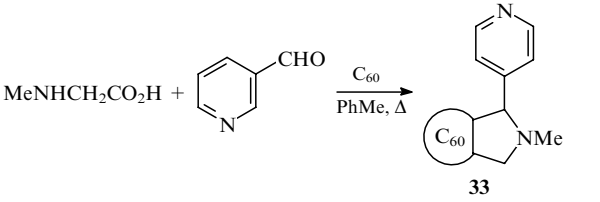
Compound **31** forms Langmuir–Blodgett films and monolayers on an air/water interface; these films are also formed when 22-tricosenoic acid is added. They possess good transparency and thermal stability.[73,74]

Fluorescence of aryl-substituted fullerenopyrrolidines has an interesting feature, namely, its intensity is much higher than that of C_{60}, which is due to the decrease in the symmetry of the molecule. At the same time, the electron-withdrawing ability of the C_{60} spheroid in these adducts is markedly lower than that of fullerene.[77]

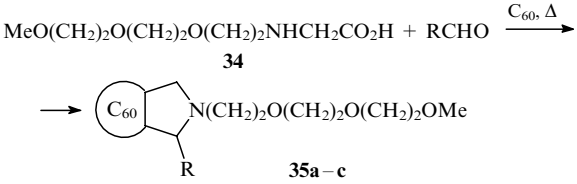
Silylamines can be used in this type of synthesis instead of the amino acid; the compound **32** obtained in this way has been oxidised to a quinone.[78]



By varying the amino acid and the aldehyde used, one can prepare biologically active compounds. For example, a fullerene analogue of natural nicotine **33** has been prepared in order to estimate the influence of the fullerene fragment on the toxicity of nicotine.[79] However, the solubility of compound **33** in solvents miscible with water was found to be too low.



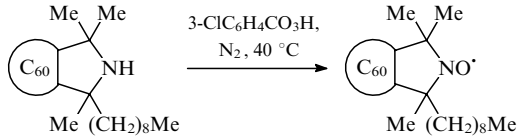
The amino acid was modified by an efficient solubilisation agent, triethylene glycol; this gave compound **34**, which reacted with aldehydes and C_{60} fullerene to give fulleropyrrolidones **35** (including those containing a nicotine fragment) soluble in an H_2O–DMSO mixture.[79]



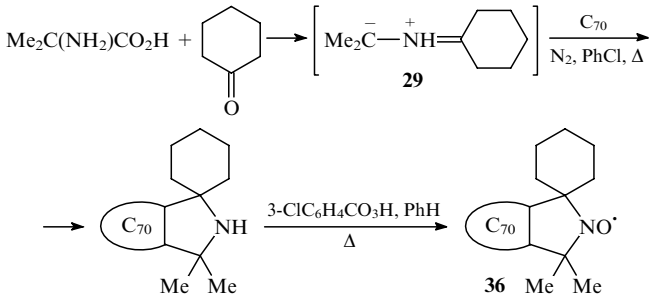
R = 3-Py (**a**), 4-Py (**b**), $CH_2O(CH_2)_2O(CH_2)OMe$ (**c**).

Compound **35c** exhibits an antimicrobial activity including that with respect to a large number of pathogenic microorganisms.[79]

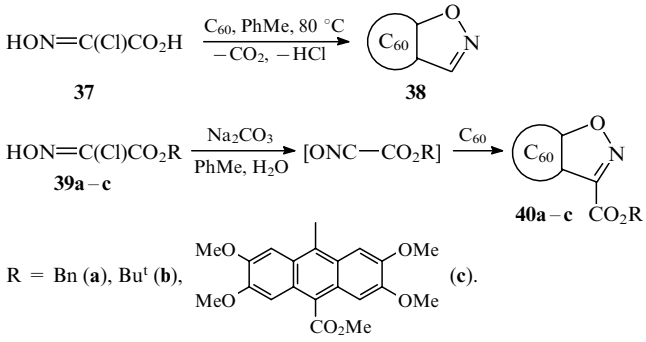
On oxidation with *m*-chloroperbenzoic acid, fulleropyrrolidines are converted into stable nitroxides possessing ferromagnetic properties.[75,76]



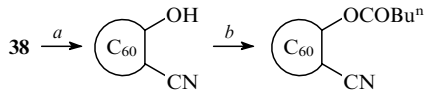
Paramagnetic nitroxide **36** with a spirocyclohexane fragment has been synthesised from C_{70} fullerene.[76]

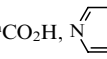
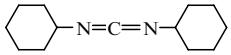


Nitrile oxides generated from oximes or in another way add to C_{60} giving rise to fullerenoisoxazolines.[77–84] Thus fulminic acid (**37**) is converted into fullerenoisoxazoline **38**, while its esters **39a–c** afford derivatives **40a–c** with retention of the alkoxycarbonyl group.[80]

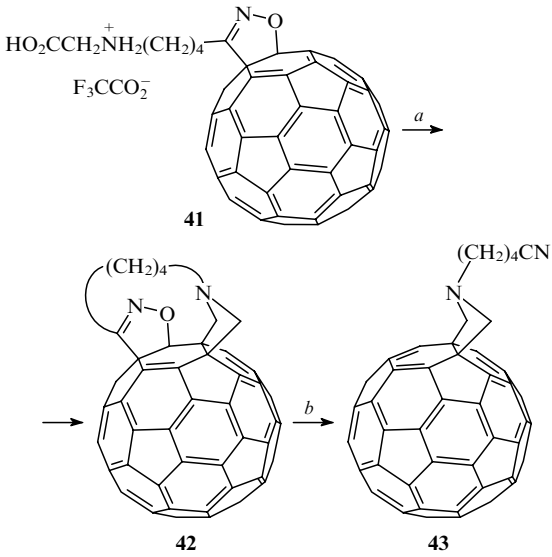


The readily available fullerenoisoxazoline **38** is a convenient starting compound for the synthesis of diverse functional derivatives of fullerene.[81]



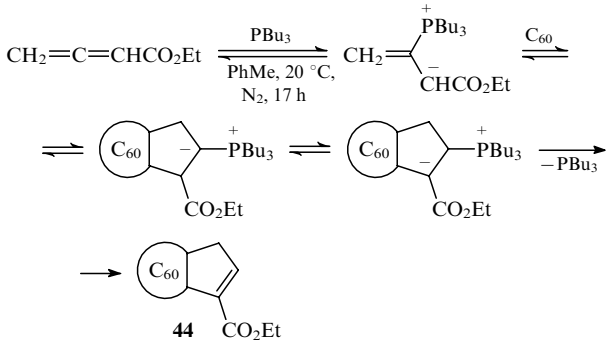
(*a*) Et_3N, N_2, PhMe, 70 °C, 6 h, ⩽10%; (*b*) Bu^nCO_2H, , , PhMe, MeCN, 25 °C (100%).

Fullerenoisoxazolines decompose under relatively mild conditions with quantitative regeneration of C_{60}. This process occurs on refluxing in chlorobenzene in the presence of $Mo(CO)_6$ or on treatment with excess diisobutylaluminium hydride in toluene at 20 °C.[82] The decomposition of the isoxazoline fragment can be used either to control fullerene functionalisation or to perform further functionalisation. Thus treatment of substituted fullerenoisoxazoline **41** with formaldehyde yields tricyclic derivative **42**. When the latter compound is made to react with $Mo(CO)_6$, *N*-substituted fullerenopyrrolidine **43** is produced.[82]

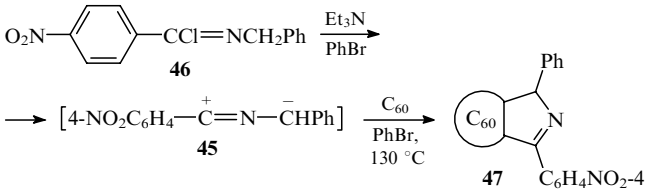


(*a*) CH_2O, PhMe, Δ, 67%; (*b*) $Mo(CO)_6$, PhCl, Δ.

The method for the synthesis of cyclopentenes based on cycloaddition of 2,3-dienoates or 2-ynoates to electron-deficient alkenes in the presence of phosphine has been employed successfully for the synthesis of fullerenocyclopentenes. The driving force of this reaction is nucleophilic attack by a tertiary phosphine on a β-allene or acetylene carbon atom. A series of successive prototropic shifts is followed by β-elimination of phosphine giving rise to fullerenocyclopentene **44**.[85,86]

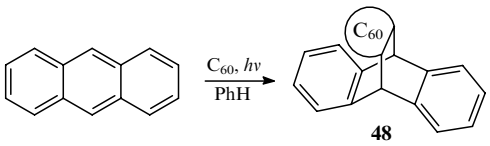


The first example of cycloaddition of ylide **45**, prepared from *N*-benzyl-1-(4-nitrophenyl)chloromethylideneamine (**46**), to C_{60} fullerene was reported.[87]



However, based on the ^{13}C and ^1H NMR data, the authors suggest that, in addition to the normal [6-6]-adduct **47**, the reaction yields an approximately equal amount of a [5-6]-adduct with an open annulene structure as a mixture of two diastereoisomers.

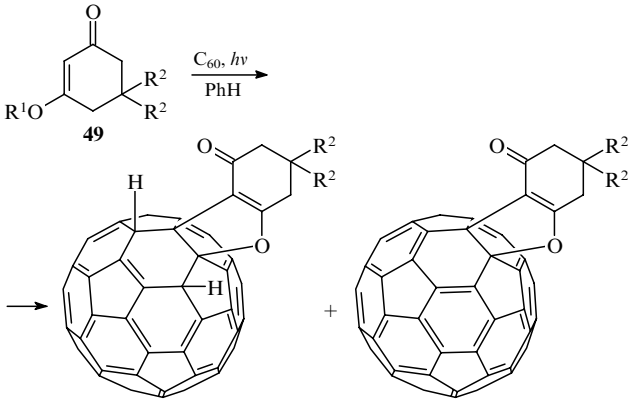
It is known that photoexcited C_{60} fullerene in the triplet state has stronger electron-withdrawing capacity than that in the ground state. Thus it is able to react with moderately electron-releasing reagents according to the [2+2]-cycloaddition pattern.[88–90] For example, anthracene adds to C_{60} on exposure to a laser radiation with $\lambda \geqslant 500$ nm giving rise to adduct **48**.[91]



48

4-Propenylanisole does not react with C_{60} fullerene without light. On exposure to the light of a xenon lamp ($\lambda > 500$ nm) at 20 °C, both *cis*- and *trans*-isomers are converted into monoadducts (yield 40%, the *trans*-compound being the major product), which, however, decompose to the initial components under conditions of mass spectroscopy.[88] Studies of the isotope effects and the ^{1}H NMR spectra of the adducts formed in the reaction of C_{60} fullerene with *cis*-2-deuterio-1-(4-methoxyphenyl)propene made it possible to propose a two-step reaction mechanism involving a bipolar or biradical intermediate.[89]

Jensen *et al.*[90] have studied the behaviour of C_{60} fullerene in the De Mayo reaction, *i.e.* [2+2] photocycloaddition of enolysable 1,3-diketones and 1,2-diketones to alkenes followed by opening of the cyclobutane ring giving rise to cyclooctadienones. The reactions of C_{60} with compounds **49** resulted in the synthesis of fused fullerenofurans, both chiral (**50a**,**b**) and achiral (**51a**,**b**).

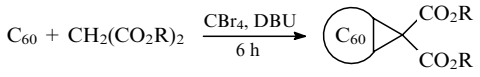


49 **50a**,**b** **51a**,**b**

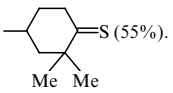
R^1 = H, Me_3Si; R^2 = H (**a**), Me (**b**).

Presumably, the reaction involves either intermolecular oxidation by singlet oxygen of the cyclobutane intermediates formed initially or intramolecular oxidation of these intermediates by a triplet fullerene fragment.

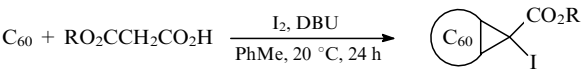
Synthesis of methanofullerenes using cycloaddition reactions is especially significant. Methanofullerenes can serve as the initial compounds for the preparation of functional derivatives of fullerene by introducing substituents into the side chains of the adducts. Routes to methanofullerenes are diverse. They include thermal addition of diazo compounds followed by thermolysis or photolysis, addition of carbenes, and reactions with ylides, which follow an addition–elimination mechanism. Cyclopropanation by diethyl bromomalonate (Bingel reaction [92]) is among the best and most widely used cyclopropanation methods. Recently this reaction has been modified [93] in such a way that bromomalonates (which are difficult to prepare) are formed *in situ* during the cyclopropanation of fullerene. Fullerene is made to react with malonates in the presence of CBr_4 and diazabicyclo[5.4.1]undec-7-ene (DBU) at 20 °C in toluene; the reagents are taken in a 10-fold excess (DBU in a 20-fold excess) with respect to fullerene.



R = 3,5-(3-BnOC$_6$H$_4$CH$_2$O)$_2$C$_6$H$_3$CH$_2$ (29%), Et (57%), $C_{18}H_{37}$ (65%),



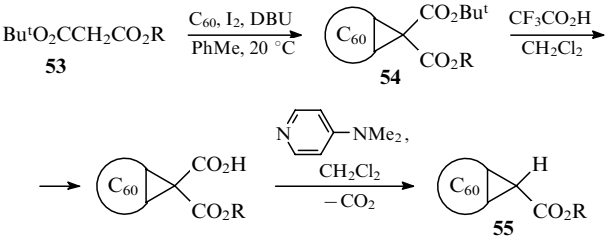
The reaction of monoesters of malonic acid, I_2 and DBU with C_{60} resulted unexpectedly in iodinated derivatives **52a**–**c**.[94]



52a–**c**

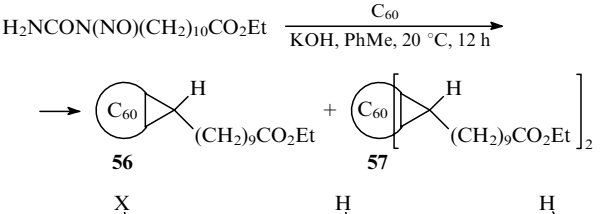
R = Bn (**a**), 3,5-(C$_{12}$H$_{25}$O)$_2$C$_6$H$_3$CH$_2$ (**b**), (CH$_2$)$_2$O(CH$_2$)$_2$OEt (**c**).

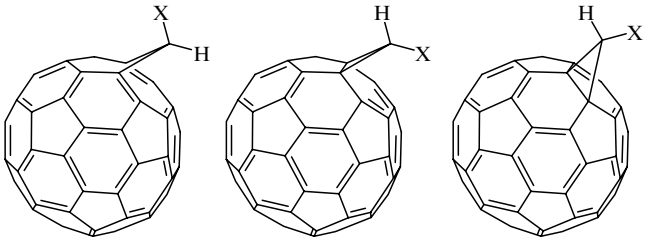
Presumably, the carbanion arising at the first stage is not sufficiently nucleophilic to be converted into diiodomalonate; instead, it is decarboxylated to give RO_2CCH_2I, which adds to fullerene. The reaction with diester **53** yielded fullerenocyclopropanedicarboxylate **54** and monoester **55**.



R = 3,5-(C$_{12}$H$_{25}$O)$_2$C$_6$H$_3$CH$_2$.

Amphiphilic C_{60} derivatives, **56** and **57**, containing an undecanoic acid fragment, have been synthesised (in 45% total yield); the purpose of the synthesis was to study the properties of thin films prepared from these compounds. The monoadduct **56** was resolved into isomers **A**–**C** using column elution chromatography.[95]



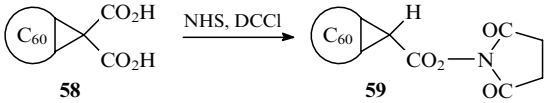


A **B** **C**

X = $(CH_2)_9CO_2Et$.

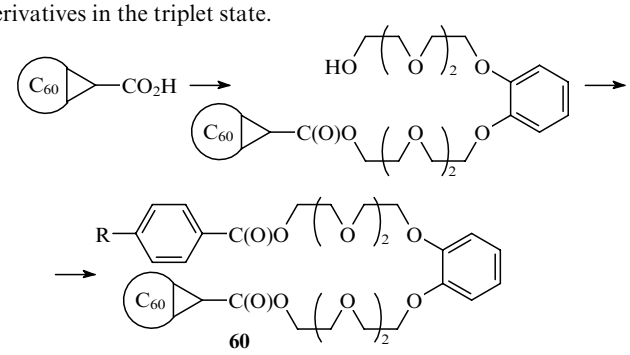
The side chain in methanofullerenes is often modified in order to obtain biologically active compounds. Mono- and di-carboxylic acids, especially 1,2-methanofullerene[60]-61-carboxylic (fulleromalonic) acid, are used most frequently as the starting compounds. Thus *N*-phenyl(1,2-methanofullerene[60])-61-formohydroxamic acid has been prepared from this acid.[96]

When 1,2-methanofullerene[60]-61,61-dicarboxylic acid (**58**) reacts with *N*-hydroxysuccinimide (NHS) and chloro-*N*,*N*-dicyclohexylcarbodiimide (DCC), it eliminates water and CO_2 being thus converted into compound **59**, which reacts with primary and secondary amines, 1-aza-12-crown-4 and 1,6-azahomo[60]fullerene.[97]



58 **59**

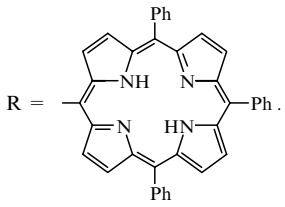
Syntheses of diesters **60** (from porphyrin, open crown ether and methanofullerenecarboxylic acid) and **61** (from azafullerene with an 'open' [6-5] bond and porphyrin) have been performed[98,99] for biological purposes, in particular, for photodynamic therapy, and with the aim of elucidating the possibility of generation of singlet oxygen in the presence of fullerene derivatives in the triplet state.



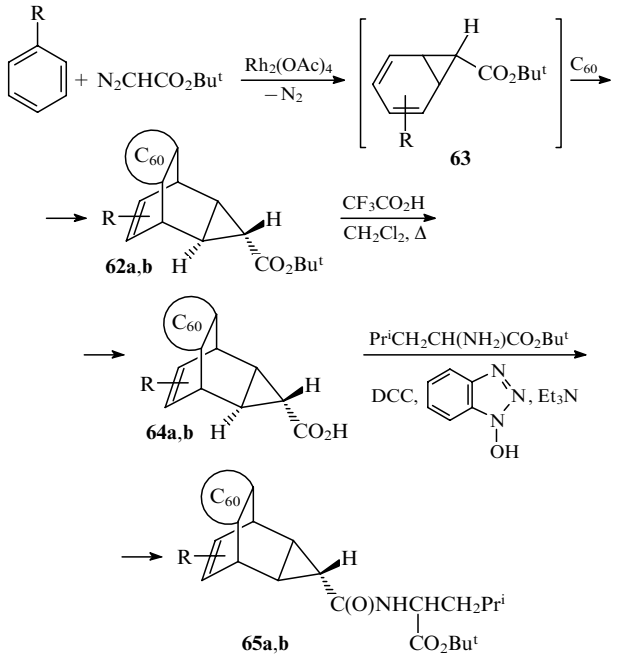
60



61

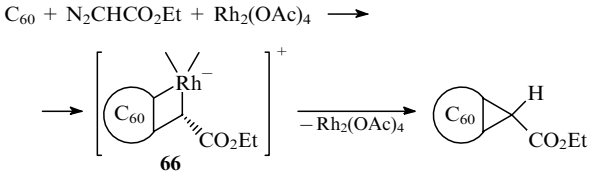


The reaction of C_{60} with *tert*-butyl diazoacetate in benzene or toluene in the presence of dirhodium tetraacetate affords a new type of cycloadducts, tricyclic compounds **62a**,**b**, instead of the expected methanofullerenes. It is assumed that initially, cyclopropanation of the solvent gives norcaradiene **63**, and it is this product that reacts with fullerene.[100] Hydrolysis of the ester group yields acids **64a**,**b**, which are then converted into derivatives **65a**,**b** at the amino group of leucine.



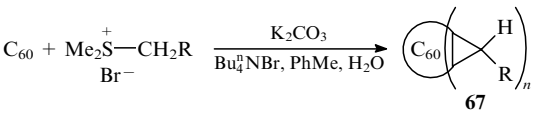
R = H (**a**), Me (**b**); DCC is dicyclohexylcarbodiimide.

However, when 1-methylnaphthalene is used as the solvent, fullerene smoothly reacts with ethyl diazoacetate in the presence of a stoichiometric amount of dirhodium tetraacetate to give normal methanofullerenes, mainly, at a [6-6] bond.[101] A mechanism including the formation of metallacycle **66** was proposed for the reaction.



66

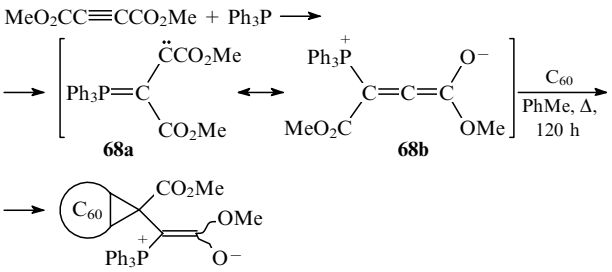
The addition to C_{60} of sulfonium ylides stabilised by cyano, carboxy or carbonyl groups followed by elimination of dimethyl sulfide affords fullerene derivatives which are highly promising as the starting compounds for subsequent functionalisation. The reaction is carried out either under phase transfer catalysis conditions or by generating the ylide *in situ* upon disproportionation of a sulfonium salt on treatment with K_2CO_3.[102] This gives rise to a mixture of mono-, bis- and tris-adducts **67**. Unlike methanofullerenes prepared from diazo compounds, products **67** have a methylene bridge at a [6-6] bond; no isomers containing an 'open' [6-5]-ring system (type **A**, see above) were detected.



67

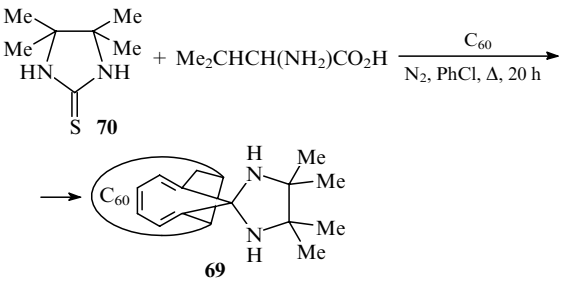
R = CN, CO_2Et, COPh, $COCMe_2CH_2CO_2Et$, CO_2Bu^t; n = 1–3.

A new methanofullerene containing a fragment of a stable phosphonium ylide has been prepared by the reaction of C_{60} with a mixture of equal amounts of triphenylphosphine and dimethyl acetylenedicarboxylate.[103] The reaction involves the formation of carbene ylide intermediate **68a** or zwitter-ion **68b**.



68a **68b**

Spiro derivative of C_{60} fullerene, adduct **69**, containing an 'open' [5-6] bond has formed unexpectedly in the reaction of C_{60} with 4,4,5,5-tetramethyl-1,3-diazolidine-2-thione (**70**) and DL-valine.[104]

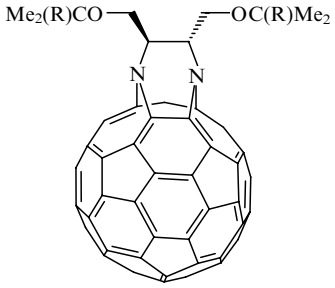


69

The mechanism assumed for this reaction includes the reaction of thione **70** with amino acid to give a carbene, which adds to fullerene.

Shen *et al.*[105] were the first to demonstrate that the reaction of C_{60} fullerene with chiral 1,4-di-*tert*-alkoxy-2,3-bisazidobutanes gives rise to chiral bisazafulleroids. Enantiomeric pairs with the

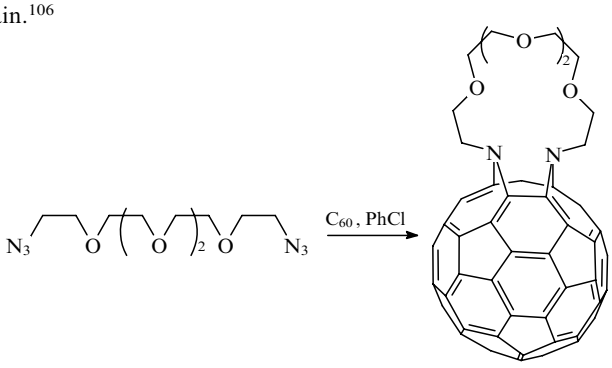
(2*R*,3*R*) and (2*S*,3*S*) symmetry were obtained in ~51% yields. The enantiomers exhibit mirror image circular dichroism curves.



71 (R = Me, Ph)

Apparently, removal of the *tert*-alkyl groups from compounds **71** would provide a route to water-soluble chiral fullerene derivatives, which is important for the investigation of their biological activities.

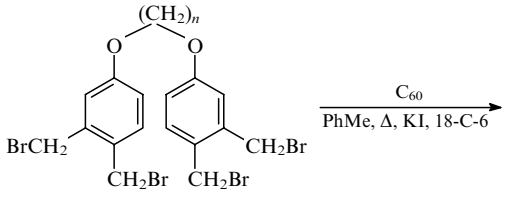
A bisazafulleroid fragment has been inserted in a crown-ether chain.[106]



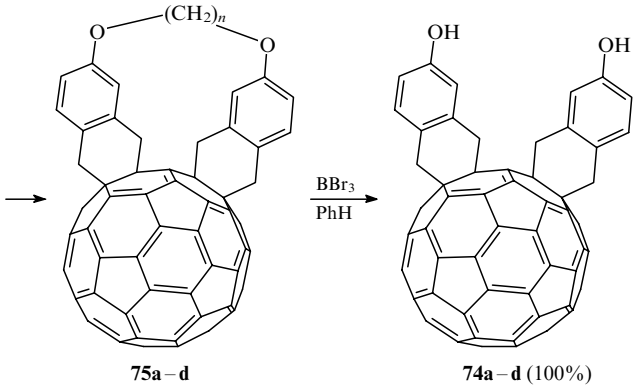
72 (28%)

According to NMR data, the bisadduct **72** has a structure with 'open' [5-6] bonds. The fullereno-crowns are excellent agents for binding metals. Perhaps, new superconducting substances would be found among these complexes.[106]

The reaction of fullerene with tetrabromides **73a**–**d** has resulted in selective multifunctionalisation of fullerene, the goal of which was to prepare disubstituted bisphenols with substituents located at particular rings in the cage.[107]



73a–**d**



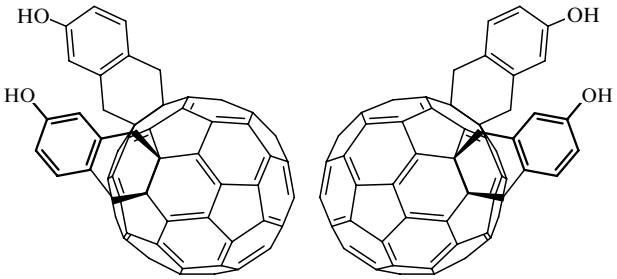
75a–**d** **74a**–**d** (100%)

n = 2 (**a**), 3 (**b**), 4 (**c**), 5 (**d**).

The reaction is carried out under conditions of high dilution (10^{-4} mol litre^{-1}) and the guiding $(CH_2)_n$ chain is subsequently split off.[107] When $n = 2-5$, the addition occurs selectively within one hemisphere of the C_{60} cage. When $n = 2, 3$, only *cis*-2- and *cis*-3-isomers are formed and for $n = 5$, bisaddition yields the *e*-adduct. When $n = 4$, the reaction gives a complex mixture of bisadducts. For both the cyclic precursors and acyclic bisadducts, types of symmetry and the relationship between the symmetry and chirality were established by analysing the data of mass, NMR, UV and visible spectra (all adducts with C_1 and C_2 symmetry are chiral and those with C_s symmetry are achiral). The chiral *cis*-3- and *e*-adducts were resolved into enantiomers using HPLC with a chiral phase [cellulose tris(3,5-dimethylphenyl carbamate)-coated silica gel (CHIRAL CEL OD), hexane–isopropyl alcohol]. For example, for $n = 2$, the bisphenol **74a** was obtained.

Both the precursor **75a** and the final diol **74a** are *cis*-2 isomers (this was observed for the first time for fullerene bisadducts) and are achiral; the compound **75a** corresponds to C_s symmetry.

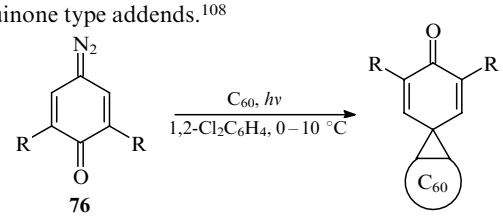
The cyclic precursor **75d** and the bisphenol **74d** for $n = 5$ are *e*-isomers with C_1 symmetry; they are chiral and optically active. The total yield of the isomers at the final stage is 100%. The $[\alpha]_D$ values for the ethers **75a**,**d** (5.7×10^2 and -5.2×10^2) and the diols **74a**,**d** (4.4×10 and -7.4×10) were determined. The structures of optical isomers of the bisphenol **74d** are presented below.



74d

The compounds **74a**–**d** belong to the few examples of chiral derivatives with achiral substituents known in the chemistry of cage compounds, in particular, in the fullerene chemistry.

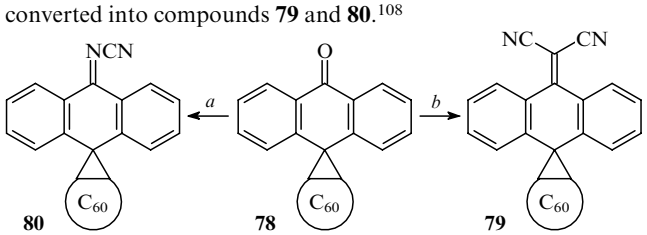
The reaction of C_{60} fullerene with diazo compound **76** has resulted in the synthesis of spirane methanofullerenes **77** with quinone type addends.[108]



76 **77**

R = H, Me, Bu^t.

Spiro[10-anthrone-9,61′]methanofullerene (**78**) and spiro[cyclohexanone-4,61′]methanofullerene (the latter as a mixture of [6-6] and [5-6] isomers) were prepared in a similar way. The conjugated dienone **78** exhibits stronger electron-withdrawing capacity than the initial C_{60} fullerene. The anthrone **78** was converted into compounds **79** and **80**.[108]



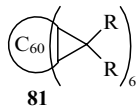
80 **78** **79**

(*a*) $Me_3SiN{=}C{=}NSiMe_3$, $TiCl_4$, $CHCl_3$, Δ, 5 days (60%);
(*b*) $CH_2(CN)_2$, $TiCl_4$, Py, $CHCl_3$ (26%).

Chemical modification of more than two double bonds in the C_{60} molecule gives, as a rule, a mixture of regio- and stereoisomers. Therefore, study of the possibility of synthesising a single isomer by multifunctionalisation of C_{60} is of interest. These molecules could serve as useful tools in the studies of functional catalysis and in the materials science; they could find application in bioorganic chemistry (for example, for reactions with DNA, enzyme inhibition, design of compounds for drug transport, and for other purposes [109]).

Hirsch has studied the regiochemistry and stereochemistry of multiple addition to the double bonds in C_{60} and has developed a theoretical substantiation of these reactions.[13, 21]

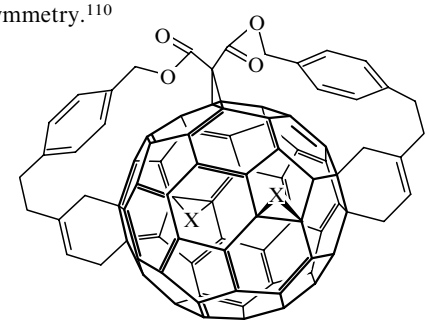
Double (and multiple) cyclopropanation with dialkyl bromomalonates according to the Bingel reaction pathway is used most often to prepare polysubstituted fullerenes.[92] Thus C_{60} has been made to react [93] with the malonate and CBr_4 in the presence of DBU on the addition of 10 equiv. of 9,10-dimethylanthracene and at longer reaction times; under these conditions, symmetrical hexakis(adducts) **81** were obtained in good yields.



81

R = CO_2CH_2Me, $CO_2(CH_2)_{16}Me$.

When pentakis(adducts) **82** with C_{2v} symmetry are again treated with diazomethane, heptakis- and octakis-adducts with C_s symmetry, pyrazoline derivatives, are formed with high regioselectivity. These products are converted into methanofullerenes by thermally induced abstraction of nitrogen. The direction of nitrogen abstraction was assumed to be controlled by orbital symmetry.[110]

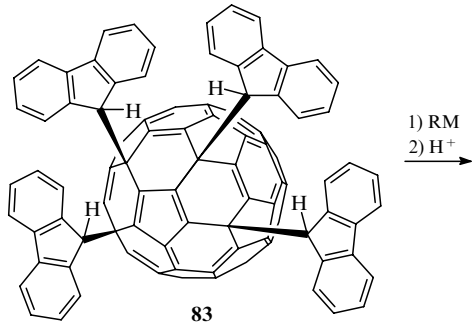


82

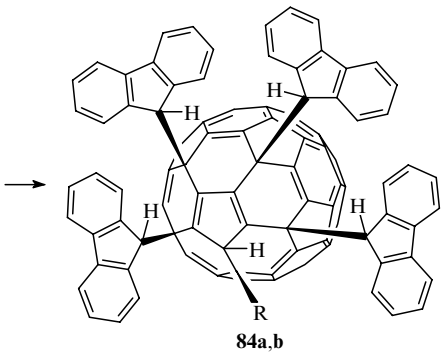
X = $C(CO_2Et)_2$, $C(CO_2CH_2CO_2Et)_2$.

The tetrakis(adduct) **83** contains a fulvene π-subsystem located on the spheroid surface. This compound is prepared from a mixture of C_{60}, fluorenylpotassium and fluorene in THF. The mixture is kept under an argon atmosphere in the presence of traces of oxygen for 72 h and the adduct is then isolated by preparative chromatography.[111]

The tetrakis(adduct) **83** adds nucleophiles, which is typical of a fulvene π-system. Thus it reacts with 1-octynyllithium in THF or with NaCN in a DMF–chlorobenzene mixture to give pentakis(adducts) **84a**,**b** in 63% and 68% yields, respectively.



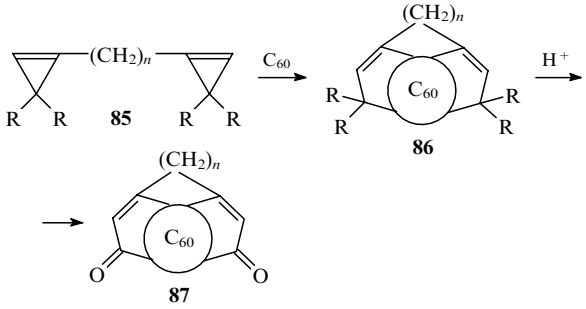
83



84a,**b**

RM = $C_6H_{13}C{\equiv}CLi$ (**a**, 63%), NaCN (**b**, 68%).

Long-term heating of C_{60} with compounds **85** in anhydrous 1,2-dichlorobenzene in the presence of 4 Å molecular sieves results in double cycloaddition giving rise to tricyclic compounds **86**.[109]



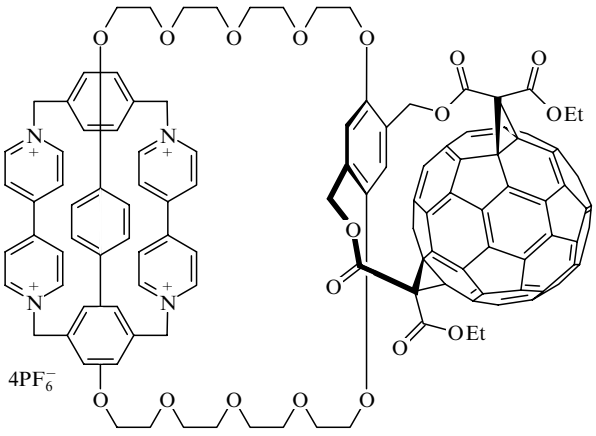
86

87

R–R = $OCMe_2O$; n = 3, 4, 6.

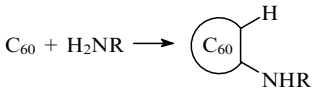
Acid hydrolysis affords quantitatively the corresponding diketones **87**.

A [2]catenane containing the C_{60} bishomofullerene fragment was synthesised for the first time using a sequence of two modified Bingel reactions (yield 18%).[112]



2. Nucleophilic, electrophilic and radical addition

Nucleophilic addition to C_{60} fullerene gives, as a rule, monoadducts; for example, C_{60} adds one amino acid molecule.[113] Dipeptides react in a similar way.[114]



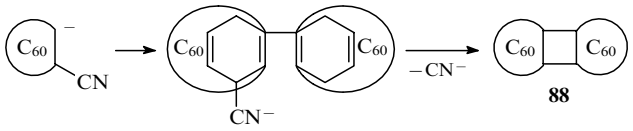
R is an amino acid or dipeptide residue.

Fullerene dipeptide derivatives are soluble in water owing to association with amino acid residues.[114] These adducts penetrate

inside the liposomes, they exhibit adjuvant‡ properties and antiviral activity.[113, 115, 116]

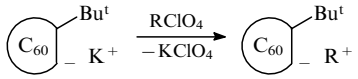
The reaction of C_{60} in 1,2-dichlorobenzene with NaCN in DMF affords not only the $[C_{60}(CN)]^-$ anion but also the $[C_{60}(CN)]^{2-}$ and $[C_{60}(CN)]^{3-}$ anions, although the monoion predominates (as shown by negative-ion mass spectrometry).[117]

Mechanochemical activation (mixing of solid reactants in a vibratory mill[118]) can be used for functionalisation of fullerenes. The reaction of C_{60} with NaCN carried out in this way gave the dimer C_{120} **88**, in which two spheroids are linked *via* a cyclobutane ring. The fact that the reaction pathway differs from that observed in solutions is due to the unique ability of the cyanide ion to serve as both a nucleophile and a leaving group.



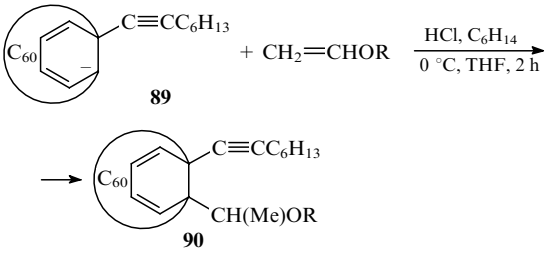
The reactivity of the dimer **88** does not differ much from that of C_{60}. For instance, it enters into the Bingel reaction with diethyl bromomalonate and DBU (in equimolar amounts) to give a mixture of isomeric monoadducts (at least, three compounds) in 44% total yield.[118]

Tanaka *et al.*[119] made use of the fact that the fullerene spheroid readily forms anions and synthesised an unusual class of compounds, hydrocarbon salts.



R^+ is tris[1-(5-isopropyl-3,8-dimethylazulenyl)]cyclopropenylium.

Vinyl ethers add to the stable 2-(1-octynyl)-1,2-dhydrofulleren[60]-1-ide ion (**89**) in the presence of HCl; this affords [6-6] bisadducts **90**, which are promising monomers for cationic polymerisation.[120]



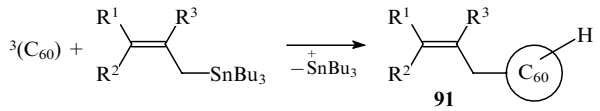
R = CH_2Pr^i, $(CH_2)_2OAc$.

The fullerene C_{60} adds Grignard reagents $ClMgCH_2SiR_3$ (R = Alk, Ar, AlkO) yielding mainly compounds $C_{60}(H)CH_2SiR_3$ in THF and only products of the formula $C_{60}(CH_2SiR_3)_2$ in toluene.[121]

Fullerenylmethylsilanes such as $C_{60}(H)CH_2SiMe_2Cl$, $C_{60}(H)CH_2SiMe_n(OR)_{3-n}$ and $C_{60}[CH_2SiMe_n(OR)_{3-n}]_2$, where R = Alk, $n = 0, 1$, are used to modify silica gel. The products thus formed are used as sorbents for HPLC, as heterogeneous photosensitisers and in catalysis.[121]

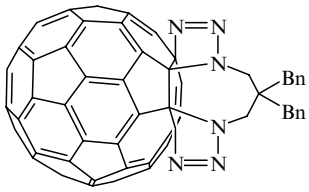
Irradiation of C_{60} and allylstannanes in a benzene or toluene solution results in the regioselective formation of fullerene monoallylation products. The process is inhibited by oxygen or benzonitrile.[122] Fullerene derivatives **91** have been synthesised in this way. This reaction occurs by a mechanism involving triplet C_{60} and single-electron transfer.[122]

‡Adjuvants are compounds stimulating an increase in the number of antibodies.

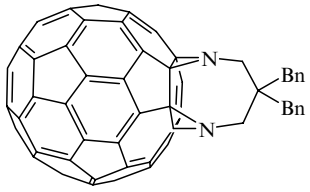


R^1, R^2, R^3 = H, Me.

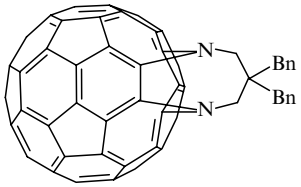
Mixed adducts **92**–**94** were directly synthesised for the first time from C_{60} and 2,2-dibenzyl-1,3-diazidopropane[123] by refluxing the reactants in chlorobenzene.



92 (18%)

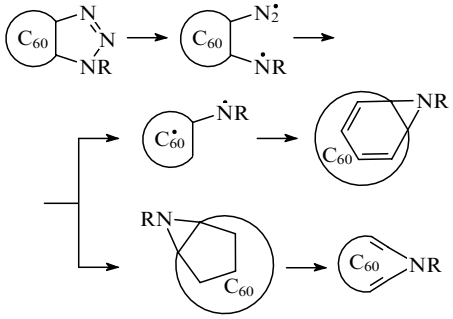


93 (25%)



94 (11%)

Bistriazolines are precursors of bisdiazolines and can be converted into the latter by thermolysis in chlorobenzene. Thermolysis of the bistriazoline **92** afforded the compound **94**. The formation of the adducts **93** and **94** was interpreted[123] in terms of a radical mechanism, similar to the mechanism of triazoline thermolysis.



3. The addition of hydrogen and the properties of hydrides

All attempts to prepare completely hydrogenated fullerene $C_{60}H_{60}$ failed. This compound appears to be highly unstable due to the enormous strain which arises upon the formation of twenty planar cyclohexane rings and numerous shielding H–H interactions.[13] By 1997, hydrides with the compositions $C_{60}H_x$ (x = 2, 4, 18, 32, 36, 36–50, 42–44) and $C_{70}H_x$ (x = 2, 4, 8, 10, 34–36, 36–38, 36–44) were known.[124, 125]

The methods used to prepare fullerene hydrides have all been considered in detail;[11, 125] they include Birch reduction, hydroboration, hydrozirconation, solid-phase and liquid-phase hydrogenation with hydrogen, electrochemical reduction, reduction with diimide or with chromium acetate, photoinitiated electron transfer and reduction with metal hydrides.

Despite the fact that fullerenes could be promising catalysts for activation of the C–H bonds in hydrocarbons *via* the formation of fullerene hydrides, as was convincingly demonstrated in a comprehensive review,[11] this aspect has not yet received adequate attention. Studies are mainly concerned with the structure[124, 125] and spectral and photophysical properties of fullerene hydrides.[124–128] It is assumed that the solid hydride $C_{60}H_{36}$ corresponds to T symmetry and contains four isolated

benzenoid rings, located in tetrahedral positions on the surface of the closed shell of the molecule.

A preparative synthesis of fullerene hydrides was carried out by treatment of fullerenes with metals and water serving as a source of protons;[125] although the number of possible isomers is enormous, only a few of them are formed. For instance, heating of a solution of C_{60} fullerene in toluene with a Zn(Cu) mixture (freshly prepared Zn dust is employed) gives rise to a mixture of hydrides, which are isolated by preparative liquid chromatography. Depending on the temperature, reaction time and the ratio of the metals, the compounds $C_{60}H_2$, $C_{60}H_4$ and $C_{60}H_6$ (two isomers) can be obtained in 66%, 45% and 38% yields, respectively. Reduction of C_{70} fullerene afforded $C_{70}H_8$ and $C_{70}H_{10}$ (three isomers) in a total yield of 62%. The hydrides $C_{70}H_n$ are all unstable in air and during storage.

Fullerene hydrides and deuterides containing up to 24 hydrogen atoms per fullerene molecule have been obtained upon hydrogenation (with either hydrogen or deuterium) at 1–2.5 MPa and 573–673 K of a mixture of fullerite (83% of C_{60}, 15% of C_{70} and 2% of higher fullerenes) and powdered intermetallic compounds $LaNi_5$, $LaNi_{14.65}$ and CeO_3.[129] At 800 K, fullerene hydrides (deuterides) decompose with evolution of gaseous hydrogen (or deuterium); at 1000 K, the reaction of fullerite with intermetallic compounds is accompanied by evolution of the corresponding 3*d* metal.[129] The hydrides prepared in this way can serve as sources of high-purity hydrogen. When fullerite (78% of C_{60} and 22% of C_{70}) is deuterated in the presence of Pd clusters (Pd powder and Pd/C), the maximum content of deuterium corresponds to $[C_{60} + C_{70}]D_{26}$ and is attained after ten repetitions of the heating–cooling cycle (673–293 K) at 2.5 MPa.[130]

Fullerene dihydride $C_{60}H_2$ has been synthesised by ultrasonic treatment of C_{60} fullerene in decalin for 2–4 h in a sealed vessel under argon.[131] The hydrogen needed to hydrogenate fullerene is formed upon sonolysis of the solvent.

The dehydrating capacity of C_{60} fullerene may be useful in the studies of biological objects. Thus C_{60} dehydrates the Hantsch ester (the reaction simulates the action of dihydronicotinamide-adeninedinucleotide) at 100 °C under anaerobic conditions to give diethyl 2,6-dimethylpyridine-3,5-dicarboxylate; in this reaction, fullerene is converted into mixed hydrides $C_{60}H_n$ ($n = 2, 4, 6$).[132] It is of interest that this dehydrogenation can be carried out by leaving the reaction mixture in the light at 20 °C; in this case, C_{60} acts as a catalyst because it is recovered unchanged.[132]

On irradiation in the presence of sensitisers such as 9,10-dicyanoanthracene (and diphenyl as a co-sensitiser), the radical cation $C_{60}^{+\bullet}$ is generated from C_{60}. The radical cation reacts with hydrogen donors, for example, with *tert*-butyl methyl ether, propionaldehyde and alcohols giving rise to 1-substituted 1,2-dihydro[60]fullerenes.[133]

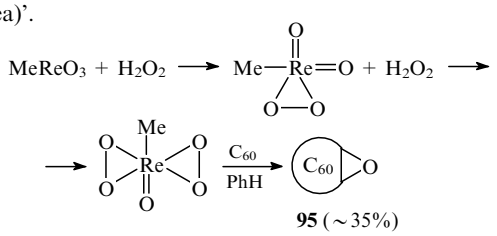
The hydride 1,2-$C_{60}H_2$ has been prepared in 70% yield by the reaction of photoexcited C_{60} fullerene with 10-methyl-9,10-dihydroacridine.[134]

The proton at the 4-position of stable 1-*tert*-butyl-1,4-dihydro[60]fullerene undergoes base-catalysed migration to give a thermodynamically more favoured isomer, 1-*tert*-butyl-1,2-dihydro[60]fullerene.[135]

4. Oxidation

The electronegative fullerene molecules can be easily reduced but cannot be readily oxidised; however, the reaction of fullerene with oxygen on exposure to UV light (in hexane) or heating of fullerene in the presence of oxygen results in vigorous oxidation accompanied by fragmentation, *i.e.* rupture of the C=C bonds in the cage.[13] Upon irradiation, C_{60} passes initially into the triplet state; the transfer of energy from this species affords singlet oxygen, which oxidises the fullerene.[9]

Oxygen derivatives of fullerenes receive little attention yet. The monoxide, namely, 1,2-epoxy[60]fullerene (**95**), is prepared by reactions with various oxidants including systems with cytochrome P450;[136] however, the yields are relatively low. A preparative pathway to 1,2-epoxy[60]fullerene (**95**) has been described[137] in which fullerene is treated with the system 'methyltrioxorhenium–hydrogen peroxide (as a complex with urea)'.



95 (~35%)

Interestingly, either component of this oxidative system taken alone give virtually no target product.

The epoxide $C_{70}O$, which is fairly difficult to obtain, has been isolated in ~0.5% yield upon the use of an arc-discharge reactor with a rotating cathode and an anode made of carbon plates (the reactor operation time was 24 h).[138] Study by ^{13}C NMR spectroscopy showed the presence of two isomers, 1,2-epoxy-C_{70} and 5,6-epoxy-C_{70} in 47 : 57 ratio. The predominance of the [5-6] isomer was interpreted[138] as being due to the lower strain in its molecule.

The compound $C_{120}O$ (its synthesis has been reported[139]) disproportionates at 400 °C to give 60% of C_{60}, 15% of $C_{120}O_2$, and a mixture containing oligomeric $(C_{60})_nO_m$ oxides ($n = 3, 5$; $m = 3–9$).[140]

The dioxide $C_{120}O_2$ is stable at room temperature both in a pure state and in solutions. After thermolysis of $C_{120}O$ at 550–560 °C, product C_{119} containing two C_{58} cages was isolated from the reaction mixture in 2% yield. The cages are connected by a bridge comprising three sp^3-hybridised carbons, two of which are equivalent.[141]

Oxidation of C_{60}^- permits the preparation of an aqueous colloidal solution of C_{60} fullerene.[142] The C_{60}^- anion is formed when a solution of C_{60} in THF is treated successively with an Ni–Al alloy and an aqueous solution of sodium hydroxide; C_{60}^{2-} can be prepared in a similar way except that DMSO is used in place of THF. The anions are inert with respect to water but highly sensitive to oxygen. Oxidation occurs *via* consecutive steps

$$C_{60}^{2-} \longrightarrow C_{60}^- \longrightarrow C_{60},$$

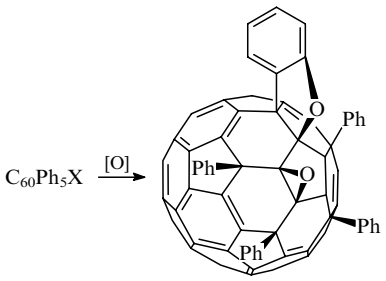
the overall reaction being written as

$$4C_{60}^- + O_2 + 2H_2O \longrightarrow 4C_{60}\,(soln) + 4OH^-.$$

If the oxidation is performed in an aqueous medium, C_{60} forms a colloidal solution containing non-crystalline and quite homogeneous particles with a dimension of ~10 nm (as established by electron microscopy); in an anhydrous organic solvent, C_{60} precipitates as a black powder.

Electrochemical reduction of $C_{60}O$ affords an electrochemically active film; a different active film is formed upon the reduction of C_{60} to the dianion in the presence of O_2.[143] Films of conducting polymers, which are deposited on the electrodes upon electrochemical reduction of $C_{60}O$, are promising for the design of important materials for engineering (*e.g.*, for microelectronics).[144]

An interesting feature of pentaphenyl-substituted fullerenes has been discovered.[145] The compound $C_{60}Ph_5Cl$ was kept for two weeks in air and in the light, and $C_{60}Ph_5H$ was stored for a year. Both substances were spontaneously oxidised yielding complex mixtures of products. In both cases, a compound with the composition $C_{60}Ph_4C_6H_4O_2$ was isolated from the mixture in 60% yield. Relying on NMR and mass spectroscopy, it was established that elimination of hydrogen or chlorine atoms linked to the cage and an *ortho*-hydrogen atom of the neighbouring phenyl group followed by oxidation gives rise to fullerenobenzo[*b*]furan **96**. The mechanism of this reaction is not yet entirely clear.



96 (X = H, Cl)

The radicals generated in the reaction of fullerene with *tert*-butyl peroxide on irradiation are highly stable under a nitrogen atmosphere and react only slowly with oxygen, water and with radical traps such as nitrobenzene.[146]

$$(Bu^tO)_2 \xrightarrow{h\nu} 2\,Bu^tO^\bullet$$

$$n\,Bu^tO^\bullet + C_{60} \longrightarrow (Bu^tO)_nC_{60}^\bullet$$

$n \geqslant 1$.

Fullerenols eliminate active oxygen radicals including superacidic radical anions formed in biological systems,[147] which opens up the way for using them in biochemistry and pharmacology.

No compounds containing the C_{60}^+ cation have been obtained. However, the salt **97**, containing the C_{76}^+ cation, which has a much lower electrochemical oxidation potential, has been synthesised.[148]

$$R_3N + Ag(CB_{11}H_6Br_6) + \tfrac{1}{2}Br_2 \xrightarrow[-AgBr]{CH_2Cl_2}$$

$$\longrightarrow [R_3N]^+[CB_{11}H_6Br_6]^- \xrightarrow[-R_3N]{C_{76},\ 1,2\text{-}Cl_2C_6H_4} [C_{76}]^+[CB_{11}H_6Br_6]^-$$

97

R = 2,4-$Br_2C_6H_3$.

The salt **97** can be stored for several weeks under a nitrogen atmosphere. Apparently, this is the first compound with a carbocation consisting only of carbon.

5. Halogenation

It was shown back in 1991–1992 that C_{60} fullerene reacts with gaseous chlorine and fluorine and with liquid bromine giving complex mixtures of addition products.[13] Subsequently, these studies have not progressed greatly due to the difficulties in the isolation of individual compounds and in controlling halogenation reactions.

It had been considered[9] that iodine does not react with fullerene; however, later,[40,41] CTC involving iodine and C_{60} were prepared.

The C_{60} fullerene readily reacts with chlorine under free radical reaction conditions to give $C_{60}Cl_{40}$ (see Ref. 149). This compound can be used as an intermediate in the further fullerene functionalisation, namely, synthesis of polyfullerol and polyfluorofullerene.

The reaction of C_{60} with excess iodine chloride (toluene, 20 °C) gives rise to an individual compound, $C_{60}Cl_6$; the reaction with liquid bromine affords $C_{60}Br_2$, while the reaction in CS_2 solvent results in $C_{60}Br_5$ (see Ref. 9).

Fluorination of fullerenes is receiving somewhat more attention because fluorinated derivatives might be of interest for materials science.[150]

Thus fluorofullerenes containing up to 60 fluorine atoms per molecule, including $C_{60}F_{48}$,[151] can be prepared by fluorination with fluorine gas, while hyperfluorofullerenes $C_{60}F_{76}$ can be synthesised on treatment with fluorine with exposure to UV radiation; this reaction is accompanied by cleavage of the spheroidal cage.[149] When C_{60} is treated with MnF_3 at 330 °C (24 h), $C_{60}F_{36}$ is formed.[152] Judging by the mass spectrometric data, the mixture of fluorinated derivatives resulting from the reaction of C_{60} with KrF_2 in anhydrous HF contains mainly $C_{60}F_{44}$ and $C_{60}F_{46}$ (see Ref. 150). Treatment of C_{60}/C_{70} with vapours of the fluorides WF_6, TaF_5, NbF_5 and TiF_4 results in the preparation of fluorides $MF_n \cdot C_{60}$ (the $MF_n : C_{60}$ ratio is $< 1:2$).[153]

A preparative route to fullerene derivatives with organofluorine substituents (for instance, derivative **98**) involves the reaction of C_{60} with halofluoroalkanes and tributyltin hydride under free-radical reaction conditions.[154]

$$Bu_3SnH \longrightarrow Bu_3Sn^\bullet$$

$$BrCF_2CO_2Et \xrightarrow[-Bu_3SnBr]{Bu_3Sn^\bullet} {}^\bullet CF_2CO_2Et \xrightarrow[PhH,\ N_2,\ \Delta,\ 30\ h]{C_{60}}$$

$$\longrightarrow EtCO_2CF_2C_{60}^\bullet \xrightarrow[-Bu_3Sn^\bullet]{Bu_3SnH} C_{60}[6\text{-}6](H)CF_2CO_2Et$$

98

When n-$C_6F_{13}I$, $BrCF_2Br$, n-$C_{12}F_{25}I$ and $I(CF_2)_6I$ are used, initiation of the reaction requires the addition of azoisobutyronitrile. The hydrogen atom in the C_{60} ring in the resulting compounds is highly acidic and can be replaced by other functional groups in a weakly alkaline medium.[154]

V. Fullerenes in polymerisation reactions

When C_{60} fullerene pellets are exposed to a pressure of 1.2 GPa at 600 K for 5 h, [2+2] cycloaddition occurs to give polymers including linear polymers in which the C_{60} fragments are linked by cyclobutane rings.[155] The C_{70} fullerene is more difficult to polymerise,[156] which has been explained by steric hindrance to the [2+2] cycloaddition involving the double bonds in the equatorial region of the ellipsoidal cage. Judging by spectroscopic data,[156] heating solid C_{70} fullerene at 750 °C under a pressure of at least 7.5 GPa affords dimers.

Shvartsburg *et al.*[157] have designed a setup permitting generation of the $C_{120}^{+/-}$, $C_{130}^{+/-}$ and $C_{140}^{+/-}$ ions, which are formed upon laser-induced desorption of crude C_{60} films, and measured their mobility and the trajectories. The trajectories of these ions were in satisfactory agreement with those calculated for the dimers produced upon [2+2] cycloaddition. This study is the first experimental proof of the structure of fullerene dimers.[157]

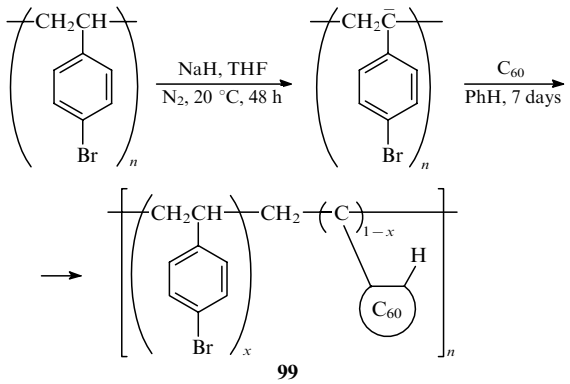
Simultaneous laser-induced vaporisation of C_{60} and graphite at a low helium pressure and a temperature of 400–500 °C or 1900–2400 °C gives rise to polymers of the composition $C_{60}(CC_{60})_{n-1}$ ($n = 2-7$), the dimer C_{121} being the predominant species.[158] When the laser radiation intensity is low, polymers dissociate to give the monomeric components, whereas high radiation intensity results in the elimination of C_2.

During polymerisation of ordinary monomers, C_{60} can be introduced both in the backbone and in the side chain of the polymer formed.

The chain growth reaction during polymerisation of polystyrene in the presence of C_{60} yields stable free radical (polystyrene)$C_{60}^\bullet$ (see Ref. 159). The C_{60} and C_{70} fullerenes copolymerise with styrene by a standard free radical mechanism both in block and in aromatic solvents;[160] this affords dark-brown polymers soluble in the same solvents as polystyrene and fluorescing more intensely than polystyrene (fluorescence is shifted to the blue region).

High-pressure (0.1 to 1.5 GPa) polymerisation of styrene in the presence of C_{60} gives rise to a mixture containing products both soluble and insoluble in chloroform.[161] An insoluble polystyrene with the chains cross-linked by fullerene molecules was isolated from this mixture.

Modification of polymers by C_{60} fullerene fragments changes markedly their physicochemical properties and, in some cases, substantially increases the solubility. A new method for the synthesis of soluble fullerenated polymers by the reaction of carbanionic polymeric intermediates with C_{60} has been developed.[162]

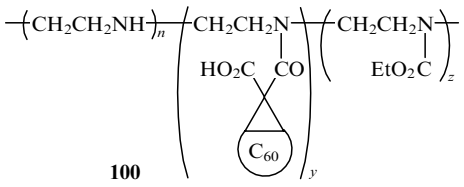


99

Poly-4-bromostyrene **99** with pendant fullerenes is readily soluble in most common organic solvents (CCl_4, $CHCl_3$, PhH, THF). Poly(vinylbenzyl chloride) modified with C_{60} fullerene and soluble in organic solvents has been prepared in a similar way.[163] It was found[164, 165] that C_{60} fullerene substantially inhibits free-radical polymerisation of vinyl monomers in the presence of AIBN by reacting with the initiator and/or by terminating the chain growth.[164, 165] This is true for copolymerisation with methyl acrylate, methyl methacrylate, acrylonitrile, vinyl acetate and *N*-vinylpyrrolidine.[164] Only with highly reactive monomers such as cyanoethyl acrylate and cyanovinyl acetate, does C_{60} give copolymers (yields 53% and 65%, respectively). Free-radical copolymerisation of 4-vinylbenzoic acid and 2- or 4-vinylpyridine with C_{60} results in polyelectrolytes.[166] Apparently, in addition to non-linear copolymers, the process yields homopolymers and microparticles, which can be separated from copolymers only using microporous filters.

When styrene or methyl methacrylate is subjected to radical polymerisation in the presence of C_{60} (1 mass % in the reaction mixture), fullerene reacts at early steps of the process. This gives rise to branched structures; the proportion of the linear polymer increases with time. Physicochemical properties of these polymers have been characterised in detail.[167]

As noted above, the synthesis of water-soluble fullerene derivatives, in particular water-soluble polymers, is important regarding the investigation of the biological properties of fullerenes. Derivatives of this type have been prepared by covalent attachment of hydrophilic linear polymers to the fullerene fragment.[168] Thus the poly(propionylethyleneimine–ethyleneimine) copolymer is added to methano[60]fullerenedicarboxylic acid in the presence of 1-ethyl-3-(dimethylaminopropionyl)carbodiimide. The reaction is carried out in chloroform at 0 °C. This gives water-soluble polymer **100** with pendant C_{60} groups (molecular mass 49 000) in about 15% yield.

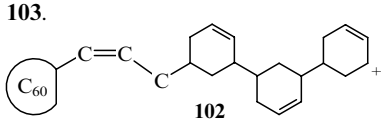


100

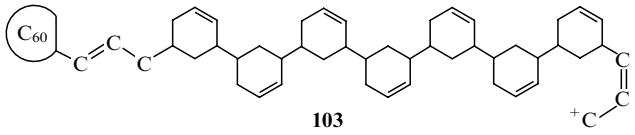
The high solubility of this polymer is due to the presence of the *N*,*N*-diethylenepropioamide fragment, which is structurally related to *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide, miscible with water.

New copolyamides containing dimethanofullerene fragments in the backbone have been synthesised[169] using [60]fullerene-bismethanocarboxylic acid (**101**) (Scheme 2). The polymer forms a brown brittle film capable of coating glass.

Cationic polymerisation involving C_{60} fullerene has been studied.[170] Multicharged cations derived from C_{60} (they are generated[171] using a special ion source) are highly reactive in the gas phase. Dications and trications initiate cyclochain polymerisation of allene or propyne under these conditions.[170] More than sixteen allene molecules add to the C_{60}^{2+} dication, odd-numbered adducts reacting approximately 10 times faster than even-numbered ones. It is assumed that multiaddition occurs during the chain growth; the alternation of the reaction rates is attributed to the difference between charge distribution and stability due to the formation of either acyclic or cyclic cation, for example, **102** or **103**.



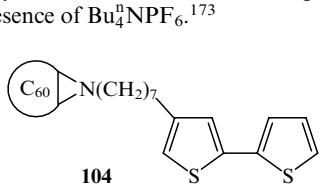
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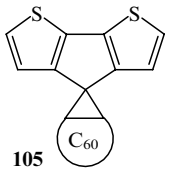
103

Studies dealing with the development of conducting and semiconducting polymeric systems involving C_{60} are in progress. One method for the synthesis of conducting polymeric composites is polymerisation on a supporting template.[172] The template is a cross-linked fullerenol–polyurethane elastomer. It is impregnated with aniline; this gives a film, which is brought in contact with an oxidising aqueous solution containing LiCl, $(NH_4)_2S_2O_8$ and HCl at −15 °C and is thus converted into a new elastomer with inserted polyaniline. This product is characterised by much higher conductance than the initial 'prepolymer' without losing the elasticity and tensile properties. The presence of the template hampers migration of the conducting species, which is a significant reason for deterioration of the physical properties of the material.

The bisthiophene derivative **104**, functionalised with fullerene, polymerises at the electrode during voltammetry in CH_2Cl_2 in the presence of $Bu_4^nNPF_6$.[173]



104

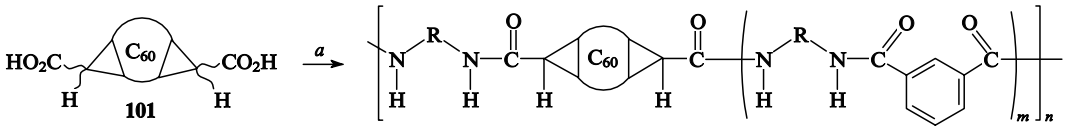


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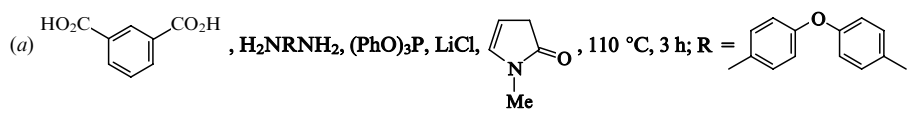
An electrically conducting polymer of the 'necklace with a pendant' type was prepared for the first time by anodic oxidation of the bisthiophene derivative containing a fullerene fragment **105**.[174]

The change in the photophysical and optical properties of conducting polymers upon the formation of composites with C_{60} fullerene is due to complex formation (resulting in the change in

Scheme 2



101



the polymer conformation [175]) and, what is more important, to the transfer of electrons from the polymer to C_{60} (see Ref. 176). The spectrum of the film prepared from a mixture of C_{60} with poly(3-hexylthiophene) exhibits a substantial shift in the UV and visible region.[175] Doping of poly(3-octadecylthiophene) with C_{60} causes quenching of the polymer photoluminescence.[176] The poly-2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylvinylene film doped with C_{60} fullerene is promising for the manufacture of holographic recording materials.[177]

VI. Fullerenes in catalysis

Fullerene C_{60} participates in catalysed processes as either a part of the catalyst and/or a substrate which modifies the action of the catalyst.

The complex η^2-$C_{60}Pd(PPh_3)_2$ has been used as the catalyst in the homogeneous (in toluene) and heterogeneous (supported on Sibunit) hydrogenation of 3,7-dimethyloct-6-en-1-yn-3-ol (dehydrolinalool).[178] The process occurs almost selectively (99.5%) as hydrogenation of the triple bond to a double bond; the catalyst activity in the heterogeneous process is maximal and is an order of magnitude higher than that of the traditional catalyst, namely, Pd supported on Sibunit.[178]

The tetralin extract of carbon was subjected to hydrocracking in petroleum ether with the addition of a dispersed C_{60}/C_{70} mixture (90 : 10) and without this mixture. Fullerenes exerted no noticeable effect on the course of hydrocracking.[179]

The complex $C_{60}[Pd(OAc)_2(PPh_3)]_3$ was reduced with hydrogen on heating to give a $Pd-C_{60}$ complex. Phenylacetylene, diphenylacetylene, cyclohexene and hex-1-ene were hydrogenated in the presence of 1 mol. % of this catalyst.[180] Alkenes were completely reduced. The yields were comparable to those attained in the hydrogenation over Pd/C but the reaction occurred faster. The mechanism of the catalytic influence of the C_{60} substrate is unknown; however, it is assumed that metal fragments form active sites on the C_{60} spheroid.[180]

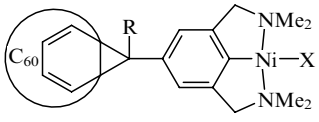
Photochemical oxidation of alkenes in the presence of silica gel modified with $C_{60}(H)CH_2SiMe_2(OPr^i)$ has been carried out.[121]

In order to prepare new film-forming materials including those promising as semiconducting films (for example, for the manufacture of diodes), polyaddition of benzene to fullerene in the presence of Kovacik catalyst ($CuCl_2 + AlCl_3$) has been carried out.[181] This gave the compound $C_{60}Ph_{19}H_{19}$, which might have resulted from the reaction of protonated C_{60} with benzene. At 400 °C, this compound eliminates hydrogen to give $C_{60}Ph_{19}$. Both compounds form films from toluene solutions and $C_{60}Ph_{19}$ exhibits clear-cut luminescence in the blue-green region.

The structure and catalytic properties of ruthenium on the C_{60} substrate (as well as on crude and extracted fullerene black and on the fullerene cathodic deposit) have been studied.[182, 183] Highly dispersed amorphous Ru was prepared from $Ru_3(CO)_2$ by the impregnation/activation method. This system serves as an active catalyst for hydrogenation of CO and 2-cyclohexanone under atmospheric pressure.

The molecular sieve MCM-41 is used to prepare catalysts with high surface areas for reactions with bulky molecules. The addition of C_{60} changes substantially the behaviour of the sieves during their dehydroxylation on heating, due to the abstraction of the hydroxy groups from the silanol fragments of the sieve to give C—H and C—OH groups followed by condensation of the C—OH groups or combination of C—OH with C—H.[184]

Precursors of fullerene-containing chelates of the type



R = H, Me; X = H, Br,

have been synthesised;[185] these compounds may find application as supported catalysts and in homogeneous catalysis.

VII. Prospects for the practical use of fullerenes

Extensive practical use of fullerenes would be largely determined by their availability. According to the data for 1995,[13] fullerenes were supplied by the Hoechst AG (Germany), SES Research (USA) and MER (USA) companies. The price of C_{60} fullerene was about \$500 per kg in 1997.[186] Back in 1995 the MER company developed a contact arc process which provided a daily output equal to 30 kg of carbon soot with a high fullerene content. Methanofullerene[60]-61-carboxylic acid is also commercially available (Fluka, Switzerland).

According to the data of MER,[186] attention is attracted first of all by the possibility of using fullerenes for the production of rechargeable galvanic cells, with electrodes made of C_{60}/C_{70} films applied onto various substrates and for the storage of hydrogen, in particular, in the fuel cells of electric cars, and the storage of adsorbed oxygen (which may be useful in medicine and in military engineering). Fullerenes have been patented as precursors of diamonds and diamond coatings, production of which from fullerenes is energetically more favourable than that from graphite. The use of fullerenes for strengthening metal surfaces upon insertion of carbide particles into a metal matrix is also promising. Films of compounds containing fullerene fragments could be used in nonlinear optics, optical computerisation and in sensor technology as solid sensors.

Molecular donor–acceptor charge transfer complexes can present considerable interest as the initial compounds for the manufacture of new materials,[187] for example, superconductors[43, 153, 188] (superconductivity transitions up to 40 K have been observed).[188].

Nitroxides with a fullerene fragment and various fullerenopyrrolidines can find use in the synthesis of organic ferromagnets.[75, 76] Films possessing valuable properties have been prepared based on fullerenopyrrolidines.[73, 74] Methano- and pyrrolidinofullerenes are efficient photosensitisers for the generation of singlet oxygen.[102] The formation of C_{60} and C_{70} fullerene adducts with porphyrins of phthalocyanines increases the photoinitiated electrical conductivity of the latter (see Ref. 53 and references therein). Nitrogen-containing fullerene derivatives immobilised on silica gel make it possible to develop new adsorbents.[70]

The potential use of fullerenes as biologically active compounds has stimulated vigorous development of the chemistry of functional derivatives of fullerene, especially after 1993, when it was shown[189] that water-soluble fullerene derivatives with methane bridges inhibit HIV enzymes, namely, protease and reverse transcriptase; data on the biological properties of fullerene derivatives have been published.[190, 191]

For biological assays, it is necessary to prepare functional derivatives soluble in water or in polar media with a stabilising fragment linked to the fullerene by a covalent bond. Nakamura *et al.*[191] have classified the biologically active fullerene derivatives into two types: the detergent type (in which the side chain is modified by, for example, attachment of carboxylic acid residues *via* organic binding groups) and the spherical type, in which there are polar groups distributed over the fullerene sphere (this class includes fullerenols and amino adducts).

VIII. Conclusion

In recent years, exohedral addition and, especially, cycloaddition has remained the main line of functionalisation of fullerenes. These reactions have been employed to prepare a large number of new oxygen- and nitrogen-containing derivatives such as quinones, pyridones, nitrile oxides and pyrrolidine derivatives. The photophysical and photochemical properties of these compounds (fluorescence, phosphorescence) and the redox potentials of these derivatives depend on the degree of functionalisation and posi-

tions of functional groups in fullerene fragments. Fullerene derivatives containing heteroatoms can be used to model the photosensitisation and photosynthesis processes, including those involving singlet oxygen, which is important for the research into biological systems. An important aspect in the studies is development of the methods for selective multifunctionalisation, which would direct the addend to a particular site of the carbon cage.

Among the fundamental studies devoted to the properties of fullerenes, the syntheses of a catenane with a fullerene fragment, the preparation of hydrocarbon salts and the generation of the carbocation consisting of only carbon atoms deserve attention. While Kroto, one of the fullerene discoverers, was amazed by the ability of pure carbon to be dissolved in organic solvents, the preparation of an aqueous colloidal solution of C_{60} seems even more remarkable.

The potential practical application of fullerenes and their functional derivatives is being studied along several paths. In the case of C_{60} fullerene, this is mainly production of films deposited on various substrates including diamond-like ones, sensitisers and adsorbents for gases. The synthesis of new complexes and incarceranes (fullerenes containing an element incorporated in the cage) is aimed at the preparation of new superconductors, dielectrics and ferromagnets. Numerous publications have been devoted to the synthesis of C_{60} adducts in order to use them as the starting compounds in the synthesis of biologically active products.

The preparation of fullerene-based catalysts and catalytic systems and the synthesis of fullerene-containing polymers have been less developed. The progress along these lines might be expected in the future.

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