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Halogenated fullerenes as precursors for the synthesis of functional derivatives of C_{60} and C_{70}

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The review is devoted to the use of halogenated fullerenes as precursors for the synthesis of functional derivatives of fullerenes C_{60} and C_{70}. Data on chemical transformations of halogenated fullerenes $C_{60}Cl_6$, $C_{70}Cl_8$, $C_{70}Cl_{10}$, $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ are described systematically, with the focus being placed on the preparation of compounds with valuable properties. In particular, new approaches to the synthesis of water-soluble fullerene derivatives are considered and prospects for their practical use in biomedicine are evaluated.
The bibliography includes 108 references.

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I. Introduction

Many derivatives of fullerenes exhibit valuable properties and find application in practice. Fullerenes and their derivatives are used as additives in motor oils † and ingredients of anti-ageing cosmeceuticals ‡ (the data can be moved by the owners of the websites). Water-soluble derivatives of fullerenes, which can be employed as potent antiviral (including anti-HIV),[1–3] antibacterial[4] and neuroprotective agents,[5] were described. Some fullerene derivatives exhibit high antitumour activity in photodynamic cancer therapy[6,7] and chemical cancer treatment.[8] Besides, composites of C_{60} and C_{70} derivatives with conjugated polymers serve as the basis for the development of plastic solar cells.[9]

The electronic and physicochemical characteristics of fullerenes, such as electron affinity, film-forming properties, solubility, tendency to aggregate in polar and nonpolar media and so on, can be modified by varying the nature and number of organic addends attached to the fullerene cage.[10] The nucleophilic addition and cycloaddition reactions can be used for the selective synthesis of fullerene derivatives, in which one multiple bond in the fullerene cage is broken. The utilization of these reactions for the synthesis of polyaddition products usually results in the formation of complex mixtures of regioisomers.[11,12] On the contrary, the halogenation of fullerenes, which proceeds *via* a radical mechanism under thermodynamic control, affords a single addition product of many (>6) halogen atoms to the fullerene cage. Further chemical modifications of halogenated fullerenes can be applied for the selective synthesis of compounds containing several organic addends on the fullerene cage. Therefore, the use of halogenated fullerenes as precursors offers great opportunities for fullerene cage functionalization.

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† http://www.lelong.com.my/bardahl-c60-super-lube-semi-synthetic-engine-oil-sae-10w40-sn-cf-12volts-I1492057-2007-01-Sale-I.htm (08.06.2017)
‡ http://jp1023114521.trustpass.alibaba.com/(08.06.2017)

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In recent years, considerable progress has been achieved in the synthesis of polyfunctional derivatives of fullerenes using halogenated fullerenes as precursors. The goal of this review is to bring together the data on chemical transformations of halogenated fullerenes published over the past two decades.

Extensive studies of halogenation reactions of fullerenes and properties of the resulting halogenated derivatives became possible after the development of procedures for the synthesis of fullerenes on a gram scale. The fluorination, chlorination and bromination of fullerenes under different conditions have been investigated in sufficient detail, and a large number of fluorinated, chlorinated and brominated fullerenes were synthesized and characterized.[13] Attempts to synthesize iodinated fullerenes failed. The reactions of iodine with C_{60} under different conditions produce clathrates rather than compounds containing a C–I covalent bond. Apparently, the eclipsing strain (torsional strain) between bulky iodine atoms attached to the fullerene cage is too high, thus making the reaction thermodynamically unfavourable.[14]

Stability of halofullerenes, the number of attached addends and their positions on the fullerene cage depend on the size of halogen atoms and the C–Hal bond energy. Thus, the maximum degree of halogenation of the carbon cage increases and stability of the resulting products is enhanced in the series of Br, Cl and F with increasing C–Hal bond energy.[13] Several reviews devoted to halogenation of fullerenes were published in the past decade (see, for example, reviews [13, 15–17]). Therefore, in this review, methods for the preparation of halogenated fullerenes will be considered only briefly.

Here, we merely note that efficient methods are currently available for the gram-scale synthesis of various halogenated fullerenes C_{60} and C_{70}: $C_{60}F_{18}$,[18] $C_{60}F_{36}$,[19] $C_{60}F_{48}$,[20] $C_{60}Cl_6$,[21] $C_{70}Cl_{10}$,[22] $C_{70}Cl_8$,[23] $C_{60}Br_6$ and $C_{60}Br_8$.[24] Most of the above-mentioned halogenated fullerenes, except for $C_{60}F_{36}$ and $C_{60}F_{48}$, are individual isomerically pure compounds. Unfortunately, brominated fullerenes have very low solubility in organic solvents, which interferes with their use as precursors in the synthesis of fullerene derivatives.[25] On the contrary, the halogenated derivatives $C_{60}F_{18}$ (Fig. 1), $C_{60}Cl_6$ and $C_{70}Cl_{10}$ (Fig. 2) are soluble in organic solvents. Owing to good solubility and availability, these derivatives can be considered as promising precursors for the synthesis of various functional derivatives of fullerenes.

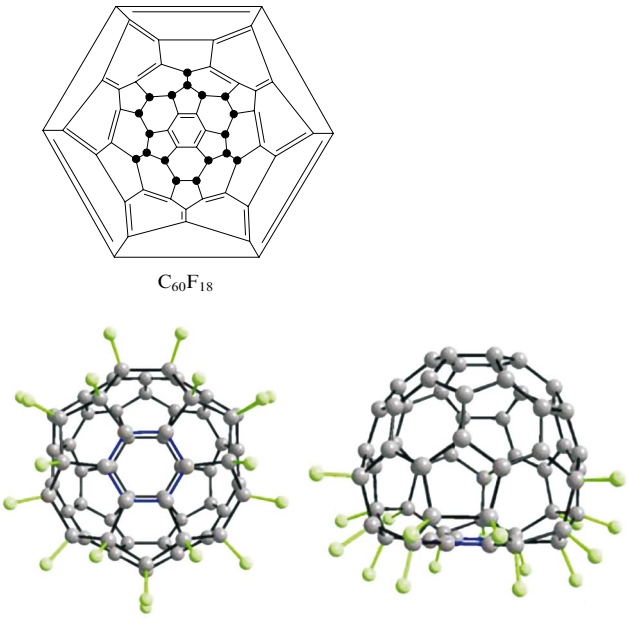


Figure 1. Schlegel diagram and the molecular structure of $C_{60}F_{18}$ in two projections (X-ray diffraction data).[26]

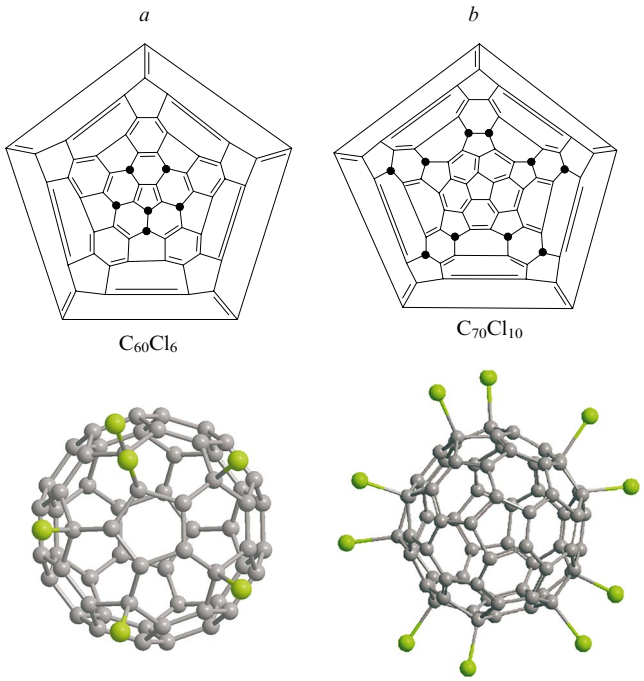


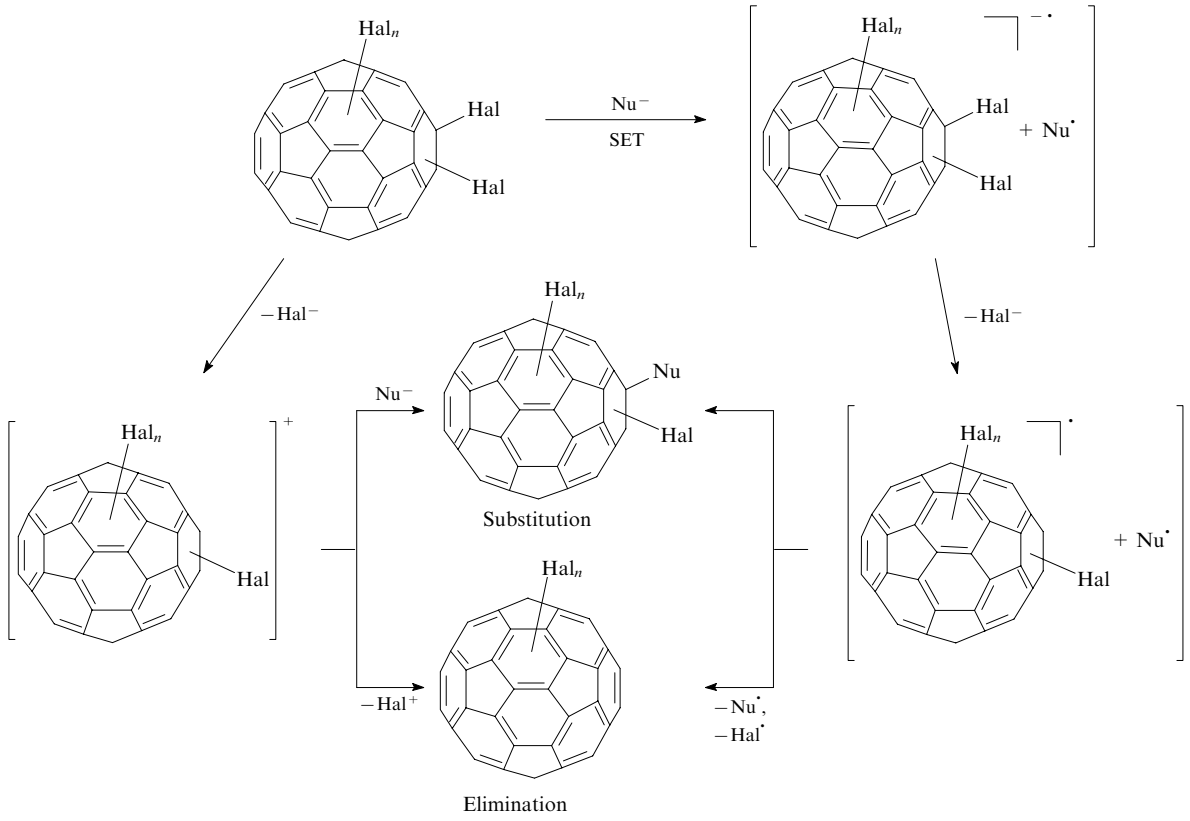
Figure 2. Schlegel diagrams and three-dimensional models of the $C_{60}Cl_6$ (*a*)[27] and $C_{70}Cl_{10}$ (*b*)[13] molecules (X-ray diffraction data).

II. Halogenated fullerenes as precursors for the synthesis of derivatives of C_{60} and C_{70}

The replacement of halogen atoms by different functional groups is one of the most well-known and commonly used reactions in organic chemistry. However, these transformations of halofullerenes are difficult to accomplish. The reason is that the substitution *via* the traditional S_N2 mechanism requires the attack of the nucleophile from the inside of the carbon cage of halofullerenes, which is impossible. Particular halofullerenes with a specific molecular structure can react by concerted bimolecular S_N2' and S_N2'' substitution mechanisms.

The replacement of halogen atoms in halofullerenes can occur either *via* the monomolecular S_N1 nucleophilic substitution mechanism (usually in the presence of Lewis acids) or through the radical single-electron transfer (SET) mechanism. Extreme instability of fullerene cations interferes with the monomolecular S_N1 substitution. Therefore, the cation produced by heterolytic cleavage of the C–Hal bond should immediately react with a nucleophile to form a substitution product. If the cation has no time to encounter a nucleophilic species, it eliminates Hal^+ (in the case of

Scheme 1



Hal = Cl, Br) giving the elimination product (Scheme 1).§ The elimination is the predominant reaction pathway if the concentration of the nucleophile in the reaction system is low.

The elimination product can be generated in the last step of the radical SET mechanism if the fullerene radical has no time to react with the Nu$^{\cdot}$ radical or if the latter is deactivated *via* the reaction with the solvent or other reactive species that are present in the reaction medium.

The ratio of substitution to elimination products generated in reactions with nucleophiles also depends on the composition and molecular structure of the starting halogenated derivative. For example, the reaction of $C_{60}Cl_6$ with arenes (in the presence of Lewis acid) affords compounds of the composition $C_{60}Ar_5Cl$ as the major products and minor amounts of $C_{60}Ar_4$ and $C_{60}Ar_2$.[28] However, the reaction of chlorofullerene $C_{60}Cl_{24}$ with toluene gives an inseparable mixture of products $C_{60}Ar_n$ ($n = 8-18$). The compound of the composition $C_{60}Ar_{24}$ was not detected apparently because of steric hindrance (it is sterically very difficult to bind 24 tolyl groups to one C_{60} cage).¶

It should be noted that of the total diversity of known halogenated fullerenes, only $C_{60}Cl_6$, $C_{60}F_{18}$, $C_{70}Cl_8$ and $C_{70}Cl_{10}$ exhibit high selectivity in reactions with nucleophiles. All other halofullerenes generally form inseparable mixtures of products. Chemical transformations of halogenated C_{60} and C_{70}, which are the most important derivatives from the synthetic point of view, are considered below.

II.1. Chemical transformations of chlorofullerene $C_{60}Cl_6$

II.1.a. Reactions with C-nucleophiles

Chlorofullerene $C_{60}Cl_6$ reacts with aromatic hydrocarbons *via* Friedel–Crafts electrophilic aromatic substitution. The replacement of chlorine atoms by aryl or hetaryl moieties occurs directly in an aromatic hydrocarbon medium or in an appropriate inert solvent (dichloromethane, nitrobenzene, Scheme 2).[3,29] This reaction affords mainly products *para*-substituted with respect to the substituent in the aromatic nucleus. It is interesting that the treatment of compounds $C_{60}Ar_5Cl$ with a PPh_3-H_2O mixture results in the replacement of the Cl atom by H to form $C_{60}Ar_5H$.[30] The reduction of chlorinated fullerene derivatives $C_{60}Ar_5Cl$ with triphenylphosphine proceeds through the intermediate formation of the aromatic cyclopentadienyl anion $[C_{60}Ar_5]^-$, the negative charge of which is stabilized by the inductive ($-I$) effect of five Ar groups. The reaction of the $[C_{60}Ar_5]^-$ anion with water that is present in the solvent results in its protonation to give $C_{60}Ar_5H$.[30]

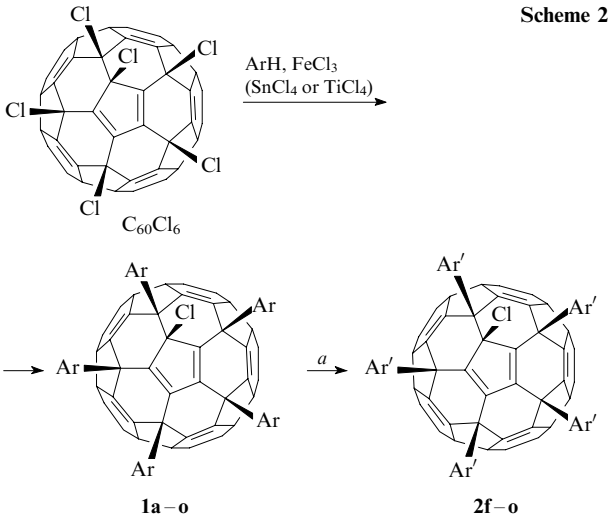
Compounds **1f–o** synthesized by the Friedel–Crafts reaction are used in the synthesis of water-soluble fullerene derivatives (see Scheme 2).[3,31] The acid hydrolysis is accompanied by the cleavage of ester groups in compounds **1f–o** to form the corresponding carboxylic acids **2f–o** in quantitative yield. The salts of these acids with alkali metal cations (sodium, potassium, caesium) are highly soluble in water.

Since the reaction of $C_{60}Cl_6$ with aromatic hydrocarbons does not cause a change in the addition pattern of addends on the fullerene cage, it was suggested that the replacement

§ Hereinafter, the structures of fullerenes are represented schematically, including the number of double bonds in the rings.

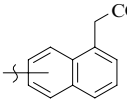
¶ P.A.Troshin, R.Taylor. Unpublished data.

Scheme 2



1a–o **2f–o**

(*a*) 1) HCl–HOAc, PhMe, Δ; 2) K_2CO_3;
Ar = 4-RC_6H_4: R = H (**a**, 58% yield), F (**b**, 63%), OMe (**c**, 54%), Me (**d**, 61%), CH_2CO_2Me (**f**, 60%), $CH_2CH(CO_2Me)_2$ (**g**, 50%), $(CH_2)_2CO_2Me$ (**h**, 49%), $(CH_2)_3CO_2Me$ (**i**, 44%), $(CH_2)_2CH(CO_2Me)_2$ (**j**, 36%), OCH_2CO_2Me (**k**, 30%), $O(CH_2)_2CO_2Me$ (**l**, 33%), $O(CH_2)_3CO_2Me$ (**m**, 38%), $C_6H_4CH_2CO_2Me$-4 (**n**, 48%); Ar = 2-Th (**e**, 49%),

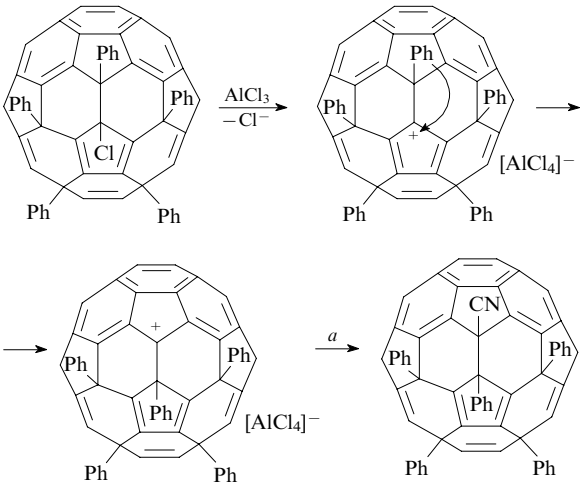


(**o**, mixture of isomers, 46%);

Ar′ is an acidic moiety of the corresponding ester

of chlorine atoms proceeds *via* the S_N1 mechanism and is accompanied by the formation of a carbocation as an intermediate. Later, ^1H and ^{13}C NMR spectroscopic studies demonstrated that $C_{60}Ph_5Cl$ reacts with $AlCl_3$ to form the C_s-symmetric $[C_{60}Ph_5]^+$ cation in solution (Scheme 3).[32] Upon the elimination of the chloride ion from the fullerene cage, the compound $C_{60}Ph_5Cl$ is transformed into the unstable C_{5v}-symmetric carbocation containing an antiaromatic moiety. The cation is stabilized *via* 1,2-migration of one phenyl group, resulting in the formation of C_s-$[C_{60}Ph_5]^+$. Apparently, the phenyl group migration occurs in parallel with the release of the chloride ion. The localization of the positive charge on the C_s-$[C_{60}Ph_5]^+$ cation was confirmed by X-ray diffraction study of the compound C_s-$[C_{60}Ph_5]CN$ prepared by the reaction of C_s-$[C_{60}Ph_5]^+$ with Me_3SiCN (see Scheme 3).[33]

Scheme 3

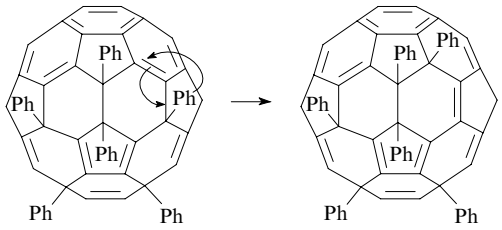


(*a*) Me_3SiCN; $-Me_3SiCl$, $-AlCl_3$

Electrochemical processes that occur in a solution of $C_{60}Ph_5Cl$ in dichloromethane were studied by cyclic voltammetry. It was shown that the electrochemical reduction of this compound affords $[C_{60}Ph_5]^-$ and Cl^- anions. Then both anions undergo one-electron oxidation followed by recombination of radicals to the starting molecule $C_{60}Ph_5Cl$.[34]

The reaction of $C_{60}Cl_6$ with benzene in the presence of $FeCl_3$ gives the compound C_s-$[C_{60}Ph_6]$ as a by-product, which can be generated by the reaction of the C_s-$[C_{60}Ph_5]^+$ cation with benzene. The unsymmetrical isomer C_1-$[C_{60}Ph_6]$ was identified as one of reaction products. According to the NMR spectroscopic data, this isomer has the structure shown in Scheme 4.[33] In addition, the reaction of $C_{60}Cl_6$ with benzene in the presence of $FeCl_3$ yields $C_{60}Ph_2$ and $C_{60}Ph_4$ as by-products (Fig. 3).[35]

Scheme 4



It should be noted that the reaction of $C_{60}Ph_5Cl$ with cyanogen bromide in the presence of $FeCl_3$ proceeds through nucleophilic substitution of the chlorine atom followed by intramolecular electrophilic substitution of the *ortho*-proton of the adjacent phenyl moiety to give compound **3** (Scheme 5). The reaction of compound **3** with the hydroxide ion produces fullerene derivative **4**.[36]

Recently, it was shown that the reaction of a mixture of oligomers $(C_{60}Cl_n)_m$ (n = 4, 5; m = 2, 3) of unknown structure[37] with benzene under Friedel–Crafts reaction conditions at elevated pressure affords a mixture of compounds $C_{60}Ph_x$ (x = 6–14).[38] Individual isomers $C_{60}Ph_9OH$ and $C_{60}Ph_{12}O_2$ were isolated from this mixture, and their structures were established by X-ray diffraction (Fig. 4).

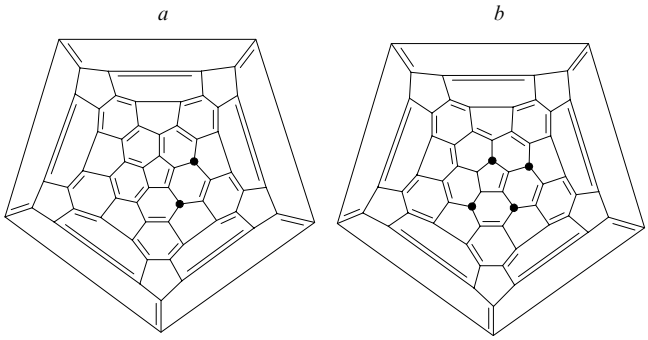
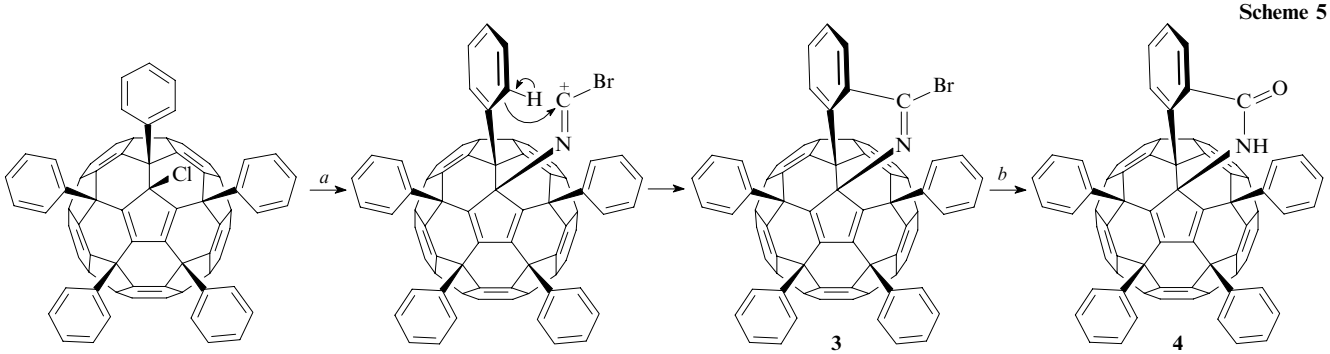


Figure 3. Schlegel diagrams of the $C_{60}Ph_2$ (*a*) and $C_{60}Ph_4$ molecules (*b*).[35]

Scheme 5



(*a*) $FeCl_3$, BrCN; (*b*) HO^-

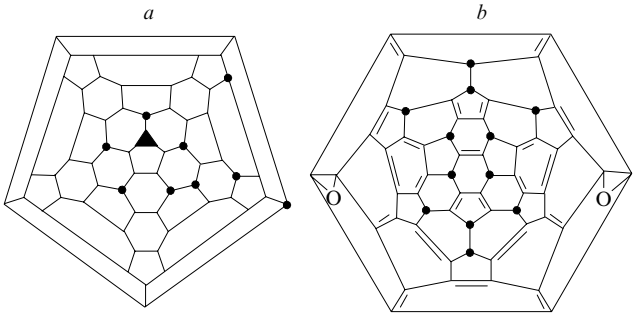
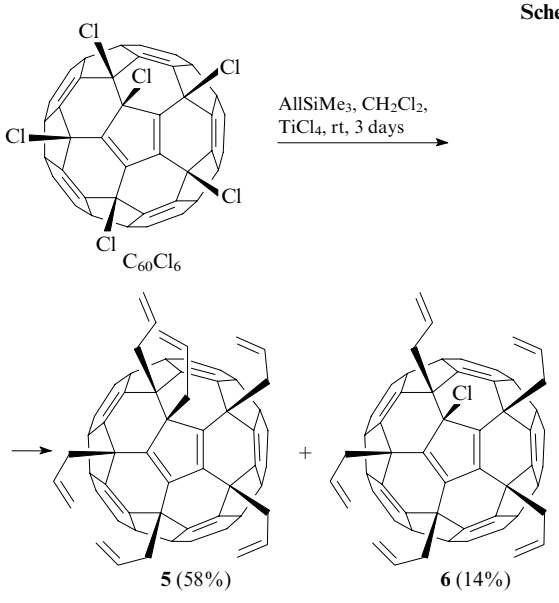


Figure 4. Schlegel diagrams of the $C_{60}Ph_9OH$ (*a*) and $C_{60}Ph_{12}O_2$ compounds (*b*).[38]

It is interesting that not five but all six chlorine atoms are replaced by allyl groups in the reaction of $C_{60}Cl_6$ with allyltrimethylsilane in the presence of $TiCl_4$, resulting in the formation of compound **5** in 58% yield. Compound **6** containing five allyl groups is also produced in this reaction but in a yield of only 14%. Apparently, the predominant formation of compound **5** in the reaction of chlorofullerene with allyltrimethylsilane is attributed to the smaller size of the allyl moiety compared to the aryl group and, as a consequence, to lower steric hindrance (Scheme 6).[39]

Scheme 6



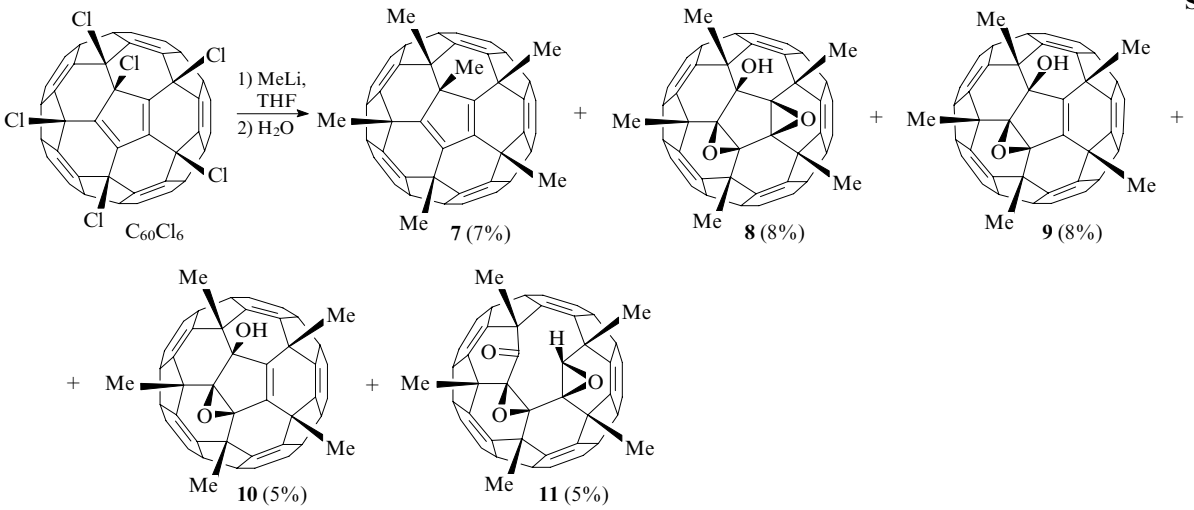
The reaction of chlorofullerene $C_{60}Cl_6$ with organometallic compounds, in particular with methyllithium, is characterized by very low selectivity. Derivatives **7**–**11** were isolated from a mixture of numerous products of this reaction followed by hydrolysis.[40,41] Some of the compounds synthesized have an unusual structure. For example, bisepoxide ketone **11** is an open-cage fullerene derivative (Scheme 7).[42]

The low-temperature reaction of chlorofullerene $C_{60}Cl_6$ with freshly prepared C_2F_5Li, like the above-described reaction with methyllithium, affords a complex mixture of products.[43] Compounds **12**–**16** were isolated from this mixture with a purity >98% (Scheme 8). The molecular structures of compounds **12** and **13** were ultimately established by X-ray diffraction. The molecular structure of compound **14** was proposed based on results of NMR and optical absorption spectroscopy. For compounds **15** and **16**, only the composition was identified.[43]

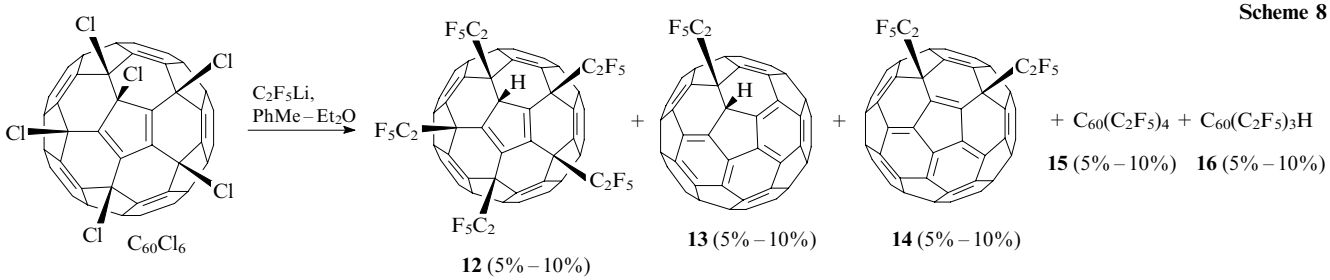
Apparently, the transmetallation side reaction is one of the main factors responsible for low selectivity of the reactions of chlorofullerene $C_{60}Cl_6$ with organolithium compounds. Due to the high electron deficiency of the fullerene cage, the $[C_{60}]^-$ anion is thermodynamically more stable than the Me^- and $[C_2F_5]^-$ anions. This fact is indirectly confirmed by the ease of formation of different lithium fullerides, including $Li_{12}C_{60}$.[44] Evidently, the electron affinity of chlorofullerene $C_{60}Cl_6$ containing six electron-withdrawing chlorine atoms on the fullerene cage should be even higher than that of unmodified C_{60}. Therefore, it can be assumed that the reactions of $C_{60}Cl_6$ with RLi give transmetallation products $Li_nC_{60}Cl_m$ (in the general case, $n = 1-6$, $m = 6-n$) and RCl. The compounds $Li_nC_{60}Cl_m$ are thermodynamically unstable with respect to elimination of Cl^-, resulting in the formation of compounds containing a smaller number of addends on the fullerene cage. Besides, the intermolecular process can give rise to dimeric and polymeric products of condensation, which actually follows the mechanism of the Wurtz reaction well-known in organic chemistry. The reaction of $Li_nC_{60}Cl_m$ with atmospheric oxygen and moisture can also be expected to form inseparable mixtures of fullerene oxides and hydroxides.

The reaction of $C_{60}Cl_6$ with organic cyanides $R_4N^+CN^-$ results in the replacement of five chlorine atoms in the chlorofullerene by cyano groups to form cyanofullerene **17** (Scheme 9).[45] Compound **17** is a salt

Scheme 7

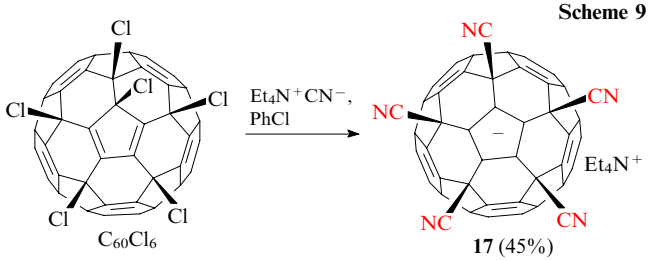


Scheme 8



containing the C_{5v}-symmetric $[C_{60}(CN)_5]^-$ anion. Some ionic salts with C_{60}^{n-} anions ($n = 1-5$) exhibit interesting electrical (conductivity and superconductivity) and magnetic (ferromagnetism) properties.[46–48] However, these compounds are unstable to moisture and air and, consequently, they are difficult to use in practice. Researchers have long attempted to address this challenge by attaching groups that are capable of stabilizing the negative charge to the fullerene cage. Recently, compounds containing the relatively stable $C_{60}Ph_5^-$ and $C_{60}Flu_5^-$ anions (Flu is 9-fluorenyl) were synthesized; however, despite the negative charge delocalization, these compounds are not quite air-stable.[49] As opposed to the $C_{60}Ar_5^-$ anions, the $[C_{60}(CN)_5]^-$ anion contains five electron-withdrawing cyanide groups, which stabilize the negative charge delocalized over the cyclopentadienyl ring. Due to this stabilization, $[C_{60}(CN)_5]^-$ is stable in the environment, as well as resistant to organic and inorganic acids and electrophiles.[45] Further investigation of ionic salts containing such anions may provide an approach to the preparation of materials possessing a unique combination of optical and electrical properties.

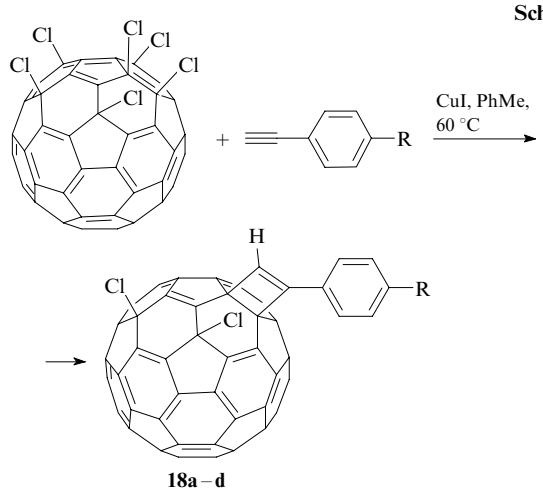
Scheme 9



Relatively recently, $C_{60}Cl_6$ was shown to react with arylacetylenes in the presence of copper(I) iodide to form fullerene derivatives **18a–d** containing the cyclobutene moiety (Scheme 10).[50] This reaction is one of the four currently available methods for the synthesis of derivatives of fullerene C_{60} containing the cyclobutene moiety.[50] Unlike other methods, this reaction can be used to prepare compounds accessible for further chemical functionalization due to the presence of two labile chlorine atoms.

The reaction of $C_{60}Cl_6$ with 4-$MeOC_6H_4C{\equiv}CH$ in the presence of CuI affords compound **19** as a by-product in 8% yield. The yield of derivative **19** can be increased by

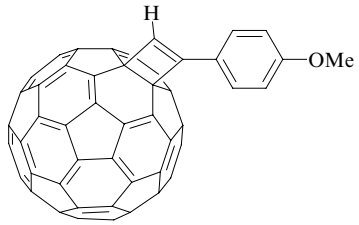
Scheme 10



R = OMe (**a**, 53% yield), n-C_5H_{11} (**b**, 48%), H (**c**, 44%), Br (**d**, 36%)

raising the temperature or increasing the reaction time. Tandem mass spectrometry showed that compound **19** is produced *via* dehalogenation of product **18a**.

Structure 19



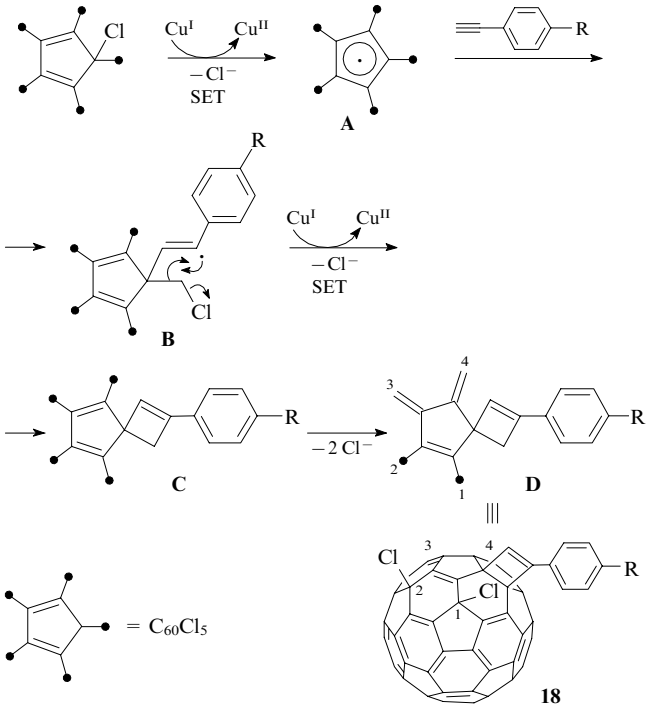
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Wang *et al.*[50] proposed a plausible mechanism of the reaction of $C_{60}Cl_6$ with arylacetylenes in the presence of CuI (Scheme 11). It is assumed that the reaction involves the single-electron transfer (SET) from Cu^I to $C_{60}Cl_6$ as the first step followed by the release of the chloride ion to form the $[Cl_5C_{60}]^{\bullet}$ radical. The possibility of the existence of this radical has been demonstrated in the earlier study of the *in situ* photolysis of $C_{60}Cl_6$ by EPR spectroscopy.[51] The reaction of arylacetylene with the radical **A** produces the radical **B**. In the presence of the second equivalent of Cu^I, the radical **B** releases the chlorine atom adjacent to the radical centre to form the intermediate **C**. After the elimination of two chloride ions, the compound **C** is transformed into the final product **D**. This mechanism was proposed based on the analysis of the reaction with different substrates and the results of earlier studies of metal-catalyzed reactions of fullerenes.[50]

II.1.b. Reactions with N-nucleophiles

The reaction of chlorofullerene $C_{60}Cl_6$ with N-substituted piperazines in the presence of potassium carbonate on heating to 80 °C is accompanied by the partial elimination of addends from the fullerene cage giving rise to a mixture

Scheme 11

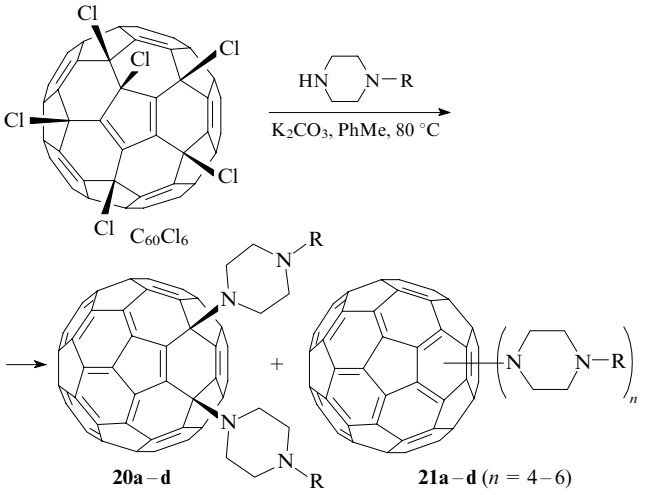


= $C_{60}Cl_5$

18

of di-, tetra- and hexaaminofullerenes. Pure 1,4-diaminofullerenes **20a–c** were isolated from these mixtures of reaction products by column chromatography (Scheme 12).[52]

Scheme 12



20a–d **21a–d** (n = 4–6)

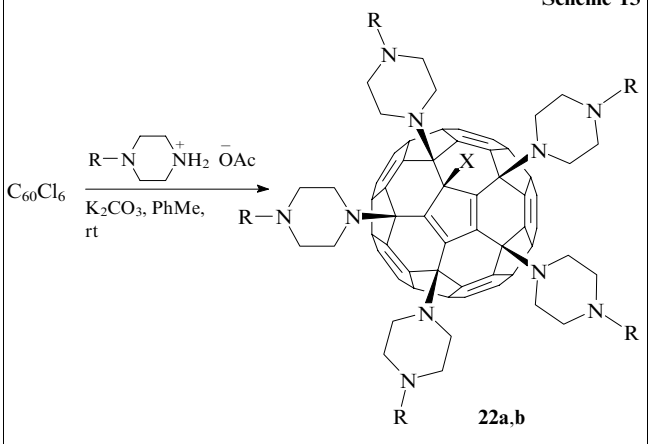
Compounds **20**, **21**	R	Yield of **20** (%)
a	2-Py	20
b	Boc	5
c	2-Pyrimidyl	10
d	Me	–

Boc = $Bu^tOC(O)$, Py is pyridyl

The reaction of chlorofullerene $C_{60}Cl_6$ with acetates of N-substituted piperazinium ions resulted in the replacement of five chlorine atoms by amino groups to form products **22a**,**b** in high yields (Scheme 13).[4] In this case, lower yields of elimination products are attributed to lower reactivity of N-substituted piperazinium salts compared to the starting amines, as well as to the fact that the reaction was performed at room temperature.

Water-soluble derivative **23** was synthesized in yield >95% by the reaction of chlorofullerene $C_{60}Cl_6$ with *N*-methylpiperazine at room temperature (Scheme 14).[4]

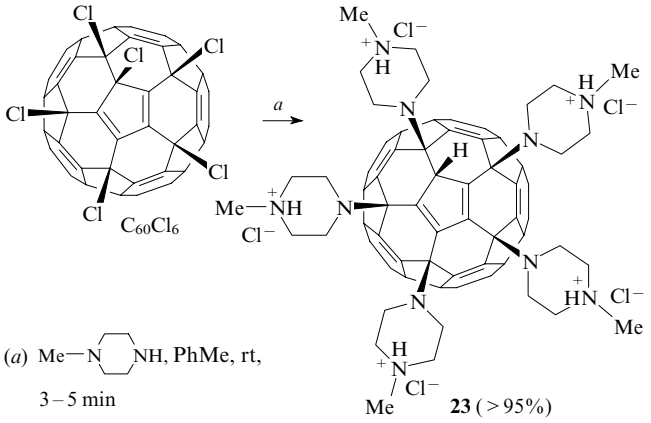
Scheme 13



22a,**b**

R = 2-Py, X = Cl (**a**, 70% yield); R = Boc, X = H (**b**, 65%)

Scheme 14



The reaction of chlorofullerene $C_{60}Cl_6$ with amino acid esters (in the salt form — hydrochlorides or hydroacetates) gave products, in which five chlorine atoms were replaced by amino groups (Scheme 15).[4] Compounds **24a–i** are valuable precursors for the synthesis of water-soluble amino acid derivatives of fullerene.

Recently, it was shown that in the presence of bases, chlorofullerene $C_{60}Cl_6$ reacts with thioamides to give fullerene derivatives **25a–f** containing the thiazole moiety (Scheme 16).[53]

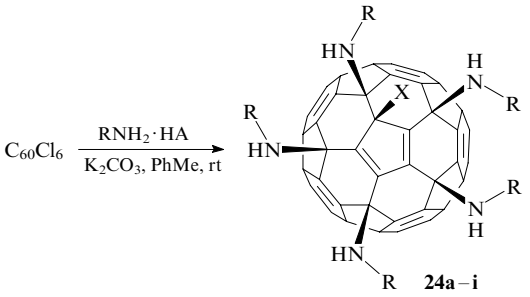
Scheme 17 shows the possible mechanism of the reaction of $C_{60}Cl_6$ with thioamides proposed by Yan *et al.*[53] based on the analysis of their own experimental results and literature data.

It was also reported that the reaction of $C_{60}Cl_6$ with diisopropylethylamine in toluene resulted in the complete dehalogenation giving unfunctionalized fullerene C_{60} (Scheme 18).[54]

II.1.c. Reactions with O-nucleophiles

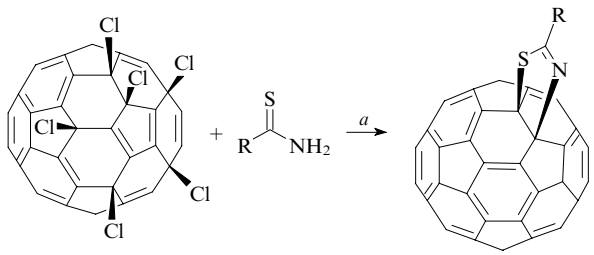
The reaction of chlorofullerene $C_{60}Cl_6$ with phenols in the presence of an aqueous KOH solution is accompanied by the partial elimination of addends from the fullerene cage to form compounds **26a–c** containing the benzofuran moiety (Scheme 19).[55]

Scheme 15



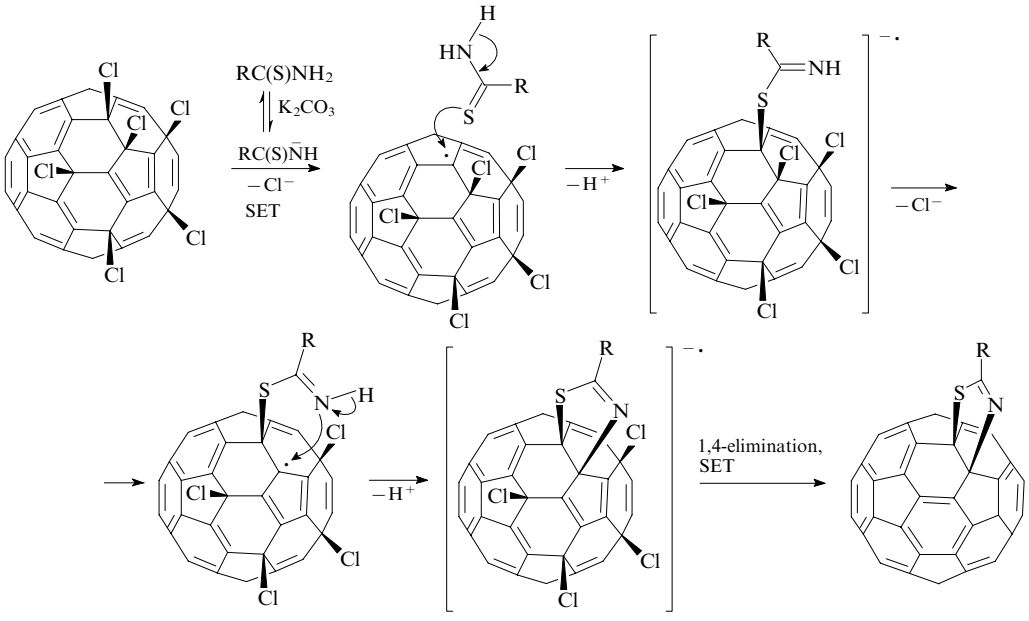
Compound **24**	R	HA	X	Yield (%)
a	$CH_2CO_2Bu^t$	HCl	Cl	65
b	$CH(Me)CO_2Bu^t$ (D)	HCl	Cl	50
c	$CH(Me)CO_2Bu^t$ (L)	HCl	Cl	47
d	$CH(Me)CO_2Bu^t$ (L)	HOAc	Cl	55
e	$CH(CH_2Ph)CO_2Bu^t$ (L)	HCl	Cl	39
f	$CH(CH_2OBu^t)CO_2Bu^t$ (L)	HCl	Cl	55
g	$(CH_2)_{10}CO_2Bu^t$	HOAc	H	60
h	$(CH_2)_2NHCO_2Bu^t$	HOAc	Cl	65
i	$(CH_2)_6NHCO_2Bu^t$	HOAc	Cl	65

Scheme 16

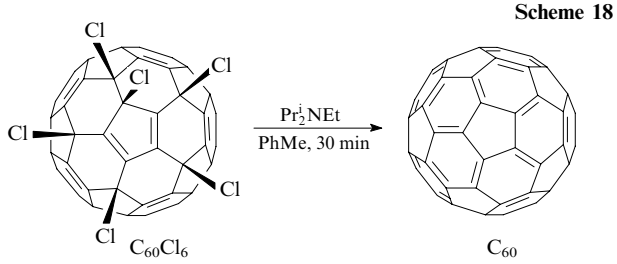


(*a*) K_2CO_3, $Bu^n_4NHSO_4$, *o*-DCB–PhMe, 100 °C;
R = 4-$Bu^tC_6H_4$ (**a**, 32% yield), 4-$Bu^nO_2CC_6H_4$ (**b**, 25%), 4-(n-C_6H_{13})OC_6H_4 (**c**, 35%), $CH(Ph)(CH_2)_3CO_2Et$ (**d**, 42%), *N*-n-pentylindol-3-yl (**e**, 28%), 5-n-pentylthiophen-3-yl (**f**, 23%);
o-DCB is *o*-dichlorobenzene

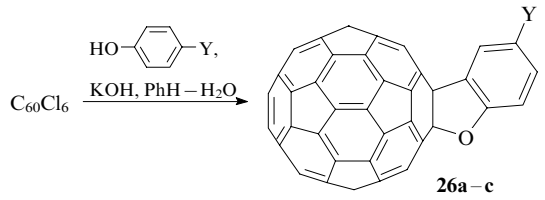
Scheme 17



Scheme 18



Scheme 19

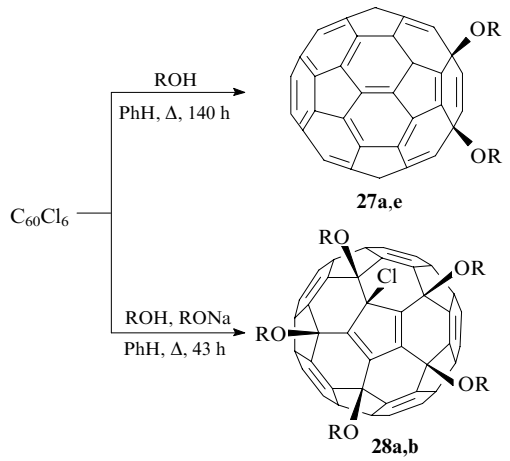


26a–c

Y = H (**a**, 23% yield), F (**b**, 6%), OMe (**c**, 3%)

1,4-Dialkoxy derivatives of fullerene **27a**,**e** were prepared by the reaction of chlorofullerene $C_{60}Cl_6$ with aliphatic alcohols (Scheme 20).[56] The reaction of chlorofullerene with alcohols in the presence of appropriate alkoxides resulted in the replacement of five chlorine atoms by alkoxy groups to give products **28a**,**b** (see Scheme 20). 1,4-Dialkoxy derivatives of fullerene are also generated under these conditions, but in insignificant yields.[56]

Scheme 20



27a,**e**

28a,**b**

27: R = Me (**a**, 11% yield), Pr^i (**e**, 30%);
28: R = Me (**a**, 15% yield), Et (**b**, 19%)

Recently, it was found that $C_{60}Cl_6$ is involved in the reaction with alcohols initiated by the addition of tetra-n-butylammonium bromide.[57] This reaction performed at room temperature affords compounds **29a**,**d** with the general formula $C_{60}(OR)_5H$ (Scheme 21, path *a*). At elevated temperature (55 °C), the reaction gives compounds $C_{60}(OR)_5Br$ (**30a**,**b**,**d**,**g**,**i**,**j**, see Scheme 21, path *b*) as the major products. In both reactions, compounds $C_{60}(OR)_2$ **27e**,**f**,**h–j** are formed as by-products. The yield of the by-products depends on the reactant structure. Thus, the use of secondary and some primary alcohols containing bulky substituents as precursors results in the formation of $C_{60}(OR)_2$ as the major reaction product. On the contrary, straight-chain primary aliphatic alcohols produce predominantly derivatives $C_{60}(OR)_5X$ (X = Br, H).

It was shown that the selectivity of the reaction of $C_{60}Cl_6$ with alcohols is substantially enhanced in the presence of small amounts of DMSO in the reaction mixture.[57] The DMSO-promoted reactions selectively produce $C_{60}(OR)_5Br$ (**30a**,**b**,**d**,**g**,**i**,**j**, see Scheme 21, path *b*) even at room temperature. In this reactions, the elimination products $C_{60}(OR)_2$ are formed only in trace amounts (< 5%). For instance, the reaction of $C_{60}Cl_6$ with *tert*-butyl 3-hydroxypropionate in the presence of DMSO gives compound **30j** in 53% yield. The same reaction in the absence of DMSO affords compound **27j** containing two organic addends as the major product, while compound **30j** is produced in trace amounts.

The reaction of chlorofullerene $C_{60}Cl_6$ with alcohols and tetra-n-butylammonium bromide in the presence of an insignificant amount of water in the solvent gives $C_{60}(OR)_5Br$ along with epoxides $C_{60}(OR)_4O$ **31b**,**c**,**i** (see Scheme 21, path *c*).[57] Apparently, this reaction proceeds through the intermediate formation of fullerenol $C_{60}(OR)_4(OH)Br$, which is transformed into epoxide $C_{60}(OR)_4O$ *via* the elimination of an HBr molecule.

It was also found that chlorofullerene $C_{60}Cl_6$ readily reacts with alcohols in the presence of triethylamine to give compounds $C_{60}(OR)_5Cl$ **28a–e**,**g–i** in 40%–50% yield (see Scheme 21, path *d*).[57]

Lou and Gan[58] demonstrated that chlorofullerene $C_{60}Cl_6$ reacts with mixtures of water and alcohols to form alkoxy derivatives $C_{60}(OR)_4Cl(OH)$ and $C_{60}(OR)_5Cl$. The reactions of chlorofullerene with bulky alcohols gave the compounds $C_{60}(OR)_4Cl(OH)$ as a single reaction product (**32l**,**m**, Scheme 22). The treatment of the derivatives $C_{60}(OR)_4Cl(OH)$ with copper iodide affords epoxide $C_{60}(OR)_4O$ (**31a**,**k**, Scheme 23). It should be noted that these epoxides can be used as precursors for the synthesis of open-cage derivatives of C_{60} **34a**,**k** (see Scheme 23).[58]

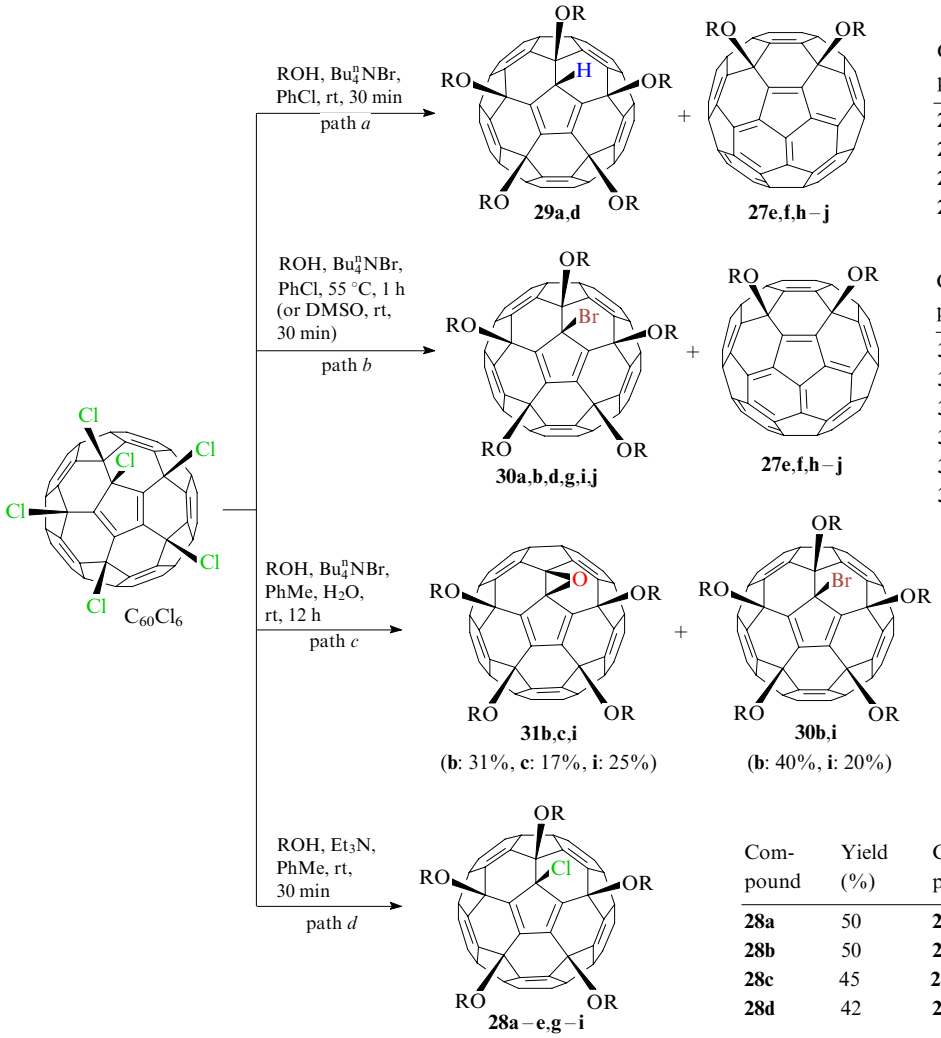
The study of the reaction of $C_{60}Cl_6$ with methanol and Bu^n_4NX (X = Br, I) by *in situ* optical absorption spectroscopy showed that the reaction mixture contained $[X_3]^-$ anions, which is indicative of the redox nature of this reaction.[57]

Besides, the reactions of $C_{60}Cl_6$ with alcohols promoted by quaternary ammonium salts and tertiary amines were studied *in situ* by EPR spectroscopy in the presence of a spin trap.[57] The EPR spectra of all the reaction mixtures under examination show an intense signal corresponding to the $MeO^{\bullet}$ radical adduct of the spin trap, which attests to the radical nature of this reaction.

Based on these results, the possible pathway of the reaction of $C_{60}Cl_6$ with alcohols was proposed (Scheme 24). This mechanism accounts for the formation of all three main types of reaction products $C_{60}(OR)_5X$ (X = H, Cl, Br) under variable reaction conditions.

Therefore, the reactions of chlorofullerene $C_{60}Cl_6$ with alcohols promoted by quaternary ammonium salts and tertiary amines can be used to synthesize different types of alkoxy derivatives of fullerene under mild conditions in satisfactory yields. This method offers wide possibilities for the design and preparation of polyfunctional fullerene derivatives for biomedical applications and materials science.

Scheme 21



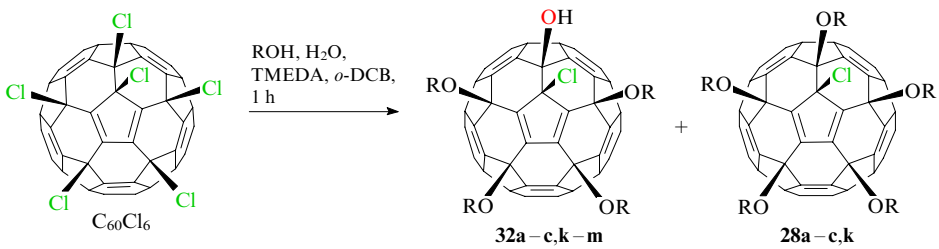
Compound	Yield (%)	Compound	Yield (%)
29a	45	**27h**	34
29d	43	**27i**	36
27e	90	**27j**	21
27f	73		

Compound	Yield (%)	Yield in the presence of DMSO (%)
30a	25	60
30b	38	70
30d	30	62
30g	33	70
30i	11	60
30j	Traces	53

Compound	Yield (%)	Compound	Yield (%)
28a	50	**28e**	38
28b	50	**28g**	52
28c	45	**28h**	40
28d	42	**28i**	43

Compounds **27** – **34**	R	Compounds **27** – **34**	R	Compounds **27** – **34**	R
a	Me	**e**	Pr^i	**i**	$(CH_2)_2O(CH_2)_2O(CH_2)_2OMe$
b	Et	**f**	$CHEt_2$	**j**	$(CH_2)_2CO_2Bu^t$
c	Pr^n	**g**	$(CH_2)_2OMe$	**k**	$(CH_2)_2C{\equiv}CH$
d	Bu^n	**h**	$(CH_2)_2O(CH_2)_2OMe$	**l**	$(CH_2)_3C{\equiv}CH$
				m	$(CH_2)_4C{\equiv}CH$

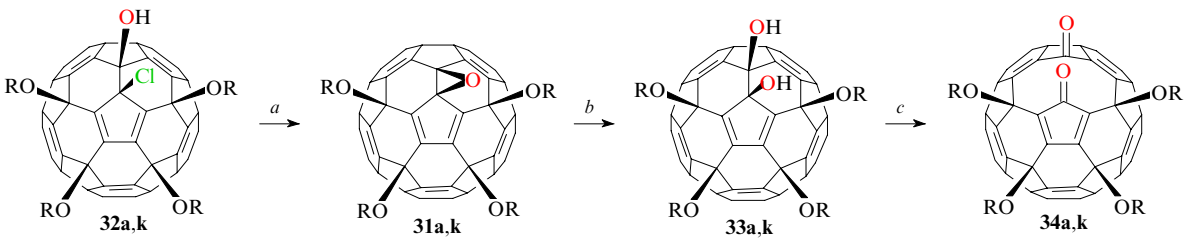
Scheme 22



Compound	Yield (%)	Compound	Yield (%)
32a	29	**28a**	48
32b	38	**28b**	33
32c	29	**28c**	20
32k	37	**28k**	19
32l	33		
32m	38		

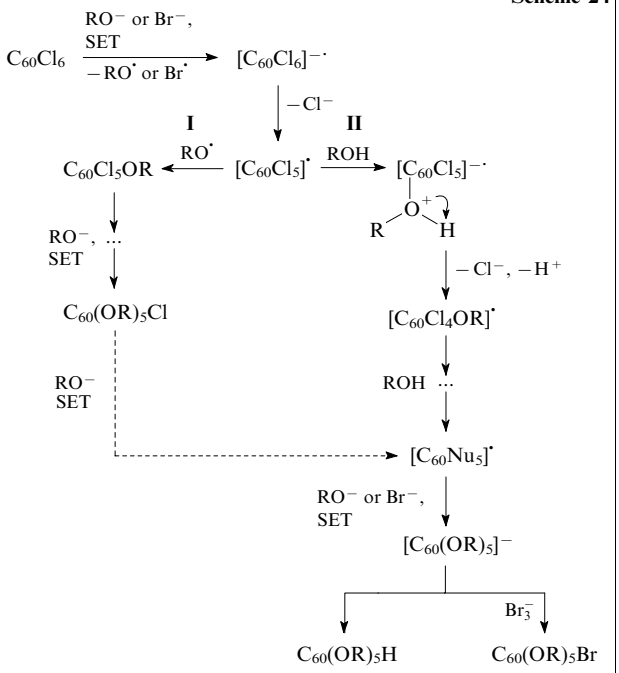
TMEDA = $Me_2NCH_2CH_2NMe_2$

Scheme 23



(*a*) CuI, TMEDA, $CHCl_3$, rt; (*b*) $B(C_6F_5)_3$, H_2O, 35°C; (*c*) $PhI(OAc)_2$, 35–40 °C

Scheme 24



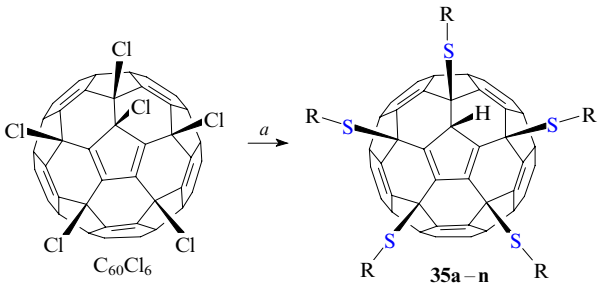
II.1.d. Reactions with thiols

Recently, it was found that chlorofullerene $C_{60}Cl_6$ readily reacts with thiols to form a new class of sulfur-containing derivatives of C_{60} of the composition $C_{60}(SR)_5H$.[59] This reaction proceeds at room temperature over 2–5 min in the presence of organic bases and gives products in 63%–95% yield (Scheme 25). Pentacarboxylic acids **35f**–**l**,**n** are insoluble in toluene and precipitate from the reaction mixture during the synthesis. Therefore, these compounds can be isolated in the pure form without using chromatographic methods.

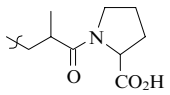
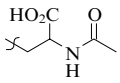
Individual derivatives of fullerene C_{60} containing sulfo groups were synthesized for the first time by the reaction of chlorofullerene $C_{60}Cl_6$ with sodium sulfanylsulfonates in the presence of 15-crown-5 (Scheme 26).[59] Like pentacarboxylic acids **35f**–**l**,**n**, compounds **36a**,**b** containing five SO_3Na groups precipitate from the reaction mixture, due to which these derivatives can be isolated in the pure form without using labourious and expensive chromatographic purification.

Scheme 27 shows the possible pathway of the reaction of chlorofullerene $C_{60}Cl_6$ with thiols, which involves the single-electron transfer from the RS^- anion to $C_{60}Cl_6$ as the first step.[59] This reaction pathway is similar to the above-considered mechanism of the reaction of chlorofullerene

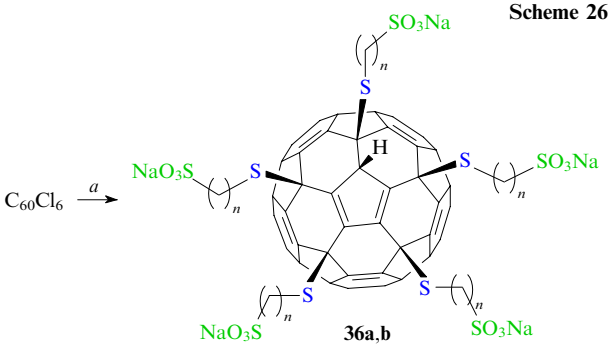
Scheme 25



(*a*) HSR, Pr^i_2NEt, PhMe, rt, 2–5 min

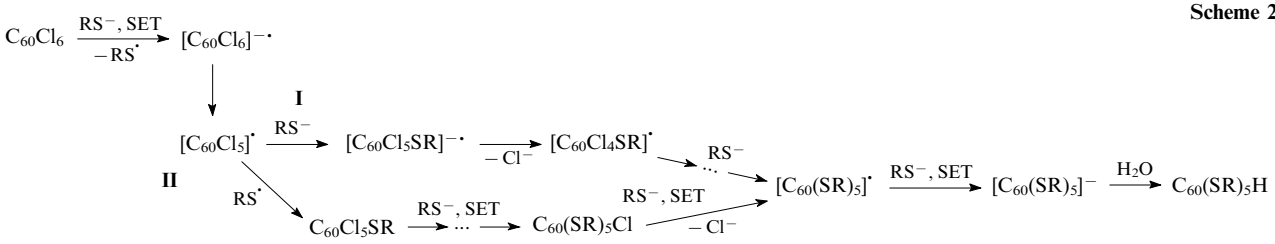
Compound **35**	R	Yield (%)
a	CH_2CO_2Me	80
b	CH_2CO_2Et	92
c	$CH_2CO_2CH_2CH(Me)Et$	83
d	$(CH_2)_2CO_2Me$	85
e	$(CH_2)_2NHCO_2Bu^t$	86
f	CH_2CO_2H	87
g	$(CH_2)_2CO_2H$	95
h	$(CH_2)_{10}CO_2H$	84
i	$(CH_2)_5CO_2H$	67
j	$(CH_2)_7CO_2H$	76
k	$(CH_2)_{11}CO_2H$	64
l		63
m	$(CH_2)_2NEt_2$	47
n		58

Scheme 26



(*a*) $HS(CH_2)_nSO_3Na$, 15-crown-5, PhMe, rt, 5 min; n = 2 (**a**, 84% yield), 3 (**b**, 79%)

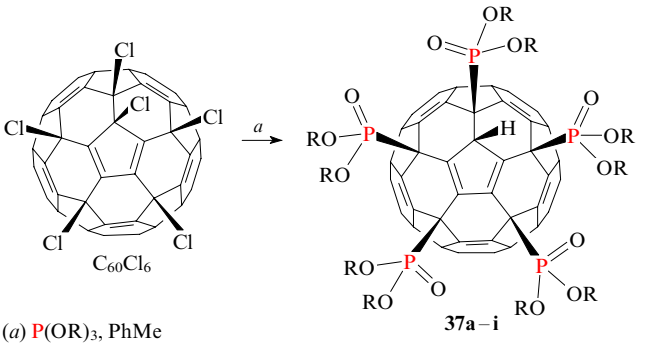
Scheme 27



with alcohols. The radical nature of the reaction was confirmed by EPR spectroscopy.

Therefore, the reactions of $C_{60}Cl_6$ with thiols and sulfanyl-substituted acids provide an efficient route to water-soluble derivatives of fullerene C_{60} containing carboxyl and ammonium groups, as well as sulfo groups. By means of this approach, water-soluble derivatives of C_{60} with a specified composition and structure were synthesized for the first time starting from chlorofullerene. The synthesis is a one-pot procedure, and the products can be isolated in gram quantities without using the labourious chromatographic purification.

Scheme 28



(*a*) $P(OR)_3$, PhMe

Compound **37**	R	Yield (%)	Compound **37**	R	Yield (%)
a	Me	80	**e**	$(CH_2)_2Cl$	75
b	Et	92	**f**	$(CH_2)_2OMe$	25
c	Pr^i	94	**g**	$(CH_2)_2O(CH_2)_2OMe$	45
d	Bu^n	87	**h**	$(CH_2)_2NMe_2$	30
			i	$(CH_2)_2O(CH_2)_2NMe_2$	23

II.1.e. Reactions with phosphites

The Arbuzov reaction of alkyl halides with trialkyl phosphites is commonly used in organic chemistry.[60,61] Relatively recently, it was shown that chlorofullerene $C_{60}Cl_6$ easily reacts with trialkyl phosphites even at room temperature to form derivatives $C_{60}[P(O)(OR)_2]_5H$ **37** as the major products (Scheme 28).[62]

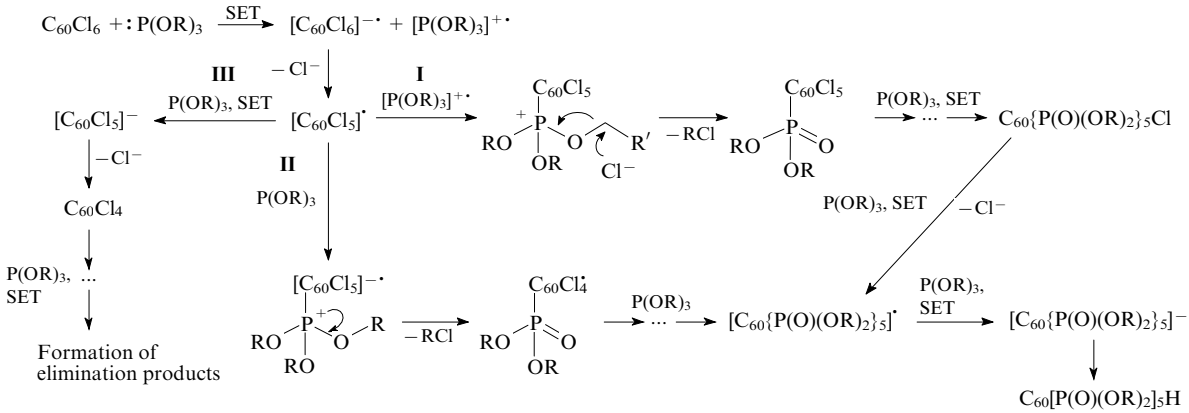
It was hypothesized that the mechanism of the reaction of chlorofullerene with trialkyl phosphites is similar to that proposed for the reaction of $C_{60}Cl_6$ with thiols (Scheme 29). Later, this mechanism was confirmed by EPR spectroscopy.[63]

Phosphorus-containing derivatives of fullerenes have unusual properties. For example, compounds **37a**,**f**–**i**, as well as **37b**, are characterized by high water solubility (> 20 mg ml^{-1}), which is quite untypical of fullerene derivatives lacking ionic or ionogenic groups. Besides, these compounds are soluble in weakly polar organic solvents, such as toluene and even hexane. Due to such behaviour, these compounds can be purified by extraction without using column chromatography.[62]

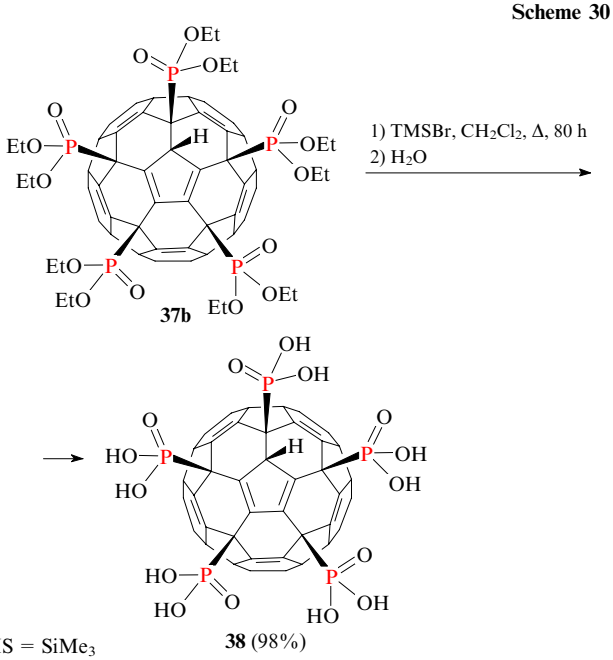
Compounds **37a**–**i** belong to a new class of C_{60} derivatives and are [60]fullerene pentaphosphonic acid esters. The acid by itself (**38**) was synthesized by heating compound **37b** under reflux in dichloromethane in the presence of a large excess of TMSBr for 80 h (Scheme 30). The solubility of acid **38** and its sodium and potassium salts in distilled water is higher than 200 mg ml^{-1} (Ref. 62).

As can be seen from the above-considered data, the chemistry of chlorofullerene $C_{60}Cl_6$ was studied in sufficient detail. The reactions of $C_{60}Cl_6$ with C-, O-, N-, S- and P-nucleophiles were investigated. It was shown that they proceed mainly *via* a radical mechanism involving the single-electron transfer as the first step, which distinguishes these reactions from most of nucleophilic substitution reactions proceeding through the S_N2 mechanism. The

Scheme 29



Scheme 30



TMS = $SiMe_3$

reactions of $C_{60}Cl_6$ with arenes, amines, thiols and phosphites serve as the basis for efficient methods for the synthesis of various polyfunctional derivatives of fullerenes, including water-soluble ones. Therefore, the employment of chlorofullerene $C_{60}Cl_6$ as a precursor for chemical modification of fullerene C_{60} makes it possible to perform the targeted design and synthesis of C_{60} derivatives containing different functional groups.

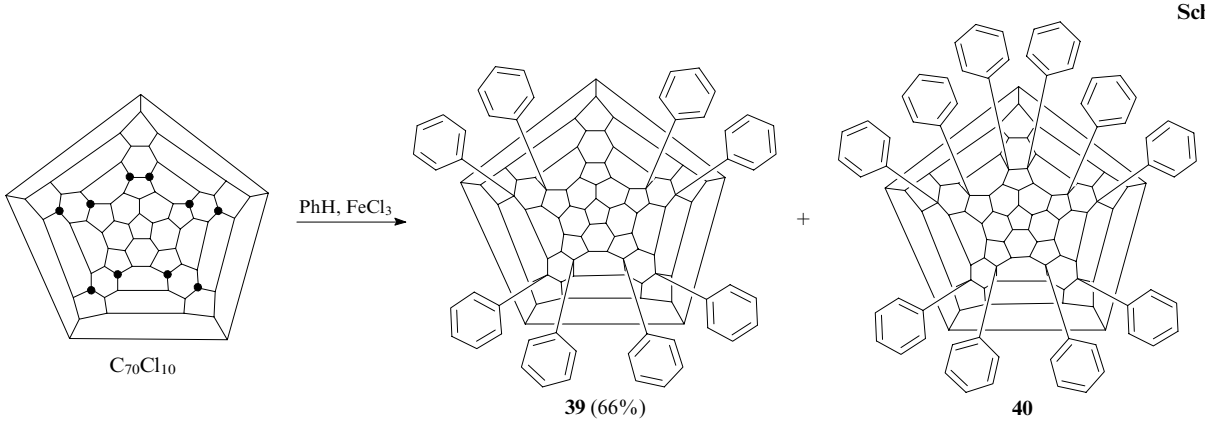
II.2. Chemical transformations of chlorinated fullerene C_{70}: $C_{70}Cl_{10}$ and $C_{70}Cl_8$

Fullerene C_{70} is less symmetric than C_{60}, which creates great difficulties in performing its chemical functionalization by classical methods (*e.g.*, by the cycloaddition to the fullerene cage) because of the formation of difficult-to-separate mixtures of regioisomers even upon the addition of one addend. As it was mentioned in the Introduction, chlorinated derivatives $C_{70}Cl_{10}$ and $C_{70}Cl_8$ can be synthesized with a selectivity of 100%. Due to the presence of labile chlorine atoms and the gram-scale availability, these chlorinated derivatives are convenient precursors for functionalization of the C_{70} cage.

II.2.a. Reactions with C-nucleophiles

Transformations of halogenated fullerenes $C_{70}Cl_{10}$ and $C_{70}Cl_8$ are less well studied compared to the chemistry of $C_{60}Cl_6$. It was shown that the reaction of $C_{70}Cl_{10}$ with benzene is accompanied by the release of two chlorine atoms [attached to adjacent carbon atoms at the (6 – 5) bond of the cage, see the Schlegel diagram in Fig. 2] to form the derivative $C_{70}Ph_8$ (**39**) as the major product along with an insignificant amount of $C_{70}Ph_{10}$ (**40**) (Scheme 31).[64] Later, some other by-products generated in this reaction were isolated: $C_{70}Ph_9OH$,[65] $C_{70}Ph_2$, $C_{70}Ph_4$ and $C_{70}Ph_6$.[66] The structures of these compounds were proposed based on

Scheme 31



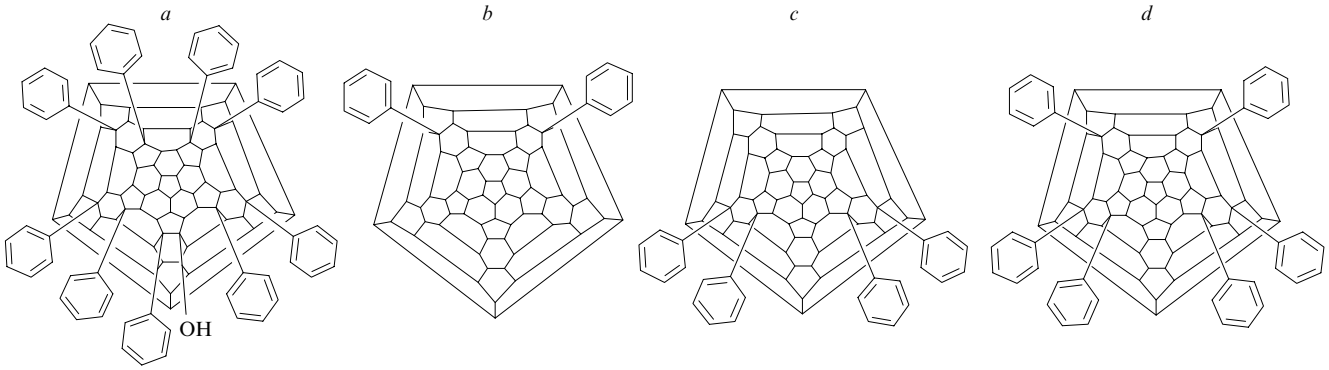
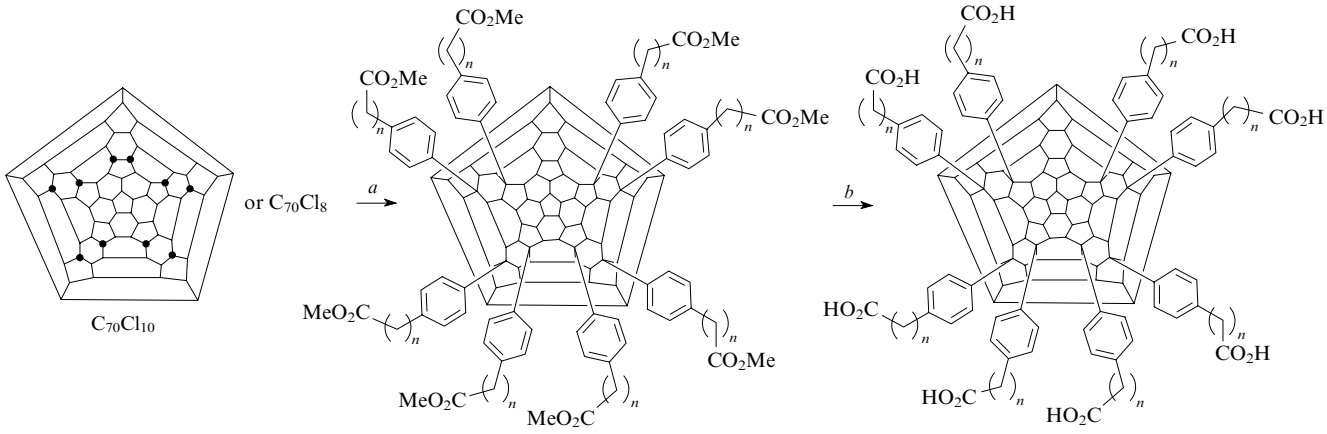


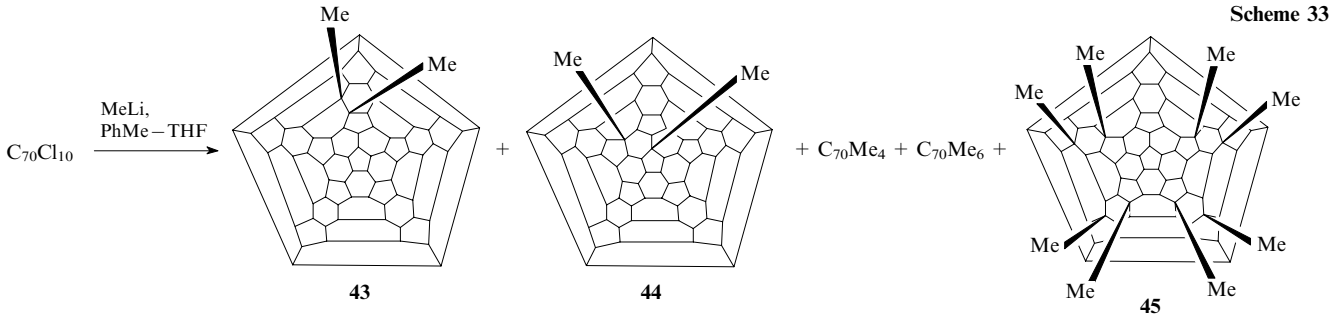
Figure 5. Schlegel diagrams characterizing the molecular structures of $C_{70}Ph_9OH$ (*a*), $C_{70}Ph_2$ (*b*), $C_{70}Ph_4$ (*c*) and $C_{70}Ph_6$ (*d*) (double bonds are not shown for sake of simplicity).

Scheme 32



(*a*) $Ph(CH_2)_nCO_2Me$, $FeCl_3$, $PhNO_2$, 90–110 °C; (*b*) $MeCO_2H-HCl-H_2O-PhMe$, 90 °C, 3 days; n = 2 (**a**), 3 (**b**)

Scheme 33



the analysis of the NMR spectra and results of quantum chemical calculations (Fig. 5).

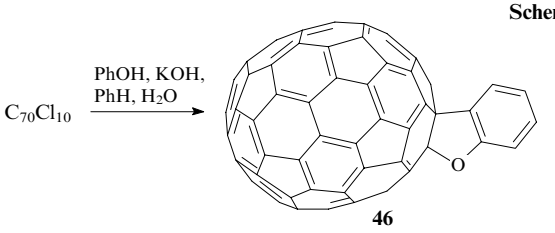
The reactions of $C_{70}Cl_{10}$ and $C_{70}Cl_8$ with methyl hydrocinnamate and methyl phenylbutyrate, like the reactions with benzene, produced compounds containing eight organic addends on the carbon cage (Scheme 32).[67] The acid hydrolysis of ester groups in compounds **41a**,**b** affords polycarboxylic derivatives of C_{70} **42a**,**b**, the salts of which are readily soluble in water (see Scheme 32).[67]

The reaction of chlorofullerene $C_{70}Cl_{10}$ with MeLi at room temperature gives a difficult-to-separate mixture of products of the composition $C_{70}Me_n$ (n = 2, 4, 6, 8). Two isomers of $C_{70}Me_2$ (**43** and **44**) were isolated from this mixture and identified. Attempts to characterize other reaction products failed. However, the compound of the composition $C_{70}Me_8$ (**45**), which was synthesized by an alternative method (reduction of C_{70} followed by the reaction of the resulting polyanion with MeI) proved to be isostructural with $C_{70}Ph_8$ (**39**) (Scheme 33).[68, 69]

II.2.b. Reactions with O-nucleophiles

Like chlorofullerene $C_{60}Cl_6$, decachlorinated fullerene $C_{70}Cl_{10}$ reacts with phenol in the presence of an aqueous KOH solution to form a derivative of C_{70} containing the benzofuran moiety (Scheme 34).[55] The reaction is accompanied by elimination of all other chlorine atoms from the fullerene cage. It is interesting that chlorine atoms in the starting chlorofullerene are located on the equator of the fullerene cage, while the benzofuran moiety in product **46** is

Scheme 34



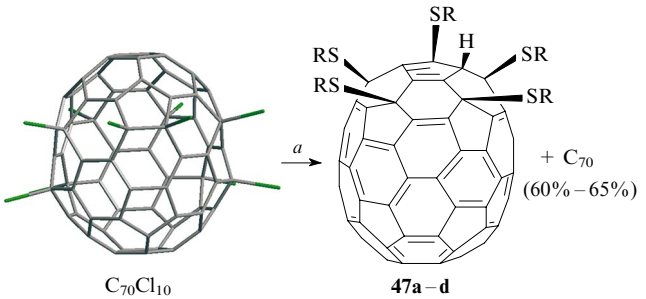
situated at one pole of the molecule, which attests to a complicated multistep reaction mechanism.

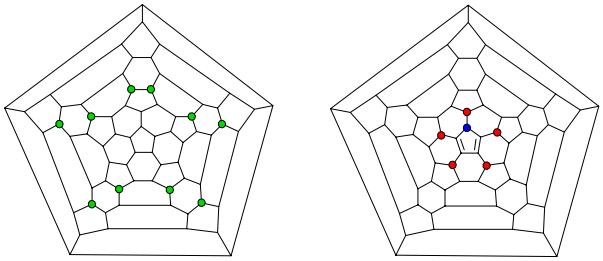
II.2.c. Reactions with thiols

Unlike the reaction of chlorinated fullerene $C_{60}Cl_6$, the reaction of chlorofullerene $C_{70}Cl_{10}$ with thiols at room temperature in the presence of Honig's base proceeds nonselectively and produces a mixture of $C_{70}(SR)_5H$ and unfunctionalized fullerene C_{70} (Scheme 35).[70] As opposed to the starting chlorofullerene $C_{70}Cl_{10}$, in which all chlorine atoms are attached to the equatorial belt region of the fullerene cage, organic addends in the compounds $C_{70}(SR)_5H$ are situated at one pole of the C_{70} cage. A change in the addition pattern of addends from the equatorial to cyclopentadienyl type is illustrated by the Schlegel diagrams, which are given below each structure in Scheme 35.

Unfortunately, compounds **47a**–**d** are thermodynamically unstable. At elevated temperature or during storage in the solid state or in solution at room temperature in the presence of even trace amounts of moisture, these com-

Scheme 35



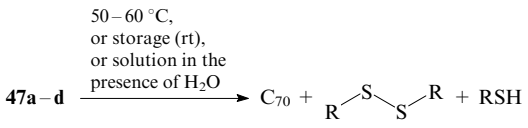


(*a*) RSH, Pr^i_2NEt, PhMe, rt; ● Cl, ● H, ● SR

Compound **47**	R	Yield (%)
a	$(CH_2)_2CO_2Me$	35–40
b	CH_2CO_2Me	38
c	CH_2CO_2Et	39
d	$(CH_2)_2CO_2H$	35

pounds undergo reductive elimination of organic addends to form unfunctionalized fullerene C_{70}, the starting thiol RSH and the disulfide derivative RSSR (Scheme 36). The elimination of organic addends is indicative of their weak binding to the fullerene cage, which was confirmed by DFT quantum chemical calculations.[70]

Scheme 36



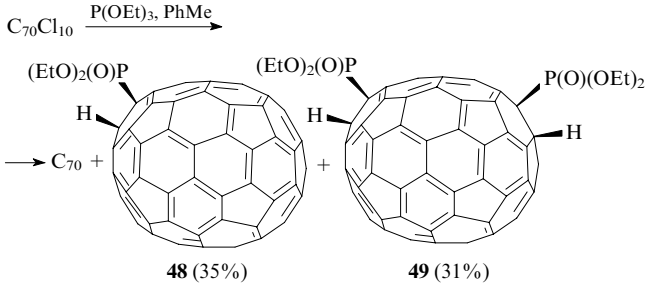
The mechanism of the reaction of chlorofullerene $C_{70}Cl_{10}$ with thiols is similar to that of the related reaction of $C_{60}Cl_6$ with the only difference that in the case of $C_{70}Cl_{10}$, the elimination makes a more considerable contribution to the process.[70]

II.2.d. Reactions with phosphites

The reaction of chlorofullerene $C_{70}Cl_{10}$ with phosphites, *e.g.*, $P(OEt)_3$, produces a mixture of compounds $C_{70}[P(O)(OEt)_2]H$ (**48**), $C_{70}[P(O)(OEt)_2]_2H_2$ (**49**) and unfunctionalized fullerene C_{70} (Scheme 37).[71] It was confirmed that the reaction of $C_{70}Cl_{10}$ with phosphites, like the reaction with thiols, proceeds with the involvement of radical intermediates.[71]

Therefore, unlike the reaction of $C_{60}Cl_6$ with phosphites, the related reaction of $C_{70}Cl_{10}$ proceeds nonselectively and is accompanied by a change in the addition pattern of addends on the fullerene cage compared to the starting chlorofullerene. The result of the reaction of $C_{70}Cl_{10}$ with phosphites substantially depends on the elimination of addends from the fullerene cage.

Scheme 37



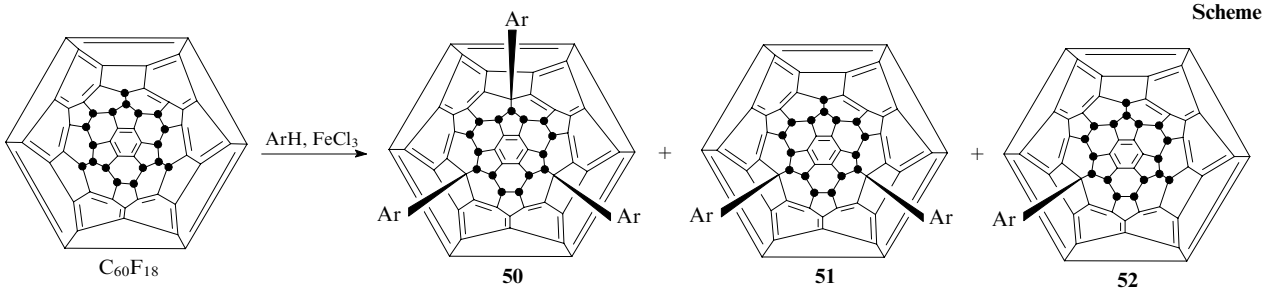
II.3. Chemical properties of fluorofullerene $C_{60}F_{18}$

II.3.a. Reactions with C-nucleophiles

Fluorofullerene $C_{60}F_{18}$ appeared to be very interesting for research. The chemistry of this compound was studied by Taylor and co-workers.[72–79] It was found that fluorine atoms in the fluorofullerene are rather easily replaced by aryl groups in reactions with ArH in the presence of $FeCl_3$ to form $C_{60}F_{15}Ar_3$ (Scheme 38). Derivatives **50** containing three aryl groups thus synthesized were named triumphenes. It should be noted that the reactions often produce mixtures of isomers because the arene is bound through different positions. Apart from triumphenes, the reactions give compounds **51** and **52** as minor products and, in some cases, even as major products. These compounds are produced *via* the replacement of two and one fluorine atoms in $C_{60}F_{18}$, respectively.[72,73] For example, the reaction of pyrene produces only monosubstituted derivative **52**.

Interestingly, a compound of the composition $C_{60}F_{14}OFPh_3$ isostructural with triumphene $C_{60}F_{15}Ph_3$ was found among by-products of the reaction of fluorofullerene $C_{60}F_{18}$ with benzene performed in the presence of $SbCl_5$ (Fig. 6).[74] The formation of this compound is appa-

Scheme 38



ArH = PhH, PhMe, PhOMe, PhOPh, PhCl, 3,4-$Cl_2C_6H_4$, , biphenyl, naphthalene, fluorene, pyrene, biphenylene

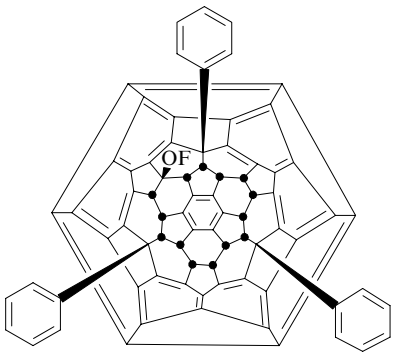
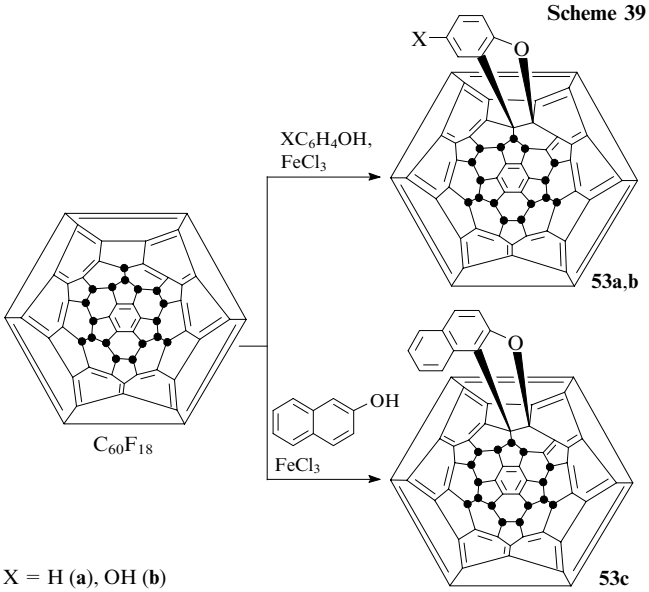
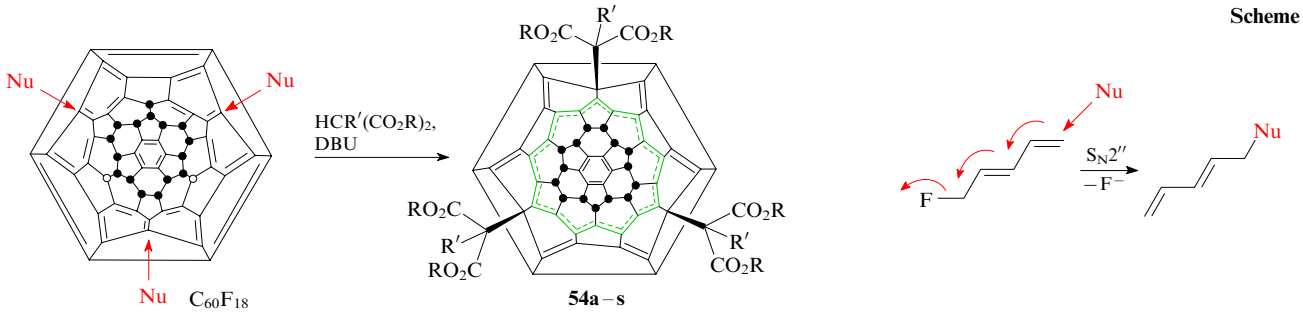


Figure 6. Schlegel diagram of the $C_{60}F_{14}(OF)Ph_3$ molecule.

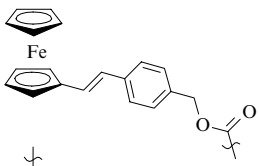
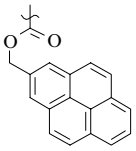
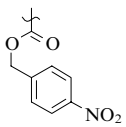
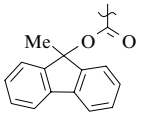
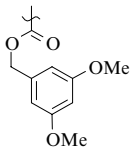
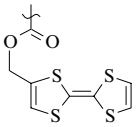
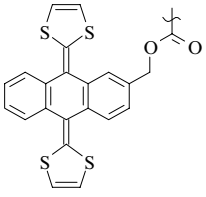
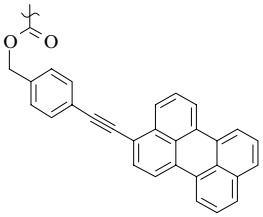
Scheme 39



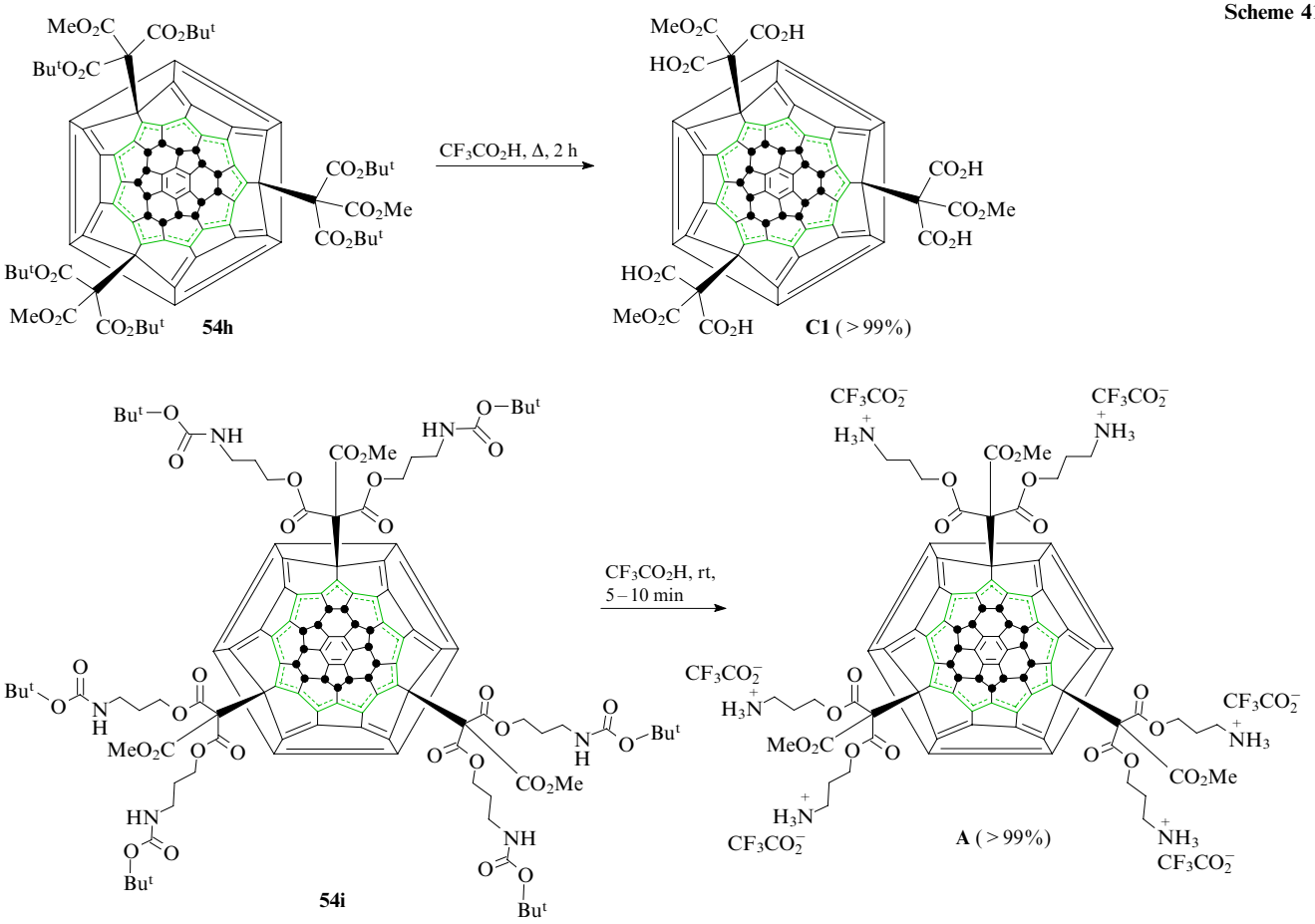
Scheme 40



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

Compound **54**	R	R′	Yield (%)	Compound **54**	R	R′	Yield (%)
a	Et	Br	30				
b	Me	Br	37				
c	Pr^n	Br	44	**o**	Et		28
d	n-C_6H_{13}	Br	30				
e	$C_6H_3(OMe)_2$-3,5	Br	32				
f	Me	CO_2Me	56				
g	Et	CO_2Et	29				
h	Bu^t	CO_2Me	46	**p**	Et		28
i	$(CH_2)_3NHCO_2Bu^t$	CO_2Me	11				
j	Et	NO_2	33				
k	Et	$P(O)(OEt)_2$	14				
l	Et		41	**q**	Et		33
m	Et		41	**r**	Et		28
n	Et		26	**s**	Et		31

Scheme 41

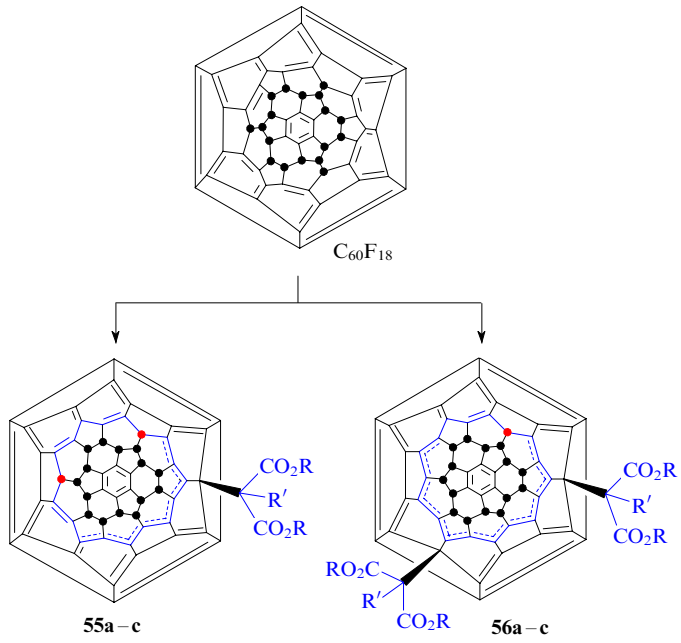


rently attributed to the presence of an impurity of oxofluorinated fullerene $C_{60}F_{17}OF$ in the starting $C_{60}F_{18}$.

Compounds **53a–c** containing the benzofuran moiety and 16 fluorine atoms attached to the fullerene cage were synthesized by the reactions of fluorofullerene $C_{60}F_{18}$ with phenol, hydroquinone and 2-naphthol, respectively, in the presence of $FeCl_3$ (Scheme 39).[75]

The reaction of $C_{60}F_{18}$ with carbanionic nucleophiles proceeds *via* an unusual S_N2'' mechanism to give trannulenes **54a–s** of the composition $C_{60}F_{15}R_3$.[76–83] The S_N2'' mechanism is unique for chemistry of fluorofullerene $C_{60}F_{18}$. It involves the nucleophilic attack on the δ-carbon atom followed by the shift of two conjugated double bonds and elimination of F (Scheme 40).

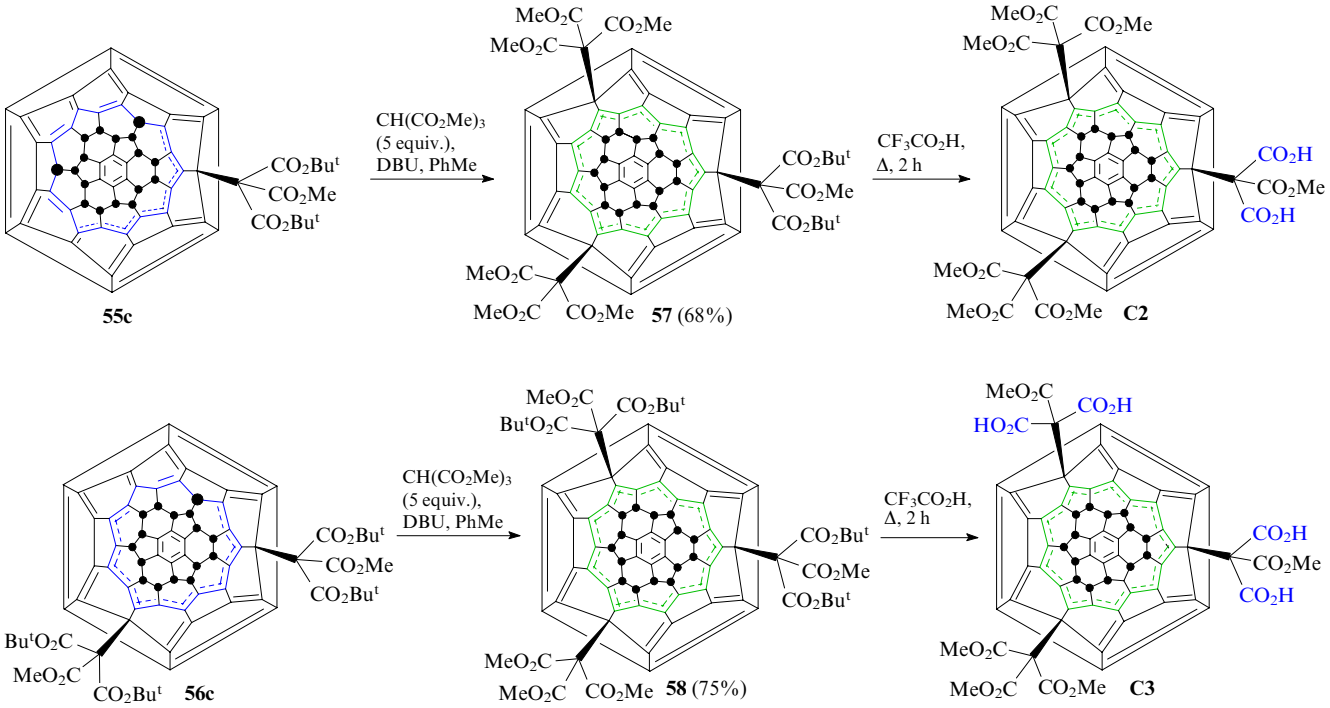
Scheme 42



Compound **55**	R	R′	Yield (%)
a	Et	Br	–
b	3,5-$(MeO)_2C_6H_3$	Br	33
c	But	CO_2Me	15

Compound **56**	R	R′	Yield (%)
a	Et	Br	–
b	Et	Perylen-3-ylmethyl-oxycarbonyl	18
c	But	CO_2Me	30

Scheme 43



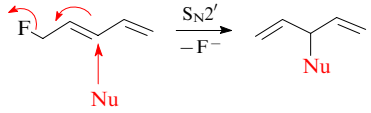
It should be noted that compounds **54h**,**i** are precursors for the synthesis of trannulenes **A** and **C1** soluble in water and polar organic solvents (Scheme 41).[81]

Monosubstituted (**55a**–**c**) and disubstituted (**56a**–**c**) products can be prepared instead of trannulenes by varying the conditions of the synthesis (Scheme 42).[78, 81]

C_s-Symmetric trannulenes **57** and **58** can be synthesized by the replacement of the remaining peripheral fluorine atoms in compounds **55c** and **56c** by organic addends (Scheme 43).[81] Trannulenes **57** and **58** are also valuable precursors for the preparation of polycarboxylic derivatives **C2** and **C3** soluble in polar organic solvents (see Scheme 43).[81]

The size of the carbanionic nucleophile reacting with $C_{60}F_{18}$ plays an important role. If the size is small, the reaction with $C_{60}F_{18}$ does not produce trannulene because it proceeds *via* the S_N2' mechanism (attack on the β-carbon atom and the shift of one double bond) (Scheme 44), which does not give rise to the trannulene system in the fullerene cage. Thus, all attempts to synthesize trannulenes by the reactions of $C_{60}F_{18}$ with diethyl fluoromalonate and diethyl cyanomalonate failed because the reaction proceeds *via* the S_N2' mechanism and gives products **59a**,**b** due to small sizes of the carbanions that are generated under the action of bases (Scheme 45).[78]

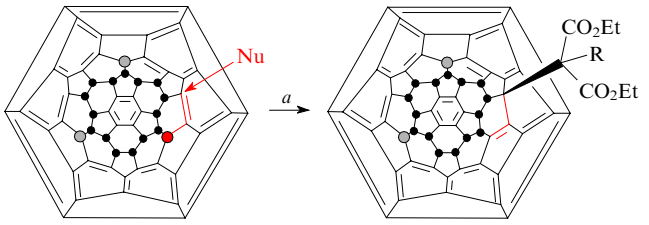
Scheme 44



Besides, it was shown that the reaction of two isomers of oxofluorinated fullerene $C_{60}F_{18}O$ with carbanionic nucleophiles affords the corresponding trannulenes **60** and **61** (Scheme 46).[79]

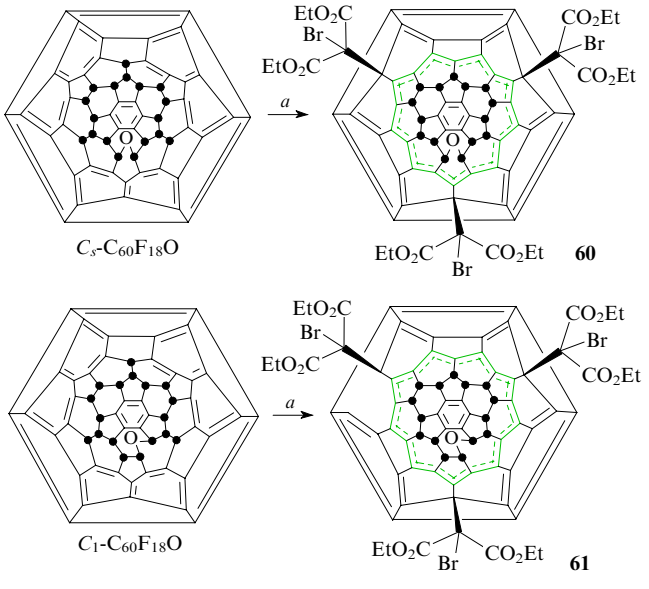
The discovery of trannulenes is of great importance not only in fullerene chemistry but also in organic chemistry in

Scheme 45



(*a*) $HCR(CO_2Et)_2$, DBU;
R = CN (**a**), F (**b**)

Scheme 46



(*a*) $HCBr(CO_2Et)_2$, DBU

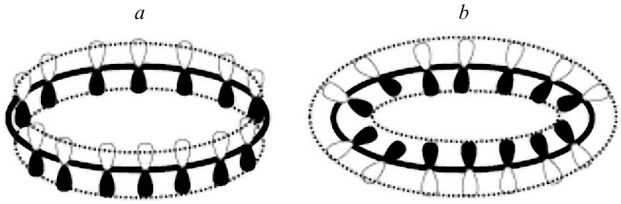


Figure 7. Overlap of orbitals in classical annulenes (*a*) and trannulenes (*b*).

general. Trannulenes (trannulene is the abbreviation of all-*trans*-annulene) are fullerene derivatives containing the aromatic 18-membered macrocycle constituting the equatorial belt of the fullerene molecule. The cyclic trannulene system is nonplanar. Due to rigidity of the fullerene cage, all conjugated π-bonds of the macrocycle are in *trans* configuration. Therefore, as opposed to classical [18]annulenes containing a planar aromatic ring, in which the π-orbitals lie above and below the ring plane and their overlap is perpendicular to this plane, the overlap of the π-orbitals in the trannulene system is parallel to the ring plane (Fig. 7). This conjugation pattern is termed in-plane aromaticity. The possibility of the existence of compounds exhibiting this type of aromaticity was predicted by Schleyer and coworkers in 1979.[84–86]

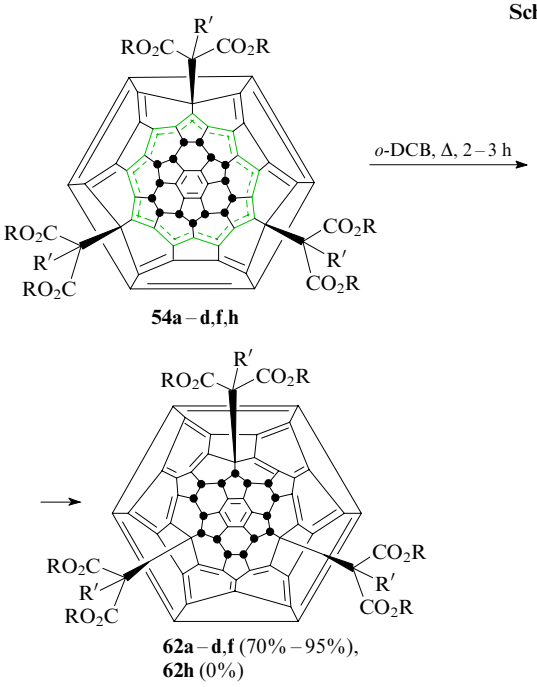
The presence of the 18-membered aromatic macrocycle is responsible for high stability of trannulenes and their unique optoelectronic properties. Thus, the trannulene system is characterized by intense absorption bands in the red and near-IR spectral region (500 – 1000 nm), resulting in a beautiful emerald-green colour of trannulenes, which is not typical of other fullerene derivatives. Unusual electronic properties of trannulenes can provide the basis for a number of practical applications.

Until recently, trannulene derivatives of fullerene C_{60} have been the only example of compounds exhibiting in-plane aromaticity. However, in 2015 Toriumi *et al.*[87] showed, by means of magnetic circular dichroism spectroscopy and theoretical calculations, that the 8-cycloparaphenylene dication ([8]CPP^{2+}) also exhibits in-plane aromaticity. Unlike trannulenes, in which all conjugated double bonds are in *trans* configuration, the conjugated bonds in [8]CPP^{2+} adopt *cis* configuration, *i.e.*, [8]CPP^{2+} is the all-*cis*-annulene with in-plane aromaticity. Based on theoretical calculations, the authors of the cited study predicted that all [*n*]CPP^{2+} cations and [*n*]CPP^{2-} anions would exhibit in-plane aromaticity.

Due to the presence of the 18-membered aromatic moiety, which greatlly contributes to stabilization of the structure of trannulene derivatives of C_{60}, these derivatives have been considered until recently as rather stable compounds with respect to different impacts. However, later it it was shown that trannulenes undergo rapid degradation under electrochemical and chemical reduction conditions.[88] Besides, trannulenes **54a**–**d**,**f** were found to undergo unique thermal isomerization to triumphenes **62a**–**d**,**f** in high yields (70% – 95%) (Scheme 47).[82]

The molecular structures of triumphenes generated through isomerization of trannulenes were established by X-ray diffraction study of compound **62f**. Two projections of the molecular structure of triumphene **62f** are shown in Fig. 8. Based on the X-ray diffraction data, it can be concluded that triumphenes are isostructural with fluorinated fullerene $C_{60}F_{18}$ with the only difference that three peripheral fluorine atoms are replaced by organic moieties.

Scheme 47



R′ = Br: R = Me (**a**), Et (**b**), Pr^n (**c**), n-C_6H_{13} (**d**);
R′ = CO_2Me: R = Me (**f**), Bu^t (**h**)

Compounds **62a**–**d**,**f** contain three aliphatic organic addends, which distinguishes them from the above-described triumphenes possessing three aryl groups.[75,76] Therefore, the thermal isomerization of trannulenes opens up a route to new triumphenes with aliphatic addends, which can be prepared directly from fluorofullerene $C_{60}F_{18}$.

Trannulenes **54a**–**d**,**f**,**h** undergo isomerization at different rates. Trannulene **54a** containing the least bulky organic addends proved to be the most reactive. This compound is completely isomerized to triumphene **62a** within 20 min by heating under reflux in *o*-dichlorobenzene (at a concentration of 7.3×10^{-4} mol litre^{-1}) in an argon atmosphere. Interestingly, as opposed to derivative **54a**, trannulene **54h** containing bulky organic addends C(CO_2Me)(CO_2Bu^t)$_2$ does not undergo a transformation into triumphene even on heating under reflux in *o*-dichlorobenzene for 8 h. Substantial differences in the reactivity of compounds **54a** and **54h** are indicative of an important role of steric effects in the isomerization of trannulenes. Apparently, the steric hindrance between the bulky moieties C(CO_2Me)(CO_2Bu^t)$_2$

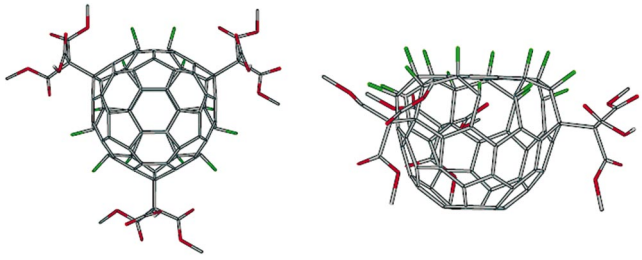
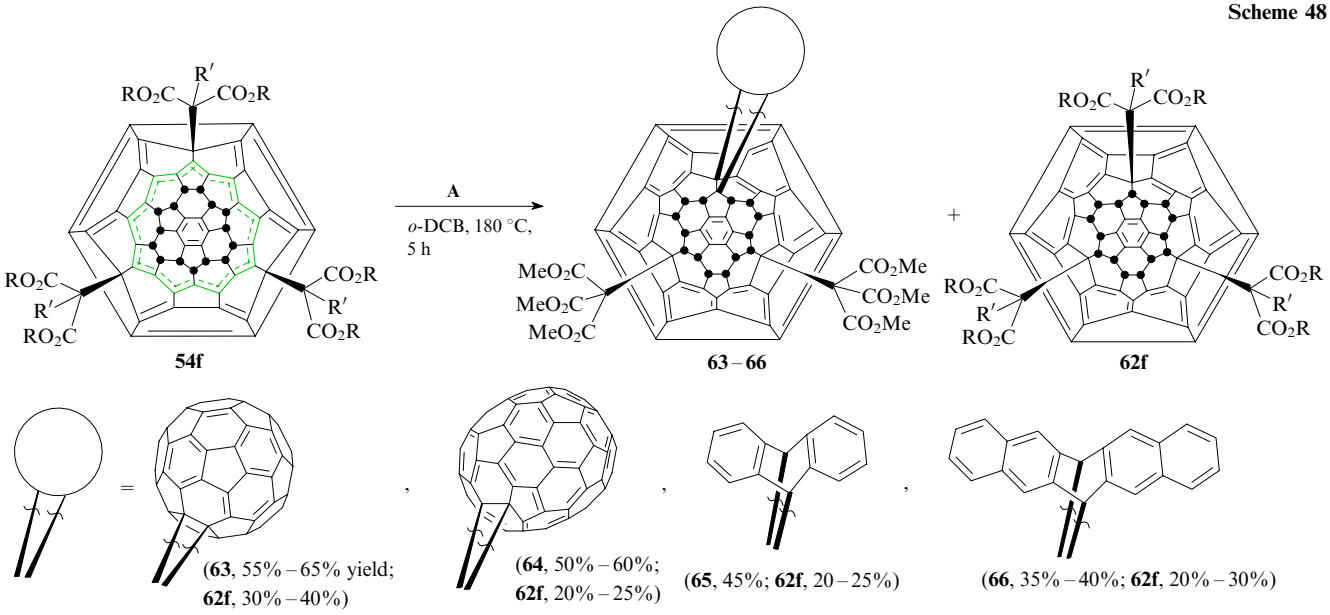


Figure 8. Two projections of triumphene **62f** molecule (X-ray diffraction data).[82]

Scheme 48



and adjacent fluorine atoms in compound **62h** is so high that its formation through the isomerization of trannulene **54h** is thermodynamically unfavourable.[82]

The *in situ* investigation of the isomerization of trannulene **54f** by optical absorption spectroscopy demonstrated that the reaction is second order with respect to the reactant. This is an indirect evidence that the rate-limiting step most likely involves the interaction between two trannulene molecules, which is apparently accompanied by the exchange of organic radicals between these molecules, resulting ultimately in the isomerization of trannulene to triumphene.[83]

Besides, it was found that the isomerization of trannulene **54f** in the presence of a number of unsaturated compounds (**A** are fullerenes C_{60} and C_{70}, anthracene, pentacene) produces, apart from triumphene **62f**, adducts $C_{60}F_{14}R_2{=}\mathbf{A}$ (Scheme 48). Compounds **63**, **64** and **65**, **66** have an unusual structure and are an acceptor–acceptor and acceptor–donor dyads, respectively. Compound **63** $C_{60}F_{14}R_2{=}C_{60}$ is structurally similar to dimeric fluorinated fullerene $C_{60}F_{16}{=}C_{60}$ synthesized earlier (Fig. 9). The molecular structure of the latter compound was determined by X-ray diffraction.[89] In compounds **64**–**66**, the addition pattern of a fragment of an unsaturated compound (C_{70}, anthracene or pentacene) on the fluorinated fullerene cage is the same as in derivative **63**.[82] It should be noted that 90% of the starting triumphene and an insignificant amount (5%) of compound **63** were isolated from the reaction mixture obtained by heating triumphene **62f** under reflux in the presence of a large excess of fullerene C_{60} in *o*-dichlorobenzene for 12 h. Therefore, adducts **63**–**66** are apparently generated mainly from trannulenes and their isomerization intermediates rather than from triumphenes.

The mechanism of formation of adducts $C_{60}F_{14}R_2{=}\mathbf{A}$ was proposed (Scheme 49). For the consideration of this mechanism, it is not essential whether the addend migration from one hemisphere of the fullerene cage to another occurs in an intramolecular manner or through a tightly bound radical or ion pair.[82]

The δ-shift of one addend in trannulene **54f** gives rise to intermediate **I1**, which can eliminate the RF molecule to form product **E1**. The sequential migration of the remaining two organic addends in product **E1** results in the formation

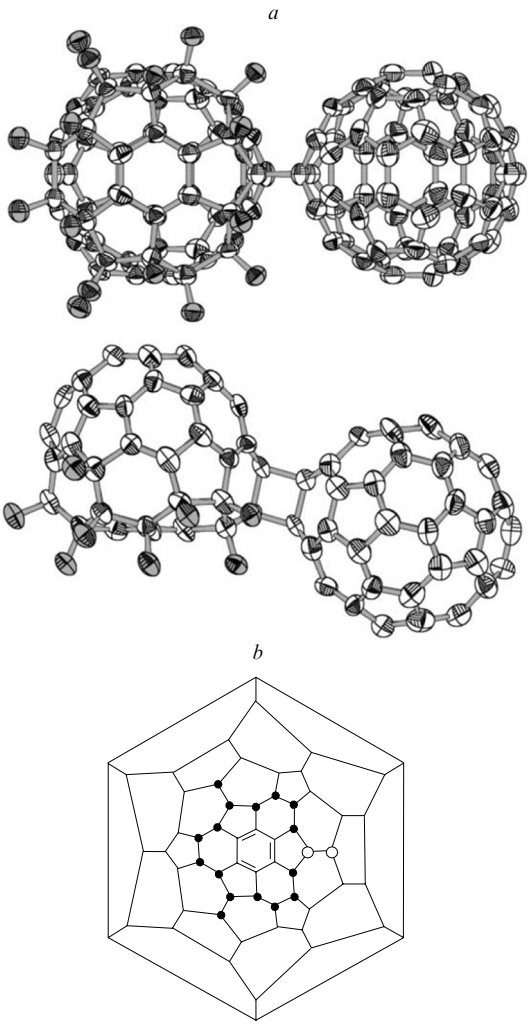
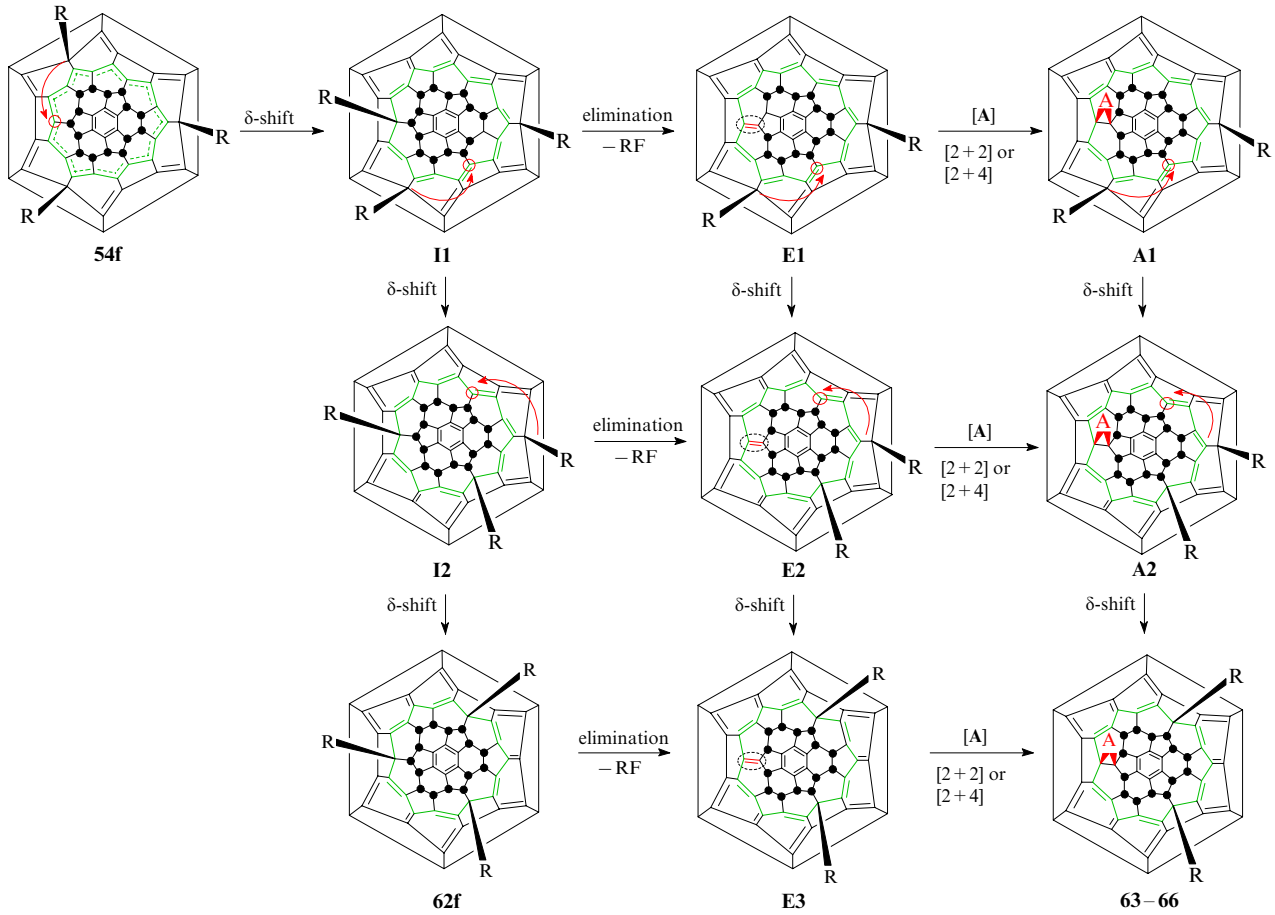


Figure 9. Two projections of the $[C_{60}F_{16}]{=}C_{60}$ molecule (*a*) and the Schlegel diagram illustrating the addition pattern of fluorine atoms on the fullerene cage (•) and the attachment site of C_{60} (○) (*b*).[89]

Scheme 49



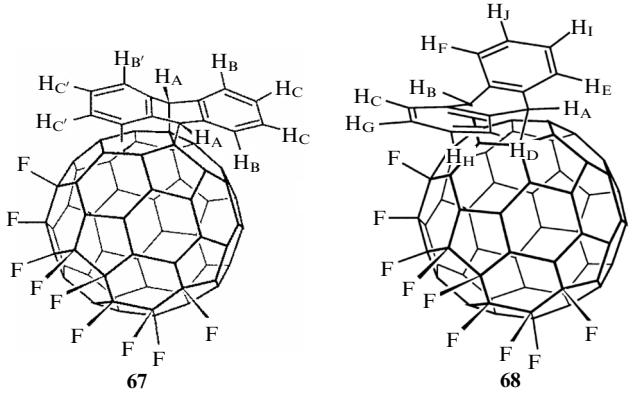
of intermediates **I2** and triumphene **62f**. They can be transformed into intermediates **E2** and **E3**, respectively, through the elimination of the RF molecule. All three elimination products (**E1**, **E2** and **E3**) have the same composition ($C_{60}F_{14}R_2$) and may undergo [2 + 2]- and [2 + 4]-cycloaddition to unsaturated compounds **A**, thus generating products **A1**, **A2** and **63**–**66**, respectively.

Intermediate **A1** can be transformed into intermediate **A2** and compounds **63**–**66** through one or two δ-shifts of organic addends R, respectively. Therefore, each of the three possible intermediates **E1**, **E2** and **E3** can be transformed into compounds **63**–**66**. However, these three reaction pathways differ in efficiency. The transformations **54f** → **I1**, **I1** → **I2** and **I2** → **62f** are thermodynamically controlled. Hence, stability of these compounds increases in the series **54f** < **I1** < **I2** < **62f**. It can be assumed that the activation barriers for the elimination reactions of compounds **I1**, **I2** and **62f** will increase in the same order. Therefore, the rate of formation of intermediate **E1** can be higher compared to **E2**, and intermediate **E2** is formed more rapidly than **E3**. In this line of reasoning, it can be concluded that the transformation of trannulene **54f** into derivatives **63**–**66** proceeds mainly through the formation of intermediates **E1** and **E2**. This is confirmed by experimental data, which indicate that products **63**–**66** are generated from trannulene **54f** in much higher yields (through intermediates **E1**, **E2** and **E3**) compared to triumphene **62f** (only through intermediate **E3**). Therefore, the formation of adducts $C_{60}F_{14}R_2$═**A** from trannulene **54f** occurs as a concerted cascade of successive reactions involving 1) isomerization (δ-shift of one or two organic addends); 2) elimination of $FC(CO_2Me)_3$; 3) [2 + 2]- or [2 + 4]-cycloaddition and 4) isomerization (δ-shift of one or two organic addends).

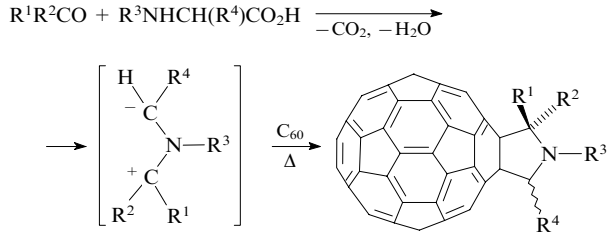
II.3.b. Cycloaddition reactions involving double bonds of the $C_{60}F_{18}$ cage

The [4 + 2]-cycloaddition of anthracene to the cage of fluorofullerene $C_{60}F_{18}$ affords two isomeric monoadducts **67** (C_s-symmetric) and **68** (C_1-symmetric) in 3 : 2 ratio.[90] The steric hindrance between the aromatic moiety and fluorine atoms is responsible for a decrease in stability of

Structures 67, 68



Scheme 50



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

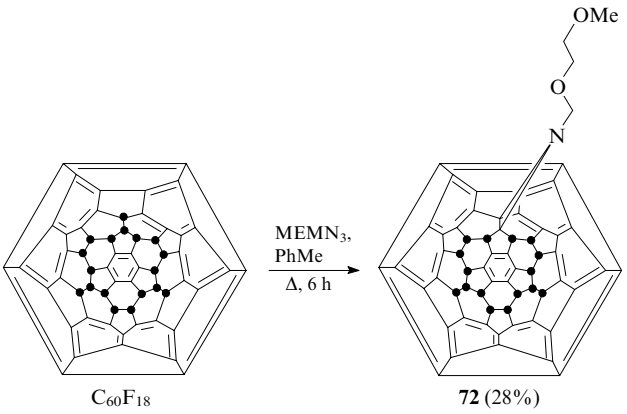
adduct **68** (C_1). The latter spontaneously reverts to the starting compounds ($C_{60}F_{18}$ and anthracene) or undergoes a rearrangement into more stable isomer **67** (C_s).

The addition of azomethine ylides, which are generated in the reaction of N-substituted α-amino acids with carbonyl compounds, to the fullerene C_{60} cage produces the corresponding pyrrolidinofullerenes (Prato reaction, Scheme 50).[91]

It appeared that fluorofullerene $C_{60}F_{18}$ can also undergo the Prato reaction with sarcosine and formaldehyde. This reaction produced a mixture of isomeric mono- and bisadducts, compounds **69**–**71** being isolated from this mixture and then characterized (Fig. 10).[92]

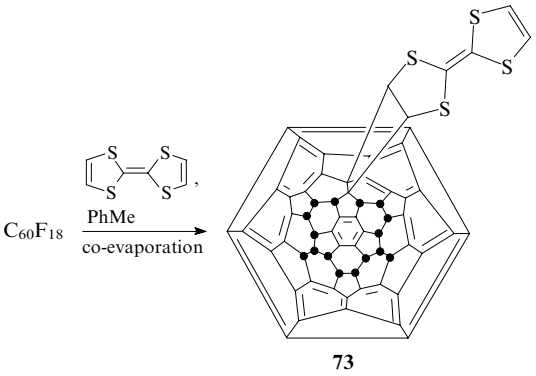
The reaction of fluorofullerene $C_{60}F_{18}$ with (methoxyethoxy)methyl azide ($MEMN_3$) gave the compound $C_{60}F_{16}NMEM$ (**72**) (Scheme 51).[93]

Scheme 51



$C_{60}F_{18}$ **72** (28%)

Scheme 52



73

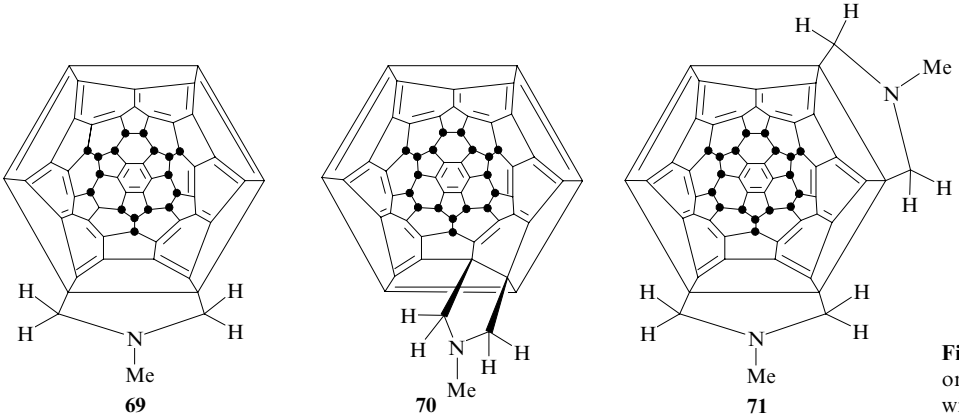
Besides, fluorofullerene $C_{60}F_{18}$ reacts with tetrathiafulvalene (TTF), resulting in the attachment of TTF to the fullerene cage to form product **73**, which is accompanied by the formal elimination of two fluorine atoms (Scheme 52).[94] The process apparently involves the redox reaction with an excess of TTF giving the $(TTF)^+F^-$ radical-ion salt as a by-product.

II.4. Chemical properties of fluorofullerenes $C_{60}F_{36}$ and $C_{60}F_{48}$

Chemistry of highly fluorinated fullerenes — $C_{60}F_{36}$ and $C_{60}F_{48}$ — is poorly understood. It is known that in organic solvents containing traces of water, the C_3- and C_1-$C_{60}F_{36}$ isomers are slowly transformed into C_3- and C_1-isomers of $C_{60}F_{35}OH$ (**74** and **75**, respectively) (Fig. 11). The hydroxylation of fluorofullerene $C_{60}F_{36}$ proceeds *via* the S_N2' mechanism (Scheme 53).[95]

The hydrolysis of fluorofullerene $C_{60}F_{48}$ in aqueous acetone or THF gave a mixture of products, in which one to twelve fluorine atoms were replaced with hydroxy groups; however, individual compounds were not isolated and characterized.[96]

Therefore, $C_{60}F_{18}$ is the most well-characterized fluorofullerene. The distinguishing feature of fluorinated fullerene $C_{60}F_{18}$ associated with the stability of the $C_{sp^3\,cage}-F$ bond is the retention of most of fluorine atoms on the fullerene cage upon the reactions with nucleophiles and cycloaddition reactions, which is not typical of chlorinated fullerenes. The use of $C_{60}F_{18}$ as a precursor allows the design and synthesis of various fullerene derivatives, which are readily soluble in organic solvents and have a high electron affinity. These



69 **70** **71**

Figure 10. Schlegel diagrams of fluorofullerene $C_{60}F_{18}$ adducts **69**–**71** with azomethine ylides.[92]

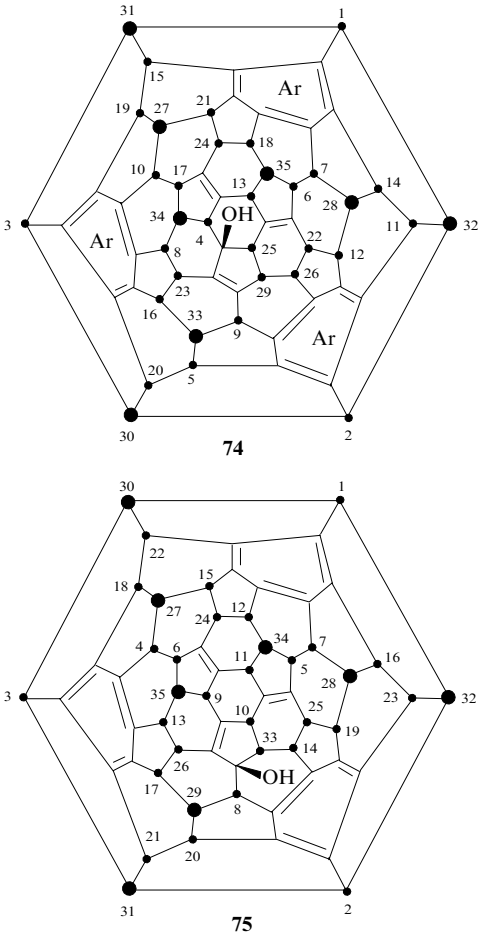


Figure 11. Schlegel diagrams of isomers $C_{60}F_{35}OH$ **74** and **75** produced by the hydroxylation of C_3-$C_{60}F_{36}$ and C_1-$C_{60}F_{36}$, respectively.[95]

compounds hold promise as materials in organic electronics.

III. Conclusion

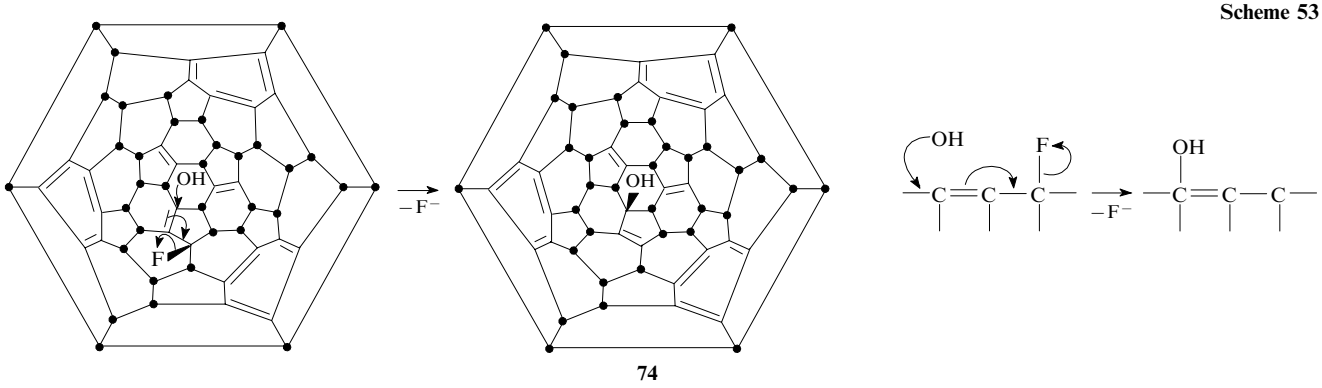
The literature data presented in this review clearly demonstrate that the use of halogenated fullerenes as precursors offers great opportunities for the design and targeted synthesis of various polyfunctional derivatives of fullerenes containing simultaneously several organic addends. Halogenated fullerenes $C_{60}Cl_6$, $C_{70}Cl_{10}$ and $C_{60}F_{18}$ are the most promising substrates due to their gram-scale availability and good solubility in organic solvents. The specific structural features of these halofullerenes provide high selectivity of their reactions with a great diversity of nucleophiles, such as aromatic hydrocarbons, amines, amino acid esters, thiols, phosphites and so on.

Many derivatives of fullerenes C_{60} and C_{70} synthesized by the reaction of halogenated fullerenes with nucleophiles are valuable materials and promising agents for biomedical research. In particular, fullerene pentaphosphonic acid **38** exhibits proton conducting properties, which significantly outperform the characteristics of Nafion, and has proved to be an efficient proton conductor at elevated temperature and low humidity.[62] Carboxylic derivatives of fullerenes C_{60} and C_{70} were employed as materials for charge-transport buffer layers utilized in highly efficient organic solar cells.[97] Sulfide derivatives of fullerenes proved to be thermally labile precursors allowing the development of a radically new technique for deposition of fullerene C_{60} thin films, which made it possible to manufacture organic field-effect transistors and solar cells with improved characteristics.[98]

It was found that water-soluble salts of fullerene C_{60} and C_{70} derivatives containing aromatic carboxylic acid moieties possess pronounced inhibitory activity against human immunodeficiency viruses type 1 and 2 (HIV-1 and HIV-2) comparable with that of the commercial antiretroviral drug Tenofovir®.[3, 31, 67] The assessment of anti-HIV activity of fullerene C_{70} derivatives containing eight phenylpropanoic or phenylbutanoic acid moieties (compounds **42a**,**b**, see Scheme 32) revealed the mechanism of their antiviral activity: inhibition of the activity of the protein gp120 responsible for the entry of the HIV virion into the host cell.[67] It should be emphasized that this mechanism was discovered for fullerene derivatives for the first time, which opens up new opportunities for designing efficient anti-HIV drugs based on these derivatives.

Derivatives of fullerenes C_{60} and C_{70} also proved to be highly active against different influenza virus strains (including avian and swine influenza viruses), herpesviruses and other dangerous viruses.[57, 59, 67] The efficiency of some fullerene-containing compounds in the suppression of influenza viruses of serotype A (H1N1 and H3N2 strains) is higher than that of the best commercial drug Tamiflu®.[59, 67] It should be noted that, apart from pronounced antiviral properties, most of fullerene derivatives exhibit low citotoxicity and acute toxicity.[4, 31, 59] Due to activity simultaneously against several viruses combined with low toxicity,

Scheme 53



fullerene derivatives are promising for the design of multiple-target antiviral agents.

It was found that fullerene derivatives containing several ammonium groups on the carbon cage exhibit high activity against Gram-negative bacteria.[4, 99] Fullerene derivatives containing attached cationoid addends were shown to be assembled on the cell walls of Gram-negative bacteria *via* electrostatic interactions, thus killing the microorganisms.[4]

Carboxyl and hydroxyl derivatives of fullerenes can destroy and prevent the formation of amyloid fibrils involved in the pathology of Alzheimer's disease.[100, 101] It was shown that fullerene derivatives can have a positive effect on the proliferation and differentiation of stem cells[102] and act as selective enzyme inhibitors.[103 – 105] Water-soluble fullerene derivatives were found to exhibit pronounced neuroprotective activity on *in vivo* models and to be able to exert a positive effect on therapeutic targets for Alzheimer's disease and improve animal cognitive characteristics.[106]

Hybrid supramolecular systems based on fullerene derivatives and dyes can act as efficient photosensitizers promising for the practical application in cancer photodynamic therapy.[107, 108]

Therefore, considerable progress in medicinal chemistry of fullerenes was made due to the development of new methods for functionalization of the fullerene cage using halogenated fullerenes as precursors. There are good reasons to expect the further successful development of this field of research.

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