Russian Chemical Reviews **80** (7) 631 – 645 (2011) © 2011 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2011v080n07ABEH004195

Exohedral and skeletal rearrangements in the molecules of fullerene derivatives

D V Ignat'eva, I N Ioffe, S I Troyanov, L N Sidorov

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Abstract. The data on the migration of monoatomic addends, perfluoroalkyl and more complex organic groups in the molecules of fullerene derivatives published mainly in the last decade are analyzed. Skeletal rearrangements of the carbon cage occurring during chemical reactions are considered. The bibliography includes 126 references.

I. Introduction

Fullerenes, a new molecular form of carbon, was discovered by a group of British and American scientists in 1985.[1] The Nobel Prize in Chemistry 1996 was awarded to Robert F Curl, Sir Harold W Kroto and Richard E Smalley for this discovery. The practical interest in fullerenes arose after elaboration of a method to obtain fullerenes in preparative amounts in 1990.[2] Since that time, numerous investigations of physical and chemical properties of fullerenes have been published and the most important results of these studies can be found in monographs.[3 – 5]

Fullerenes are the polyatomic molecules C_n, in which three-coordinate carbon atoms occupy the vertices of polyhedra. The Schlegel diagrams, *i.e.*, projections of a 3D polyhedron on a plane showing all atoms, bonds and rings of a carbon cage, are used for schematic representation of fullerenes and their derivatives. Most of experimentally studied fullerenes contain only five- and six-membered rings and comply with the Isolated Pentagon Rule (IPR).[6, 7] According to this rule, cages with adjacent pentagons (non-IPR-isomers) are supposed to be less stable as compared with cages in which pentagons have no common edges and are surrounded by five six-membered rings (IPR-isomers).

Fullerene molecules contain weakly conjugated double bonds and behave themselves as spherical electron-deficient polyolefins, 'superalkenes'.[8, 9] It is this feature of fullerenes that determines their sufficiently high activity in nucleophilic and radical addition reactions, contrary to graphite, for example. As a consequence, a considerable number of isomers form in any syhthesis of fullerene derivatives depending on the addition pattern of addends to the carbon cage.

Studies of general approaches to functionalization of fullerenes escalated gradually to the development of methods for the synthesis of individual derivatives and methods for their isolation and purification (mostly by chromatography). Intensive investigations in this field resulted in elucidation of molecular structures of numerous derivatives and elaboration of theoretical models for their formation from the parent fullerenes. It is noteworthy that in several cases characteristic features of addition can only be rationalized assuming migration of the addends on the surface of the fullerene sphere. Such rearrangements that occur in the course of synthesis were first discovered for halogen-contaning derivatives and then for derivatves with other addends.

However, it has recently been established that isomerization processes in fullerenes can involve not only the attached atoms and functional groups but the carbon cage itself. Skeletal rearrangements that have previously been postulated predominantly for the transformation mechanisms of 'hot' carbon clusters occurring in the synthesis of fullerenes, were discovered later experimentally under substantially milder conditions. It is particularly remarkable that such rearrangements can result in the formation of both 'nonclassical' fullerenes, *i.e.*, fullerenes with other rings in carbon cages in addition to usual five- and six-membered rings, and non-IPR isomers. Further studies of these processes open broad perspectives for the development of a new and practically unknown field, *viz.*, chemistry of non-IPR fullerenes.

D V Ignat'eva, I N Ioffe, S I Troyanov, L N Sidorov Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory 1, 119991 Moscow, Russian Federation. Fax (7-495) 939 12 40,
tel. (7-495) 939 13 23, e-mail: ignateva_dv@mail.ru (D V Ignat'eva),
tel. (7-495) 939 12 40, e-mail: ioffe@thermo.chem.msu.ru (I N Ioffe),
e-mail: sidorov@thermo.chem.msu.ru (L N Sidorov)
tel. (7-495) 939 53 96, e-mail: stroyanov@thermo.chem.msu.ru
(S I Troyanov)

Received 16 November 2010
Uspekhi Khimii **80** (7) 663 – 678 (2011); translated by P M Chukurov

The present review is devoted to the analysis of theoretical and experimental studies published mainly in the last decade where the problems of skeletal and exohedral rearrangements in fullerene derivatives have been dealt with.

II. Rearrangements of functional groups

1. Derivatives with monoatomic addends: hydrides, fluorides, chlorides and bromides

Halogenation and hydrogenation were the first chemical reactions of fullerenes studied.[10–18] The interest in the possible reaction products was aimed, first of all, at the design of new materials based on the fullerene derivatives with promising properties. For example, polyhalogenated fullerenes possess pronounced electron-withdrawing properties and thus they might be employed for the manufacture of donor-acceptor dyads and molecular devices.[19–22] Hydrogenated fullerenes are promising materials for hydrogen storage.[23]

In the last decade, comprehensive reviews devoted to the preparation of the above-mentioned classes of chemical compounds were published (see, *e.g.*, Refs 24–32), therefore we shall not dwell on the specific features of their synthesis. It should only be noted that preparative methods of the synthesis of different hydrogen-, fluorine-, chlorine- and bromine-containing fullerenes have recently been developed. Structures and properties of these derivatives were established based on the data from X-ray crystallography and/or different spectroscopic methods (IR, Raman, NMR) as well as quantum chemical calculations.

The maximum degree of addition of halogens and hydrogen to fullerens is relatively high. For example, fullerene C_{60} can add up to 48 fluorine atoms without destruction of the carbon cage. Therefore, paucity of the isomeric composition of these compounds appeared to be quite unexpected. Only some of these compounds with an intermediate degree of addition were prepared practically and for them one or several isomers were isolated. At the same time, theoretically 418 770 isomers are possible for the composition $C_{60}X_6$ of which 48 isomers are the pairwise additions to the double bonds. Calculations revealed that experimentally found compounds were the most thermodynamically stable. It is thus not surprising that following the appearance of the first structural data for fullerene hydrides and halides numerous attempts were undertaken to establish mechanisms of their formation.

Early studies in this field were based on a paradigm for organic chemistry implying successive addition of halogen and hydrogen atoms at those positions that have already been activated in the preceding stages of addition.[28,33–35] In particular, S- and T-mechanisms of successive additions were proposed for hydrides and fluorides (Fig. 1). According to this hypothesis, the most obvious kinetic mechanism suggests that following addition of the first two F atoms to a double bond two neighbouring double bonds in two adjacent hexagons become mostly polarized and therefore the most preferable reaction sites. As a result, two competing addition pathways arise after formation of $C_{60}F_6$, *viz.*, S and T (the third putative pathway involving the addition of six fluorine atoms to the same hexagonal ring is less favourable for steric reasons). Evolution of the T-pathway gives, in particular, compound $C_{60}F_{20}$,[36] and evolution of the S-pathway gives $C_{60}F_{18}$ and then isomer $C_{60}F_{36}$ with the *T* symmetry.

Formation of many isomeric fluorofullerenes can be explained with the use of the above-described model but substantial difficulties arose in the cases of some isomers. For example, $C_{60}F_{48}$ does not contain the substructure of $C_{60}F_{36}$ and cannot be described as the pairwise addition product to the double bonds. Similar inconsistency is observed for C_s-$C_{60}F_8$, C_1- and C_3-$C_{60}F_{36}$, for which initial hypotetical structures on the basis of S- and T- mechanisms proved afterwards to be incorrect. Analogous problems appeared for chloro-, bromo- and hydridofullerenes. Attempts to overcome these difficulties were undertaken

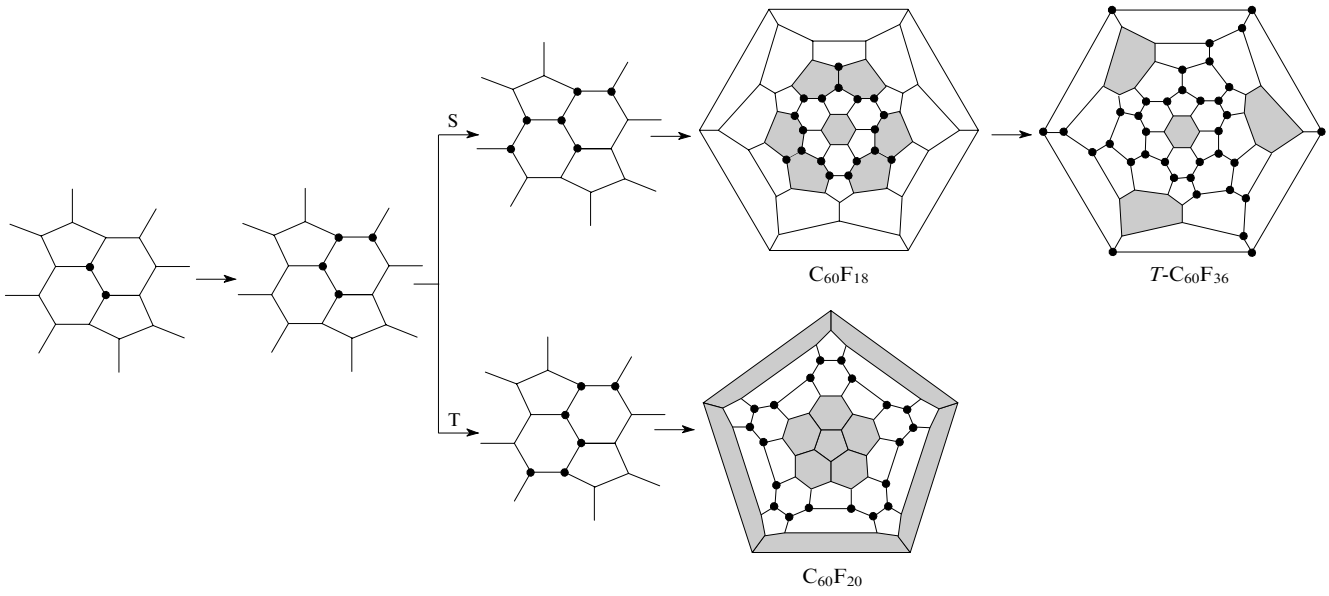


Figure 1. Scheme of succesive addition of F atoms to the fullerene cage. Here and below, the black dots are F atoms.

based on an assumption of several competing addition pathways that are terminated at different steps. However, this assumption cannot be considered as completely convincing if formation of the most stable and extremely limited range of compounds is taken into account.

An extensive bulk of structural data was accumulated in the course of subsequent studies of halogenation and hydrogenation and a phenomenon of addend migration on the fullerene surfaces was discovered. A characteristic feature of this migration is a 'concerted' behaviour of added groups unlike isomerization of conventional organic compounds. In some cases, more than ten addends can change their positions, which results in substantial changes in the overall addition process.

Indirect evidences on the possibility of such rearrangements in fact appeared in the early 1990s. For example, it was shown[14] that dissolution of C_s-$C_{60}Br_6$ in organic solvents was accompanied by its disproportionation with formation of C_{60} and C_{2v}-$C_{60}Br_8$. The latter is characterized by a substantially different bromination pattern.[14] In this case, the disproportionation can proceed through partial or even complete debromination steps (although the first pathway appears more probable) with regard of the weakness of bonds of the Br atoms with the fullerene C atoms. Later, quite convincing evidences have appeared for rearrangements of monoatomic addends much more strongly bound to the fullerene cages.[26, 37–40]

For the first time, rearrangements were proved for fluoro-derivatives of fullerene C_{60}. The fluorination products of the well-known isomers $C_{60}F_{36}$ with molecular fluorine were studied[37] and it was found that the same isomers $C_{60}F_{48}$ devoid of substructures $C_{60}F_{36}$ form, as in the fluorination of C_{60}. The formation of the major isomer D_3-$C_{60}F_{48}$ from the precursor major isomer C_3-$C_{60}F_{36}$ required that no less than five fluorine atoms changed their positions. With account of these facts it was concluded[37] that a complete reconstruction of an addition pattern to the carbon cage is possible resulting in the formation of an equilibrium mixture of isomers at the fluorination temperatures. It is noteworthy, that later a model of the solid-state fluorination has been suggested assuming the thermodynamic control; conditions of selective formation of compounds $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ were formulated.[41]

Putative mechanisms of migration of the F atoms were studied theoretically in the framework of the density functional theory (DFT).[42] Sigmatropic intramolecular shifts and intermolecular migration of the F atoms have later been considered as the most probable rearrangement pathways. An intramolecular migration was established to be possible if the stability of the product is considerably higher than that of the initial isomer. The isomerization of m-$C_{60}F_2$ to o-$C_{60}F_2$ as a result of 1,2-F transfer was given[42] as an example of such a migration. An activation barrier amounts to only 56 kJ mol^{-1} due to the lower energy of formation (by 178 kJ mol^{-1}) of the *ortho*-isomer. Thus, rearrangements of isomers with very high relative energies of formation to the more stable structures can occur in the high-temperature synthesis without kinetic hindrance. If the initial and the final isomers have comparable energies of formation, the activation barrier to the intramolecular transfer of the F atoms appears too high and close to the bond energies. Thus 1,3-F transfer, which 'connects' the preparatively accessible isomers $C_{60}F_{36}$ with symmetries C_1 and C_3 with one another (Fig. 2), is characterized by the activation barrier higher than 300 kJ mol^{-1}. The series of the corresponding 1,2-transfers appears to be even less favourable according to the results of quantum chemical calculations.

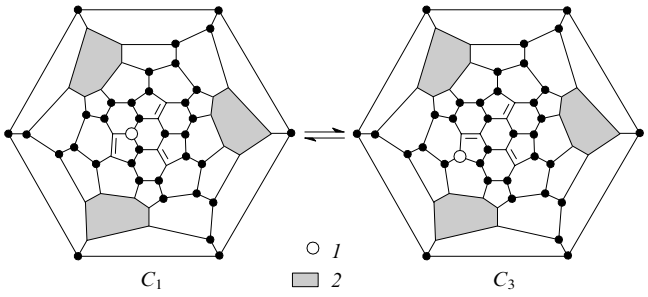


Figure 2. Scheme of rearrangements of the C_1 and C_3 isomers of $C_{60}F_{36}$.
(*1*) migrating F atom, (*2*) π-conjugated six-membered rings.

Consequently, only the mechanism of the intermolecular migration of the F atoms can explain the absence in the synthesis products of such isomers that are slightly less stable than those found experimentally. The results of calculations revealed that transition states (in which a halogen atom is situated between the neighbouring fullerene molecules and breaking of an initial bond is compensated by the formation of a new one) are characterized by rather low activation barriers. For example, the activation energy for the transfer of a F atom from $C_{60}F_{36}$ to C_{60}, (*i.e.*, in the thermodynamically unfavourable direction resulting in two radical products) is as low as 110 kJ mol^{-1}. The reverse process is virtually barrierless because the activation energy for the isomerization of $C_{60}F_{36}$ is reduced by almost 200 kJ mol^{-1} as compared with the intramolecular pathway.[42] Thus, whereas intramolecular rearrangements lead to decomposition of only very unstable isomers, the intermolecular processes should provide an equilibrium isomerization of fluorofullerenes in the solid-state synthesis at elevated temperatures.

The isomerization of fluorofullerenes can be catalyzed by not only neighbouring fullerene molecules but other species as well, while in the latter case this process is possible even in solutions at room temperatures. It is known, for example, that the isomer C_1-$C_{60}F_{36}$ isolated by chromatography converts upon dissolution in a mixture toluene + deuterochloroform with subsequent exposure in air for a few days in an equilibrium mixture of isomers with the symmetry C_1 and C_3 and predominance of the latter.[38] At the same time, the initial isomer remains unchanged in a sealed ampoule in an atmosphere of nitrogen. Theoretical studies revealed that in this case trace amounts of water can release HF owing to hydrolysis and further initiate migration of the F atoms on the carbon cage, which was realized as a chain of nucleophilic substitutions by the S_N2' mechanism. Besides, this F atom can be transferred by a donor transport ligand (D), which forms a charge transfer complex with the fluorofullerene. Migration of the F atoms from the fluorofullerene to the ligand molecule is accompanied by a simultaneous negative charge transfer in the reverse direction and this stabilizes the arisen ion pair $[C_{60}F_{2n-1}]^-[DF]^+$ with closed electronic shell and, as a consequence, lowers the activation barrier to migration.[42]

Presumably, migration between the neighbouring fullerene molecules in the solid-state synthesis can be equally important for other monoatomic addends as well. However, it is molecules with high affinity for each specific type of addends that show transport properties in solutions and melts rather than electron-donating compounds because the extremely high electron affinity for characteristic only of fluorofullerenes. In this context, it is of particular interest to consider chemical properties of fullerene C_{60} polyhydrides. An assumption about easy migraton of the H atoms on this fullerene cage was made[39] on the basis of results of the high-temperature hydrogenation of C_{60}. Only three stable isomers of $C_{60}H_{36}$ with comparable energies form. Exprimental data on the dehydrogenation of a mixture of C_1-, C_3- and T-$C_{60}H_{36}$ evidenced in favour of this assumption.

Prolonged heating of a mixture of isomers of $C_{60}H_{36}$ at the temperatures above 340 °C in molten 9,10-dihydroanthracene results in a single isomer, $C_{60}H_{18}$, with the symmetry C_{3v} as was established by NMR spectroscopy.The structure of this isomer is not compatible with either of structures C_1- and C_3-$C_{60}H_{36}$, *i.e.*, C_{3v}-$C_{60}H_{18}$ can be prepared neither from the C_1- nor from the C_3-isomers of $C_{60}H_{36}$ without rearrangements of H atoms on the fullerene cage. It should be noted that C_{3v}-$C_{60}H_{18}$ and T-$C_{60}H_{36}$ exhibit a common pattern of hydrogen addition, but the amount of T-$C_{60}H_{36}$ in a mixture before heating was so negligible, that it could not serve as the source of the final product $C_{60}H_{18}$.

It was concluded[39] that medium plays the decisive role in migration processes, particularly, exchange of the H atoms between the fullerene molecules and 9,10-dihydroanthracene can occur. It is of note that in another fullerene hydrogenation reaction, *viz.*, the Birch reduction, which is carried out under milder temperature conditions, more complex mixtures of products form[43], *i.e.*, migration of H atoms is hindered.

Specific patterns of chlorination of fullerenes differ from fluorination and hydrogenation owing to the larger size of the Cl atoms. However, in the case of chlorides similar isomerization prosesses take place, *e.g.*, multiple migration of the Cl atoms occurs in the consecutive chlorination of fullerenes in the series (Fig. 3)

$$C_{60} - C_{60}Cl_6 - C_{60}Cl_{24} - C_{60}Cl_{28} - C_{60}Cl_{30}.$$

Contrary to fullerene fluorides and hydrides, a kinetically stable isomer C_2-$C_{60}Cl_{30}$ was isolated from highly chlorinated fullerenes due to comparatively low rate of migration, but this compound converts into the thermodynamically stable D_{3d}-$C_{60}Cl_{30}$ on heating in the presence of a chlorinating agent (Fig. 4).[26] Isomerization of chlorides was found to start at the temperatures above 250 °C. For example, the chlorination of C_{60} or $C_{60}Cl_{24}$ with $SbCl_5$ in the temperature range of 280–300 °C, as well as the isomerization of C_2-$C_{60}Cl_{30}$ at 300 °C, result in the same product, *viz.*, D_{3d}-$C_{60}Cl_{30}$. It should be noted that substantial changes of the chlorination patterns from T_h-$C_{60}Cl_{24}$ (the absence of chlorines attached to the *ortho*-positions and aromatic rings, the presence of only isolated double bonds), to C_2-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$ (chains of Cl atoms, two aromatic rings in mutually inclined hexagons) and to D_{3d}-$C_{60}Cl_{30}$ (closed chains of Cl atoms, two aromatic rings in opposed hexagons of the carbon cage and the 18-*trans*-annulenic aromatic belt) are not possible without

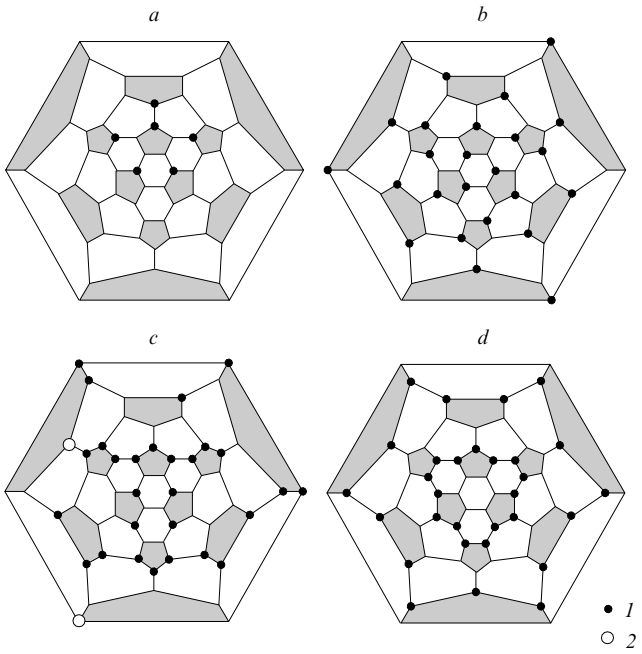


Figure 3. Schlegel diagrams for C_s-$C_{60}Cl_6$ (*a*), T_h-$C_{60}Cl_{24}$ (*b*), C_2-$C_{60}Cl_{28}$ and C_2-$C_{60}Cl_{30}$ (*c*) and D_{3d}-$C_{60}Cl_{30}$ (*d*).
(*1*) Cl atoms common to $C_{60}Cl_{28}$ and $C_{60}Cl_{30}$; (*2*) Cl atoms completing $C_{60}Cl_{28}$ to $C_{60}Cl_{30}$. Here and below the five-membered rings in carbon cages are indicated by grey colour.

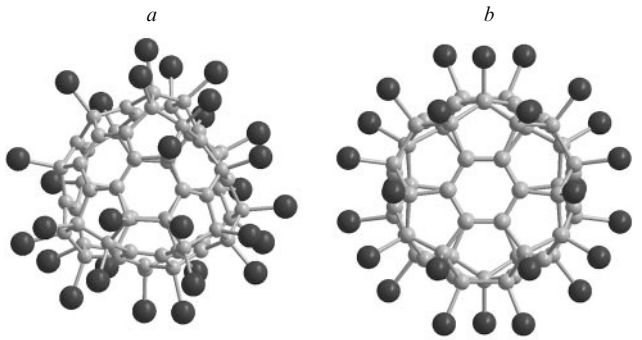


Figure 4. Structures of the molecules of C_2-$C_{60}Cl_{30}$ (*a*) and D_{3d}-$C_{60}Cl_{30}$ (*b*).

migration of a large number of the Cl atoms in the isomerization of these molecules (*e.g.*, the formation of D_{3d}-$C_{60}Cl_{30}$ from T_h-$C_{60}Cl_{24}$ requires that no less than twelve Cl atoms changed their positions). In these systems, complex anions $SbCl_6^-$ can be the effective transport agents for the transfer of the Cl atoms.

Systematic studies of the chlorination of fullerene D_2-C_{76} to D_2-$C_{76}Cl_{34}$ showed that migration of the Cl atoms proceeds under substantially milder conditions (at 220–240 °C).[44] The structures of several intermediate compounds with the compositions from $C_{76}Cl_{24}$ to $C_{76}Cl_{34}$ formed in the system D_2-C_{76}–VCl_4 in the course of the consecutive chlorination were established by X-ray diffraction analysis. Fullerene D_2-C_{76} was proved to form chloroderivatives with two substantially different chorination patterns. The less chlorinated derivatives $C_{76}Cl_{24}$ and $C_{76}Cl_{28}$ contain continuous chains of the adjacent Cl

atoms on the one fullerene hemisphere and a group of more distant Cl atoms on the other. Chloride $C_{76}Cl_{18}$ studied earlier[45] must be referred to this type. At the same time, chlorofullerenes D_2-$C_{76}Cl_n$ with a higher degree of chlorination ($n = 30-34$), are characterized by substantially different positions of the Cl atoms on the carbon cage, in spite of the presence of chain addition fragments. These latter compounds cannot be produced by just addition of the Cl atoms to either of the described above isomers (Fig. 5).

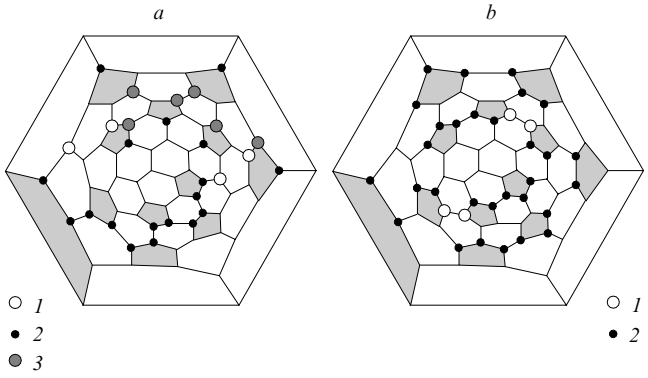


Figure 5. Schlegel diagrams for $C_{76}Cl_{28}$ (*a*) and $C_{76}Cl_{34}$ (*b*);
a: (*1*) chlorine atoms completing $C_{76}Cl_{24}$ to $C_{76}Cl_{28}$; (*2*) chlorine atoms common to $C_{76}Cl_{18}$, $C_{76}Cl_{24}$ and $C_{76}Cl_{28}$; (*3*) chlorine atoms completing $C_{76}Cl_{18}$ to $C_{76}Cl_{24}$;
b: (*1*) chlorine atoms that are absent in $C_{76}Cl_{30}$ and present on either one or the other side of $C_{76}Cl_{32}$; (*2*) chlorine atoms common to $C_{76}Cl_{30}$, $C_{76}Cl_{32}$ and $C_{76}Cl_{34}$.

In conclusion, we should note that migration of halogen atoms in molecules of unsaturated organic compounds is well known. Fullerenes are spherical polyolefins and, consequently, it is not surprising that rearrangements in alkenes and cycloalkenes have similar features with the isomerization of fullerenes derivatives. But the 'concerted' character of halogen migration involving ten and more atoms is an exceptionally interesting and specific property of fullerene derivatives.

2. Perfluoroalkyl derivatives

Processes of fullerene perfluoroalkylation were studied together with halogenation and hydrogenation. But perfluoroalkyl derivatives of fullerenes could be isolated for the first time as individual compounds much later than hydrides and halides, just as by-products of the solid-state fluorination of fullerenes.[46-49] Afterwards, experimental procedures were developed for the targeted synthesis of perfluoroalkyl derivatives with the compositions $C_{2m}(R_F)_{2n}$ ($R_F = CF_3$, C_2F_5, iso-C_3F_7, n-C_3F_7, n-C_4F_9, n-C_6F_{13}; $m = 30$, 35, 38, 39, 41–44, 46–48; $n = 1-10$). Currently, the structures of many compounds of these classes were established by either X-ray diffraction analysis or one- and two-dimensional ^{19}F NMR spectroscopy in combination with quantum chemical calculations.[31,50-100]

Qualitative composition of perfluoroalkylation products depends on many experimental factors of which the most significant are the choice of sources of the corresponding substituents, temperature, overall composition of the reaction mixture and the synthesis conditions. Thus 'lower'† trifluoromethyl derivatives can be prepared by treating a fullerene with CF_3COOAg with subsequent three-step fractional sublimation,[52,54] and also by annealing mixtures of 'higher' derivatives with a pure fullerene.[55] Derivatives with a larger number of added functional groups are prepared by trifluoromethylation of C_{60} or C_{70} in a flow-type reactor[70,71] or by heating fullerenes in a sealed glass tube in an atmosphere of CF_3I.[80]

Independently of the synthesis method, the perfluoroalkylation products are mixtures of derivatives with a wide range of the addition degree and a complex isomeric composition, which sharply differentiate them from the halogenation and hydrogenation products. The highly selective (85%) formation of S_6-$C_{60}(CF_3)_{12}$, which condenses in a cooler part of a tube in the synthesis in the atmosphere of CF_3I, is a unique exception.[81]

Certainly, the group of experimentally observed compounds is limited and determined by their thermodynamic properties. In general, relative energies of formation of isolated and described trifluoromethyl derivatives fall within 0–30 kJ mol^{-1} (the energy of the most stable isomer with the corresponding composition was chosen as the reference value). But if the products of synthesis are quickly removed from the reaction zone, as, for example, in the trifluoromethylation of fullerene in the flow of CF_3I, then kinetically stable isomers with higher energies can also be present. In particular, the isomer C_1-$C_{60}(CF_3)_{12}$ (Ref. 75), which is less stable (by 40 kJ mol^{-1}) in comparison with the most stable isomer S_6-$C_{60}(CF_3)_{12}$ (Ref. 81) according to the results of quantum chemical calculations, was succesfully isolated from the flow reaction products.

Several isomers with relatively low energies of formation are absent among the products of the direct trifluoromethylation. For example, only two isomers $C_{70}(CF_3)_{12}$ are found in the reaction products of fullerene C_{70} with trifluoromethyl iodide in a sealed tube, whereas no less than three additional compounds must exist with practically the same energies in accordance with quantum chemical calculations.[80] Interpretation of these facts was suggested with recourse to the Bell–Evans–Polanyi principle.[60] According to this principle, a correlation between the activation energies and enthalpies exists in a series of same-type reactions.‡

The essence of the Bell–Evans–Polanyi principle lies in the fact that reactions with formation of more thermodynamically favourable compounds proceed with a higher rate than those with formation of less stable compounds. Consequently, one should expect the accumulation of those compounds that are formed relatively fast and, on the contrary, undergo relatively slow subsequent functionalization. It can be assumed that the addition of the CF_3 radical to other radical species with an odd number of CF_3 groups will proceed more quickly than subsequent trifluoromethylation of a molecule $C_m(CF_3)_{2n}$ with a closed electron shell.

† Here and below, 'higher' perfluoroalkyl derivatives of fullerenes are those containing 12 to 20 added groups and 'lower' derivatives are those with 2 to 10 attached groups.

‡ In this case, reactions of the same type are the steps of succesive addition of addends to free double bonds. Reactions of other types are excluded from consideration.

Thus, the following scheme of consecutive trifluoromethylation is probable. The positions where the trifluoromethyl groups attach to the initial molecule $C_m(CF_3)_{2n}$ with the highest probability are determined by relative energies of formation of the corresponding isomers of a radical $^{\bullet}C_m(CF_3)_{2n+1}$. The position of addition of the second CF_3 group, which will complete the radical to the molecule $C_m(CF_3)_{2n+2}$, will be determined by localization of the spin density in this radical and by steric factors (the effect of the groups already attached). As a rule, competition takes place between addition to *ortho*- and *para*-positions relative to the $(2n+1)$-th group added the last. Most often, addition to the *para*-position occurs owing to the large size of the CF_3 groups, although addition to the *ortho*-position must be more favourable regarding distribution of the spin density. *ortho*-Additions mainly occur at high degrees of trifluoromethylation (when the carbon cage is rather densely occupied).[76–78] If we consider addition to a free carbon cage C_m, then it will be possible to predict products for different degrees of trifluoromethylation and genetic interrelations between them.

Using structural data on experimentally found isomers and calculated energies of formation for theoretically possible compounds, a simple criterion of a synthetic availability could be formulated: an isomer with the composition $C_{60/70}(CF_3)_n$ will more probably be accumulated in the reaction products if relative energies of formation of this isomer and all precursors fall in the range from 0 to 30 kJ mol^{-1} and if this isomer possesses low reactivity and its precursors possess high reactivity.[60] An example of such a rationale for the formation of experimentally observed products using branched chains of consecutive conversions

$$C_{60} - {}^{\bullet}C_{60}CF_3 - C_{60}(CF_3)_2 - \ldots - C_{60}(CF_3)_6$$

can be found in the study.[52] It is of note that one of the isomers of $C_{60}(CF_3)_6$ is the simplest compound of the trifluoromethyl derivatives studied in which the two groups are in the *ortho*-contact.[62] Various limitations for *ortho*-addition of the bulky CF_3 groups are often imposed on

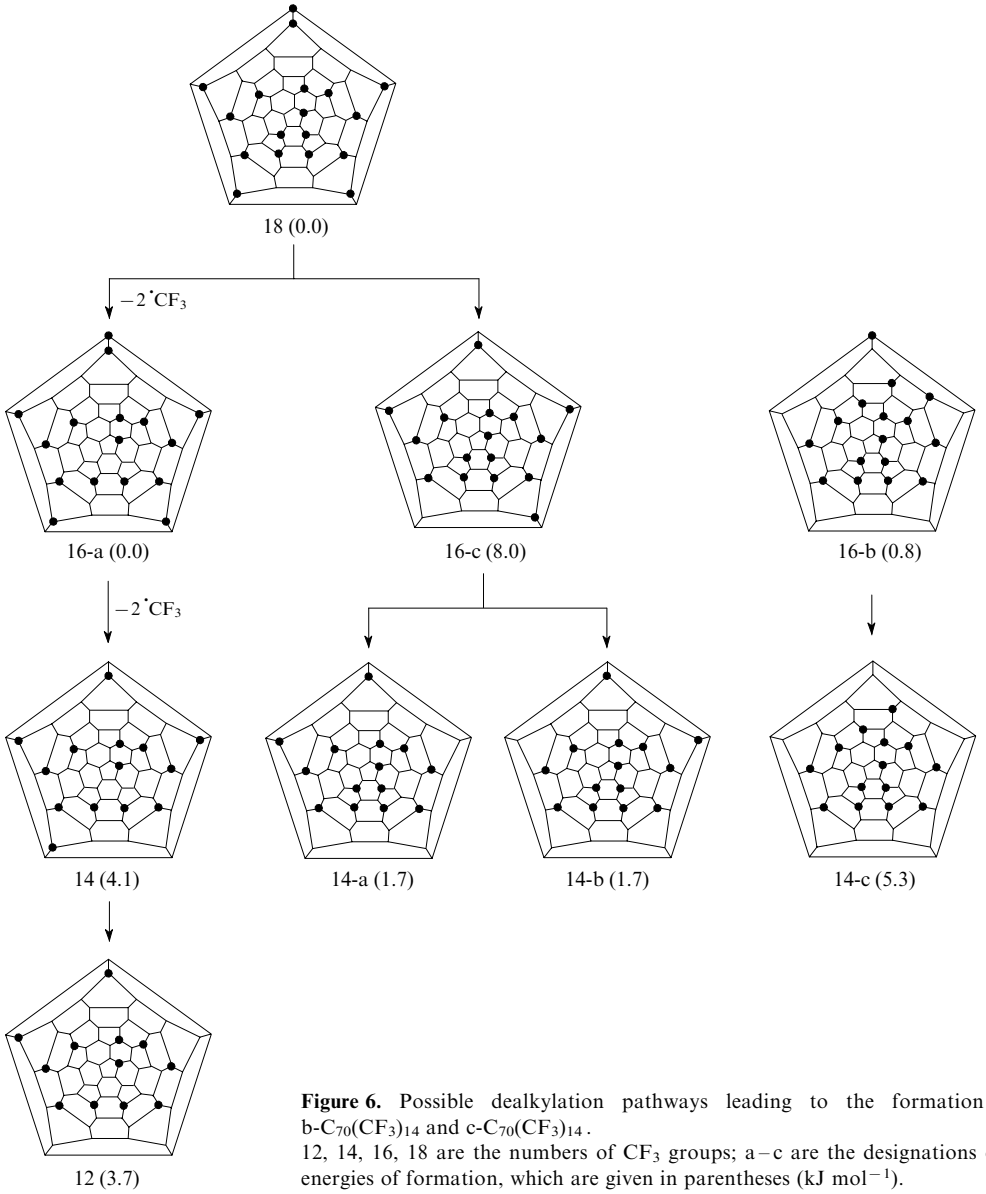


Figure 6. Possible dealkylation pathways leading to the formation of $C_{70}(CF_3)_{12}$, a-$C_{70}(CF_3)_{14}$, b-$C_{70}(CF_3)_{14}$ and c-$C_{70}(CF_3)_{14}$.
12, 14, 16, 18 are the numbers of CF_3 groups; a–c are the designations of isomers with different relative energies of formation, which are given in parentheses (kJ mol^{-1}).

theoretical calculations for limiting the number of possible isomers, but the examples of $C_{60}(CF_3)_6$ and some other compounds demonstrate that such limitations must be introduced with care.

Thus, approaches based on the Bell–Evans–Polanyi principle are convenient for analysis of the regiochemical features of the trifluoromethyl fullerene derivatives, but only as far as isomerization processes may be ignored. Up to date, the migration of trifluoromethyl groups on a fullerene cage has been much less studied than the migration of halogen and hydrogen atoms. Experiments on thermal annealing of mixtures of higher trifluoromethyl derivatives indicate indirectly the possibility of such rearrangements involving CF_3 groups. It is known that apart from other isomers, the reaction products contain thermodynamically stable but kinetically unstable (in relation to further trifluoromethylation) isomer of $C_{70}(CF_3)_{12}$ (see Ref. 60) and three $C_{70}(CF_3)_{14}$ isomers (a–c).[55,60] (Fig. 6). Certainly, these compounds could be formed upon the removal of two or more CF_3 groups from more trifluoromethylated derivatives. In particular, it can be seen in Fig. 6 that the addition pattern present in these compounds is also found in the isomers of $C_{70}(CF_3)_{16}$ (Refs 60, 78) and $C_{70}(CF_3)_{18}$ (Ref. 78) prepared by direct synthesis. However, it was shown[60] that thermal annealing does not merely increase the portion of thermodynamically stable isomers due to direct dealkylation but also shifts the composition of the starting mixture toward equilibrium. This observation means that under certain conditions, the system of trifluoromethyl derivatives can also be thermodynamically controlled, *i.e.*, the composition of the mixture can be determined by the Gibbs energies of the isomers.

In the study cited,[60] the products of trifluoromethylaton of two individual isomers $C_{70}(CF_3)_{12}$ (Fig. 7) were analyzed

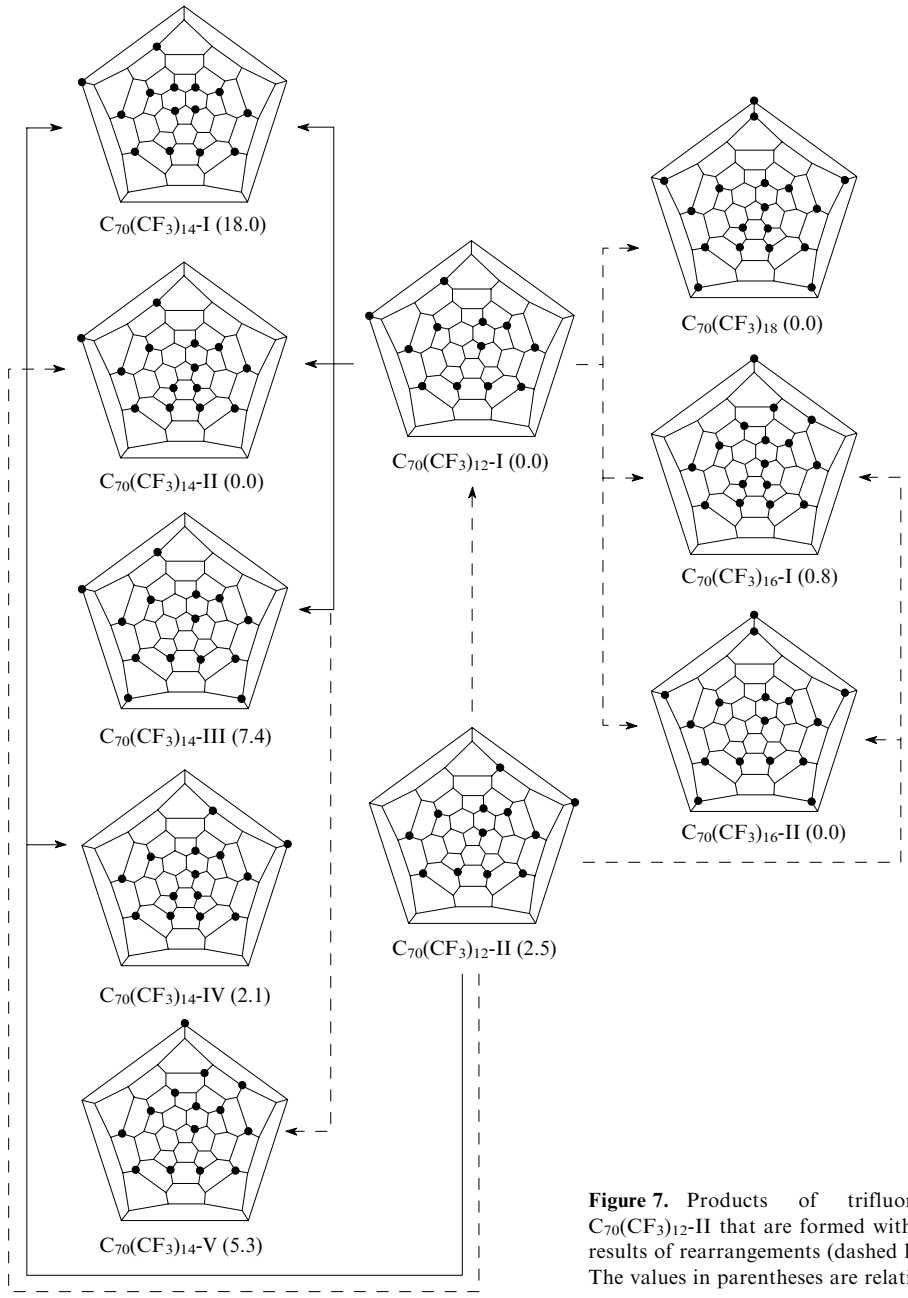


Figure 7. Products of trifluoromethylation of $C_{70}(CF_3)_{12}$-I and $C_{70}(CF_3)_{12}$-II that are formed without rearrangements (solid lines) and as a results of rearrangements (dashed lines).
The values in parentheses are relative formation energies (kJ mol^{-1}).

in detail and unique direct evidence for the CF_3 migration over the fullerene cage was given. The authors were able to show that trifluoromethylation of $C_{70}(CF_3)_{12}$-II is accompanied by the formation of $C_{70}(CF_3)_{12}$-I. In addition, the products of reactions with $C_{70}(CF_3)_{12}$-I and $C_{70}(CF_3)_{12}$-II were found to contain the isomers $C_{70}(CF_3)_{14}$-V, $C_{70}(CF_3)_{16}$-I and $C_{70}(CF_3)_{16}$-II. The formation of these isomers is impossible at any fixed positions of addends in any of the initial isomers. It is obvious that, together with above-indicated compounds, the products of direct addition of CF_3 groups to the initial trifluoromethylfullerenes were also formed. For example, $C_{70}(CF_3)_{12}$-I gives all of the expected compounds: $C_{70}(CF_3)_{14}$-I, $C_{70}(CF_3)_{14}$-II and $C_{70}(CF_3)_{14}$-III, while $C_{70}(CF_3)_{12}$-II is converted into $C_{70}(CF_3)_{14}$-I and $C_{70}(CF_3)_{14}$-IV. The formation of energetically favourable isomers is the general trend in this case. For example, the isomers $C_{70}(CF_3)_{16}$-I, $C_{70}(CF_3)_{16}$-II and $C_{70}(CF_3)_{18}$ are energetically the most stable among all possible isomers of $C_{70}(CF_3)_{16}$ and $C_{70}(CF_3)_{18}$.[78] Nevertheless, some energetically stable isomers have not been detected despite the rearrangements. In particular, the isomers $C_{70}(CF_3)_{14}$-IV (2.1 kJ mol^{-1}) and $C_{70}(CF_3)_{14}$-III (7.4 kJ mol^{-1}) were not found among the trifluoromethylation products of $C_{70}(CF_3)_{12}$-I or C_{70}; however, in both cases, $C_{70}(CF_3)_{14}$-I [which contains the substructures of both isomers of $C_{70}(CF_3)_{12}$] was found, although its relative energy is rather high (18.0 kJ mol^{-1}). Thus, in the case of trifluoromethyl fullerene derivatives, the effect of functional group migration on the isomeric composition appeared not to be crucial but is comparable with the effects of kinetic factors.

Migration of CF_3 groups on a fullerene cage was considered theoretically in a study[42] where intra- and intermolecular migrations of these groups were compared similarly to the rearrangements of F atoms. As was shown above, intermolecular migration of monoatomic addends, for example halogens, is generally more favourable, because transition states with a relatively low activation energy exist for such addends. In these transition states, the halogen atom is located between neighbouring molecules and the cleavage of the outgoing bond is counterbalanced by the formation of the new bond.[42] There are no such states for the CF_3 group because the formation of a chemical bond with a neighbouring molecule requires an inversion of this group, *i.e.*, the carbon atom of this group has to turn toward the new bond. This inversion can occur only after almost complete cleavage of the outgoing bond (Fig. 8). Thus, intermolecular migration of CF_3 groups has no advantages over intramolecular migration, and both processes can provide fast conversion of only energetically substantially unfavourable isomers.

The rearrangements of trifluoromethyl groups in relatively stable isomers should be considered as a much slower sequence of their elimination and addition steps that compete with side reactions such as decomposition to give inert C_2F_6. The isomerization processes make a significant contribution to the product composition only if the rates of trifluoromethylation and CF_3 elimination are comparable. In particular, isomers with lower relative energies usually predominate in the case of ampoule synthesis (long residence time and comparatively slow removal of products from the reaction zone). Apparently, similar trends hold for other perfluoroalkyl fullerene derivatives, for example, for the compounds $C_m(C_2F_5)_n$ and $C_m(C_3F_7)_n$.

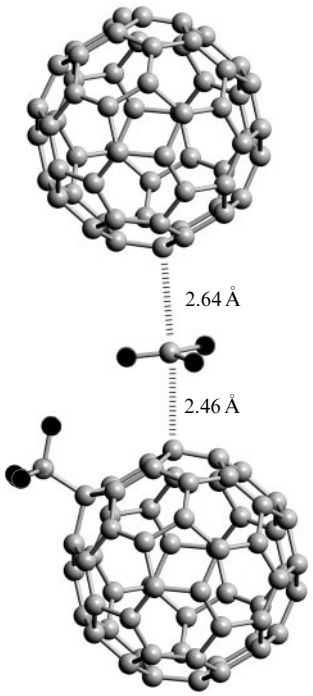


Figure 8. Optimized geometry of the transition state of the CF_3 group for the transition from $C_{60}(CF_3)_2$ to C_{60}.

3. Rearrangements with migration of bulky functional groups

The rearrangements on a fullerene cage are far from being limited by the migration of small functional groups. In some studies (see, *e.g.* Refs 101, 102), it was shown that irreversible reactions well-known in the traditional organic chemistry ([2 + 1]-cycloaddition of carbenes, nucleophillic cyclopropanation, [2 + 3]-cycloaddition of azomethine ylides) become reversible with fullerenes. These facts suggest that polyatomic organic addends attached to fullerene are sufficiently labile and can change their positions on the cage to give the most stable isomers. This assumption is supported by the solid-phase disproportionation of the anthracene C_{60} monoadduct to the *trans*-1-isomer of the corresponding bis(adduct) and the initial C_{60},[103] migration of the anthracene groups attached to $C_{60}F_{18}$ at room temperature,[20] transformation of the pyrrolidine derivatives of the endohedral fullerene $Sc_3N@C_{80}$.[104]

The rearrangements of large functional groups and the possible mechanisms of these processes were considered most comprehensively by Khakina *et al.*[105] The authors found expermentally that heating of the *trans*-annulene derivatives (trannulenes) $C_{60}F_{15}[CX(COOR)_2]_3$ in 1,2-dichlorobenzene induces the migration of three organic addends from one hemisphere of the carbon cage to the other, and this leads to the formation of thermodynamically more favourable derivatives (so-called, triumphenes) (Fig. 9). It is of interest that compounds of both types can be prepared under certain conditions of synthesis from the same precursor, $C_{60}F_{18}$. If the reaction proceeds according to the S_N1 mechanism, three F atoms are replaced by aromatic addends to give triumphene isostructural with the initial fluorofullerene. If the reaction follows less common S_N2'' mechanism, then the $^-CX(COOAlk)_2$ carbanions add in the δ-positions (relative to carbon atoms from which F atoms are detached), and this leads to the formation of the aromatic 18-membered *trans*-annulene ring at the equator of the molecule. In view of the fact that trannulenes are converted to triumphenes under comparatively mild con-

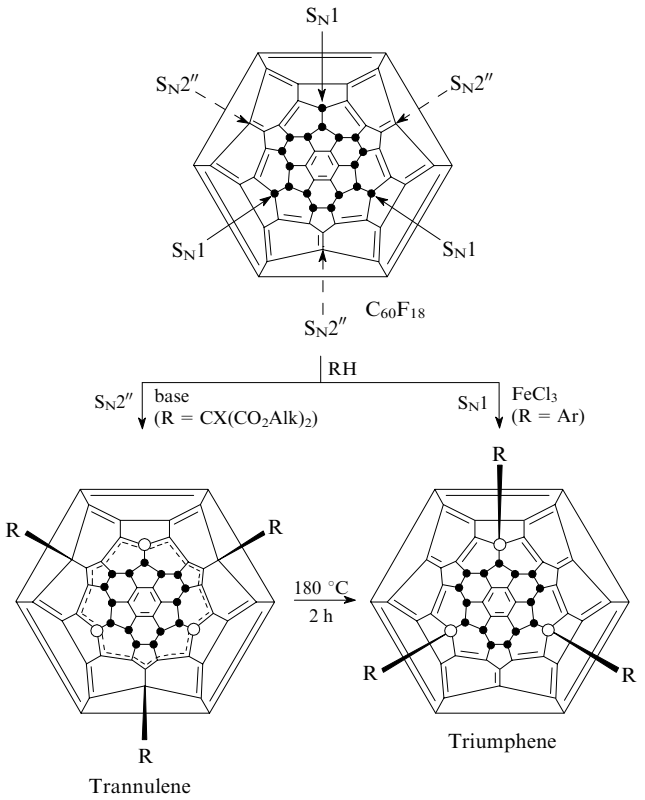


Figure 9. Schemes of formation of trannulene and triumphene derivatives from $C_{60}F_{18}$ and conversions of trannulene derivatives to triumphenes for X = Br, COOAlk.
The hollow circles indicate the sites of attachment of substituents upon the rearrangement.

ditions, the authors concluded that formation of trannulenes from $C_{60}F_{18}$ is governed by kinetic factors, whereas arylation of $C_{60}F_{18}$ to triumphenes is a thermodynamically controlled process.

Two alternatives were proposed as possible mechanisms of trannulene isomerization. On the one hand, migration of aliphatic substituents on the fullerene cage can proceed by an intramolecular mechanism where organic groups migrate from one hemisphere to the other along the chain of conjugated C=C double bonds. On the other hand, triumphenes can be formed by the elimination–addition mechanism where organic radicals or anions are first eliminated from trannulene and then attached to the thermodynamically most favourable positions on the carbon cage. In order to find out which of the mechanisms is realized in practice, isomerization of trannulenes was studied in the presence of excess unsaturated compounds capable to effectively capturing the radicals and nucleophilic anions detached from the carbon cage. It was found that even under these conditions, isomerization proceeds with high yields (up to 90%), which attests to an intramolecular mechanism of the rearrangements of trannulenes to triumphenes *via* three succesive δ-shifts of the $CX(COOAlk)_2$ groups.

III. Skeletal rearrangements

The rearrangements that directly involve the cage carbon atoms also arouse considerable scientific interest. In particular, these processes can have practical significance for the use of fullerenes as molecular containers where it will be possible to open or close a window in the carbon cage. Generally, two types of processes can be distinguished: cleavage of one or more C–C σ-bonds of the carbon cage to give fulleroids (open isomers) and changes in the topology of the bond system of the carbon cage and, consequently, the whole system of rings that form the cage.

The fullerene cage opening was studied in considerable detail. The [5,6]- and [6,6]-open isomers are formed as a result of cycloaddition to compounds such as nitrenes, carbenes, diazo compounds, azides and dienes. Examples of various isomeric structures are given in Fig. 10. In most cases, the major products of these reactions are [6,6]-closed adducts, fulleroid structures being present as impurities. Nevertheless, a series of works were published devoted to the specific features of synthesis, structures and theoretical consideration of the formation mechanisms of particularly open adducts. Detailed information on this issues can be found in recent reviews.[106–108]

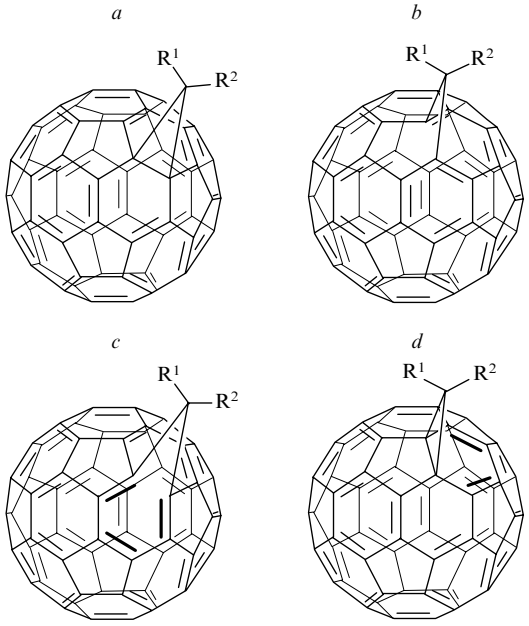


Figure 10. Four possible products of the addition of the R^1R^2C group to C_{60} fullerene.
(*a*) [6,6]-closed, (*b*) [5,6]-open, (*c*) [6,6]-open, (*d*) [5,6]-closed.

The interconversions of open and closed isomers are of particular interest. Numerous quantum chemical calculations revealed that among the cycloaddition products, [6,6]-closed isomers are thermodynamically more stable than [5,6]-open isomers, whereas [6,6]-open and [5,6]-closed compounds are even more unstable.[109,110] It is not surprising that isomerization of open adducts into closed ones is more often observed in experiments. However, thermally activated reverse rearrangements are also known.[107,108]

Skeletal rearrangements with conservation of the whole structure of the carbon cage are much less studied. Before discussing the rearrangements of this type, consider the problem of systematization and numbering of classical (containng only pentagonal and hexagonal faces) fullerene cages, a solution to which was proposed in a monograph.[6]

According to the spiral conjecture, all faces of a fullerene polyhedron can be wound up according to a spiral pattern and ordinally numbered.[111] The resulting sequence of digits 5 and 6 is called the spiral code and unambiguously describes the cage. Since the spiral can start practically with any face of the fullerene polyhedron, the same structure can be described by different spiral codes. For example, if one of pentagons is chosen as the starting face of IPR-C_{60}, the spiral code will be as follows:

5666665656565656656565656566665;

if the sequence of faces is started with the hexagon, then, depending on the selection of the second face, the spiral code will be either

6565656665665665656656565656566

or

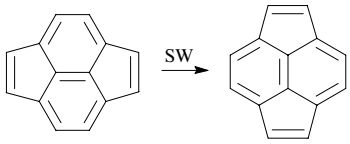
6656565656656656565665666565656.

Since for less symmetrical cages the number of different spirals will be even greater, the unambiguous correspondence between the spiral code and the structure is attained by choosing the minimum (consdering each sequence of digits 5 and 6 as a number) spiral, *i.e.*, the canonical spiral. Among the above spiral codes, the first code starting with a pentagonal face is canonical.

A unique identifier of a fullerene cage is the ordinal number of its canonical spiral in the list of canonical spiral codes of all isomers with the given number of carbon atoms arranged in the order of increasing numerical value. In particular, the most abundant IPR-fullerene C_{60} is designated by $^{\#1812}C_{60}$, since its canonical spiral occupies the last place in the list of canonical spirals for the 1812 possible [5,6]-isomers (the spiral code begins from combination 56 owing to the absence of adjacent pentagons).

The ordinal number of the canonical spiral in the list that includes only the cages that obey the IPR-rule can be employed as an alternative identifier of an IPR-isomer. For example, two isomers of C_{76} fullerene can be designated as $C_{76}(1)$ and $C_{76}(2)$, which corresponds to the general classification $^{\#19150}C_{76}$ and $^{\#19151}C_{76}$. It should be noted that this numbering has a meaning for fullerenes with more than 76 carbon atoms in the cage, since fullerenes C_{60}, C_{70}, C_{72} and C_{74} each have only one IPR-isomer. The cages of other higher fullerenes can be constructed in two or more ways, their number rapidly increasing with increase in the size of the fullerene cage: C_{76}, C_{78}, C_{84}, C_{90} and C_{96} fullerenes have 2, 5, 24, 46 and 187 IPR-isomers, respectively.[6] More rarely, skeletal isomers are identified according to their point group of symmetry. This method is not universal because there exist isomers with the same group of symmetry and, moreover, asymmetrical cages start to prevail with increase in the size of the fullerene cage.

It has been considered for a long time that the interconversions of $^{\#N}C_n$ and $^{\#M}C_n$ fullerenes can proceed only in the course of their high-temperature synthesis and result in the formation of the most stable cages, which must obey the IPR-rule in the case of unfunctionalized fullerenes. The succesive Stone–Wales (SW) rearrangements, *i.e.*, rotation of C_2 fragments by 90° with reconnection of neighbouring bonds, are considered to be the key mechanism of these cage rearrangements.



Usually such rotations are studied for pyracylene fragments consisting of two five- and two six-membered rings.[6, 112, 113] It should be mentioned that the IPR-rule can be violated for endohedral metallofullerenes, which are prepared by electric arc synthesis in the presence of metals (Sc, La, Y, *etc.*), and also for exohedral derivatives, which are obtained by injection of additives (CCl_4, Cl_2, CH_4) directly into the buffer gas during the electric arc synthesis rather than from pre-formed carbon cages. The principles of stabilization of fused pentagons both by encapsulated metal atoms and by external addends have been considered in detail.[114, 115]

The presence of addends can lead to violation of the general criterion of fullerene stability, according to which non-IPR-isomers are less stable.§ For example, the energy of formation of the non-IPR-isomer $^{\#1809}C_{60}Cl_8$, which is formed in the modified fullerene synthesis, is substantially lower than that of chlorides of the IPR-isomer $^{\#1812}C_{60}$ (Ref. 118). A series of calculations[119] demonstrated that endo- and exohedral non-IPR fullerene derivatives are energetically more favourable in some cases than the corresponding IPR-analogues. These theoretical calculations were performed only for the most abundant fullerenes, C_{60} and C_{70}, but it can be assumed that similar tendency will also be maintained for higher fullerenes.

In spite of the thermodynamic stability of some non-IPR-fullerene derivatives, their formation in functionalization of IPR-isomers has not been observed until recently. For example, the above-mentioned $^{\#1809}C_{60}Cl_8$ cannot be prepared by conventional chlorination of the IPR-isomer $^{\#1812}C_{60}$ (Ref. 118). Similarly, the fluorination of $^{\#1812}C_{60}$ does not give $^{\#1784}C_{60}F_{48}$ whose energy is more than 500 kJ mol^{-1} lower than that of the known D_3- and S_6-isomers of $C_{60}F_{48}$.[119] This is attributable to the too high, for usual chemical conditions, activation energy of the Stone–Wales rearrangements, which can reach 7 eV according to calculations for the non-functionalized C_{60} (Ref. 120) or 5 eV when the transition state is stabilized by hydrogen atoms or alkyl groups.[112] Therefore, the first reported case of the Stone–Wales rearrangement induced by chemical treatment of the carbon cage appears unexpected: among the products of chlorination of the pure IPR-isomer of $^{\#19150}C_{76}$ with antimony pentachloride at 340 °C, the non-IPR- isomer $^{\#18917}C_{76}Cl_{24}$ with five pairs of adjacent pentagons was detected and structurally characterized.[121]

Initially, considering the possible pathways of this skeletal rearrangement showed that the reconstruction of the carbon cage includes at least seven succesive Stone–Wales rearrangements and that each rearrangement proceeds through two transition states stabilized by chlorine

§ The only case where the violation of IPR-rule for non-modified fullerenes can be assumed is $^{\#11188}C_{72}$ fullerene, which is more stable than the only IPR-isomer $^{\#11190}C_{72}$ according to calculations. The fullerene $^{\#11188}C_{72}$ has not yet been isolated in a pure state but the structure of this fullerene was supported by X-ray crystallographic data for $^{\#11188}C_{72}Cl_4$ (Refs 116, 117).

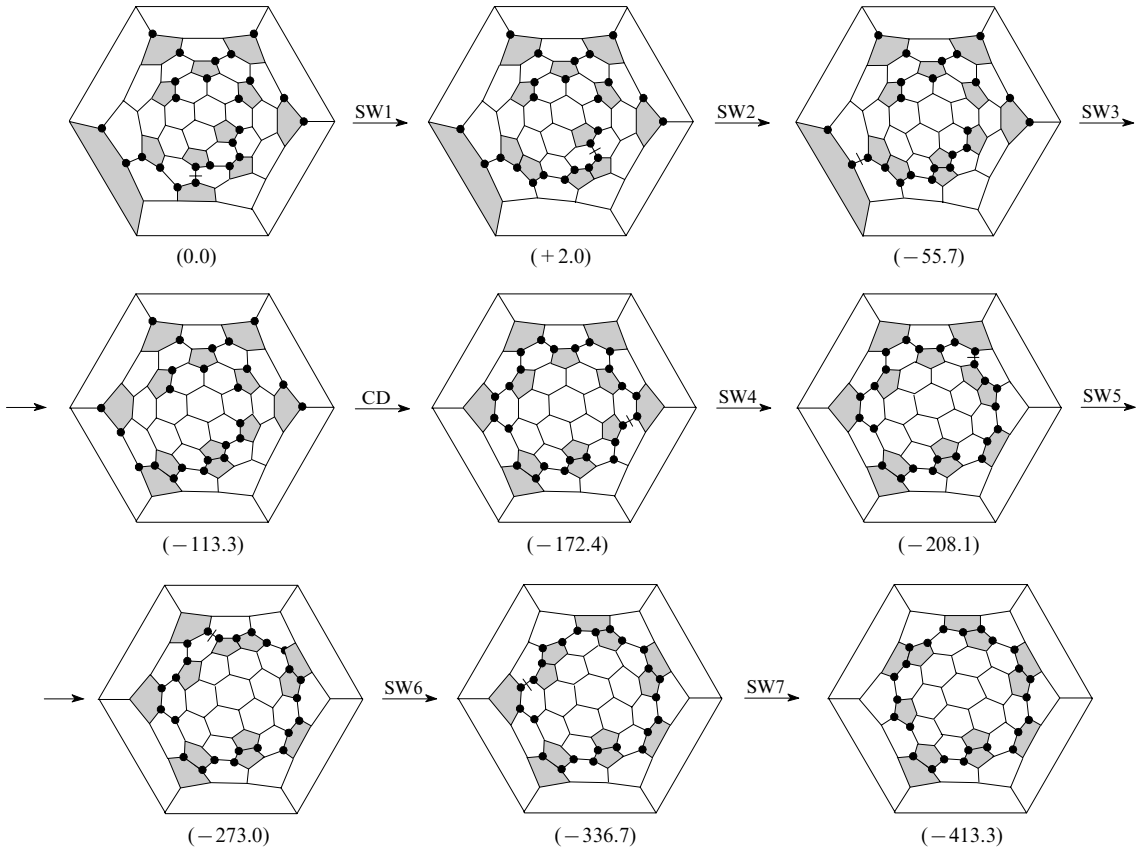


Figure 11. Scheme of transformation of $^{\#19150}C_{76}Cl_{24}$ to $^{\#18917}C_{76}Cl_{24}$.
The values in parentheses are the energies of formation (kJ mol^{-1}); SW is the Stone — Wales rearrangement; CD is the migration of Cl atoms; the bonds that are rotated by 90° are crossed.

atoms and characterized by relatively low values of the activation energy (2.1 and 1.3 eV for the last step).[121] Later, the transformation of the presumptive precursor of the IPR-isomer $^{\#19150}C_{76}Cl_{24}$ to the non-IPR-isomer $^{\#18917}C_{76}Cl_{24}$ was investigated theoretically in more detail.[44] The possible scheme of this transformation is shown in Fig. 11. This scheme includes the minimum number of steps, and in each step (except for the first one), the energy of the molecule slightly diminishes. Apart from the Stone – Wales rearrangements, this scheme includes the step of multiple migration of Cl atoms over the intermediate carbon cage. The reaction medium, antimony pentachloride, plays the key role, as it was found, both in the migration of Cl atoms and in the skeletal rearrangements. This compound forms ion pairs with chlorofullerene, $[C_{76}Cl_{23}]^+SbCl_6^-$, which can be regarded as transition states for Cl atom migration between different positions of the carbon cage. Owing to this, the activation energy does not exceed 2.5 eV even for the most unfavourable steps of the skeletal rearrangement (Fig. 12).

Apart from the Stone – Wales rearrangements where the number of carbon atoms in the cage is retained, transformations with cage expansion or contraction are also possible under certain conditions. These transformations are usually due to either incorporation or loss of a C_2 unit giving so-called non-classical fullerenes, which contain other rings in the cage together with five- and six-membered ones. The incorporaion of C_2 into the carbon cage can be achieved by conventional organic reactions. For example, the reaction of I_h-C_{60} with 1,2,4,5-tetrazines leads to the expansion of the carbon cage to C_{2v}-C_{62} with a four-membered ring in the structure.[122] It has been considered for some time that the processes accompanied by loss of C_2, like the Stone – Wales rearrangements, can be induced only by high-energy impact (according to mass spectrometry data, approximately 8 eV is needed).[123] Even the conditions of high-temperature (550 °C) fluorination of C_{60} where the exothermic effect is compensated by the formation of $C_{58}F_{18}$ and $C_{58}F_{17}CF_3$ as by-products[124] seem too mild for such processes. The structures of these compounds proposed based on ^{19}F NMR data are characterized by the presence of a heptagon adjacent to two pentagons in the carbon cage (Fig. 13 *a*). Apparently, in this case, the process should be regarded as not a rearrangement in the strict meaning of the term but rather as a thermal destruction upon local overheating. Similarly, higher fullerenes (C_{76}, C_{78}, C_{84}) degrade to C_{60} and C_{70} upon annealing at 1000 °C without any additives.[125]

Yet another unexpected experimental fact, after the preparation of $^{\#18917}C_{76}Cl_{24}$, is the formation of chlorofullerene $C_{84}Cl_{32}$ from the pure C_s-C_{86}(16) isomer upon the reaction with vanadiun tetrachloride at the temperature of only 250 °C.[126] The isolated $C_{84}Cl_{32}$ was found to be very similar to the chlorofullerene $C_{86}Cl_{28}$, which retains the initial carbon cage. This similarity relates both to the structure of the carbon cage and to the chlorination patterns, which isolate three aromatic fragments. The different

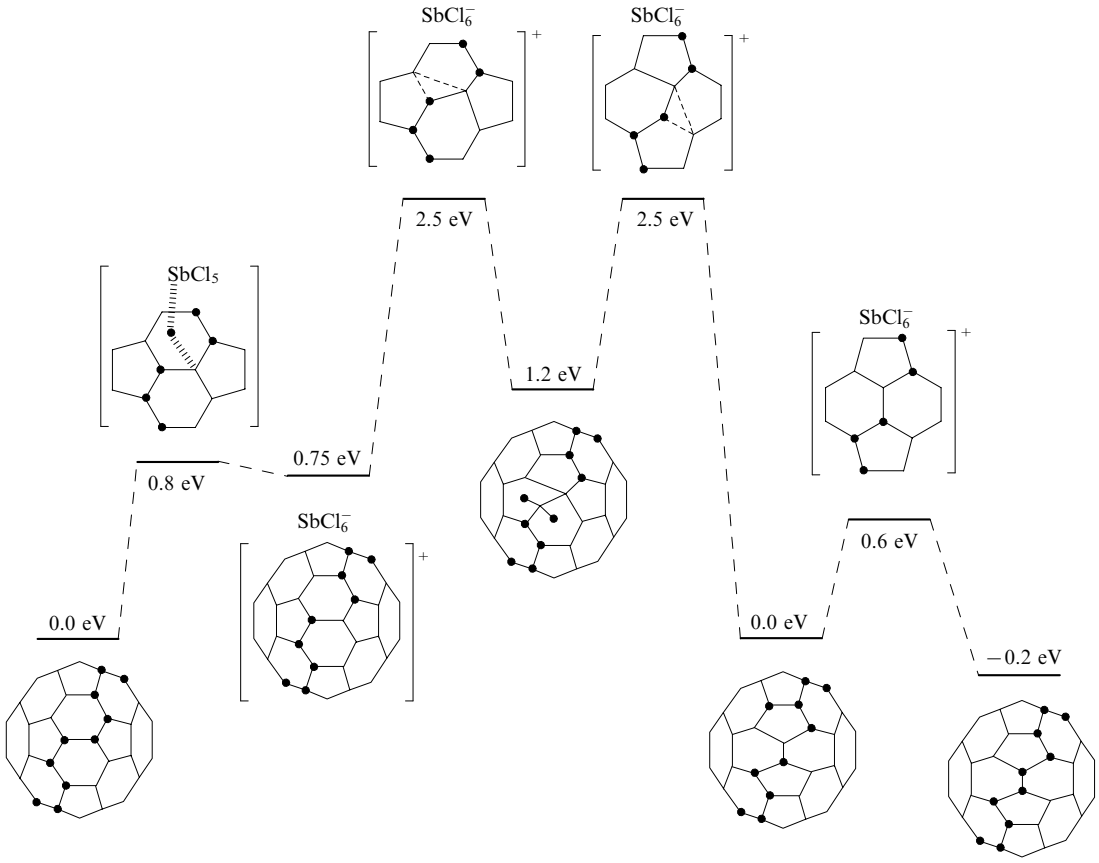


Figure 12. Energy profile of the first step of rearrangement of $^{\#19150}C_{76}Cl_{24}$ to $^{\#18917}C_{76}Cl_{24}$ (see step SW1 in Fig. 11).

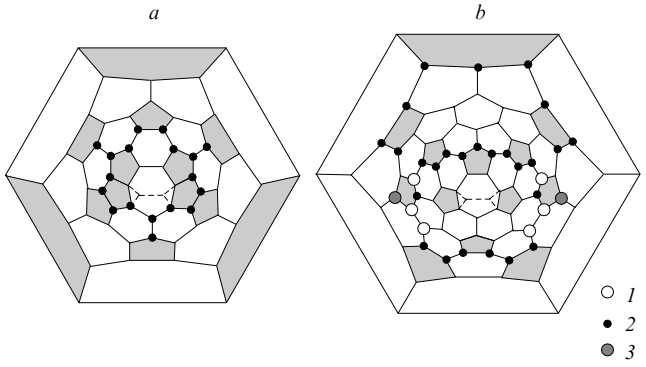


Figure 13. Schlegel diagrams for $C_{58}F_{18}$ (*a*) and $C_{84}Cl_{32}$ (*b*).
The dashed lines mark the C−C bonds present in the carbon cages of I_h-C_{60} and C_s-C_{86}(16).
b: (*1*) chlorine atoms that are absent in $C_{86}Cl_{28}$ and present in $C_{84}Cl_{32}$; (*2*) chlorine atoms common to $C_{84}Cl_{32}$ and $C_{86}Cl_{28}$; (*3*) chlorine atoms that are absent in $C_{84}Cl_{32}$ and present in $C_{86}Cl_{28}$.

numbers of carbon atoms in the cages of this fullerene and the initial one can be adequately described as being formally the result of C_2 elimination with the subsequent closure of the free bonds thus formed. However, the resulting changes of the carbon cage are very unusual. In place of the removed C_2 fragment, a seven-membered ring arises and simultaneously thirteenth five-membered ring appears to compensate the formation of the seven-membered ring (Fig. 13 *b*). The conversion of C_s-C_{86}(16)Cl_{28} to $C_{84}Cl_{32}$ differs from the destruction of C_{60} to C_{58} not only by much milder conditions and lower exothermic effects of the accompanying processes but also by the fact that carbon cage destruction has not been observed earlier even under much more rigorous conditions of chlorination.

Unfortunately, despite the simple formal relationship between $C_{84}Cl_{32}$ and the initial C_{86}, the direct mechanism of $C_{84}Cl_{32}$ formation is not entirely clear. Quantum chemical calculations have not still allowed one to propose a mechanism with the activation energy of less than 3 eV. It is only obvious that in this case, too, the reaction medium should play the key role in the skeletal rearrangement. Clarifying this issue can provide the possibility of passing from the above-described succesful experimental findings in this area of fullerene chemistry to systematical studies into the synthesis of non-classical carbon cages. Note that according to our preliminary data, skeletal rearrangements are also possible for other higher fullerenes, in particular, C_{82} and C_{88}.

IV. Conclusions

The review demonstrates that rearrangements of exohedral addends in functionalized fullerenes have been known for a long time, but reliable proof for their occurrence and descriptions of their mechanisms appeared later. Recent publications present data on skeletal transformations of fullerenes, which proceeded under milder experimental conditions than it could be expected. However, neither of these trends in fullerene chemistry has been practically implemen-

eted. Meanwhile, the prospects of application of isomerization approaches in fullerene chemistry appear quite extensive. It is sufficient to mention that non-classical carbon cages can possess even more pronounced acceptor properties than usual IPR-fullerenes and the appearance of fullerenes with larger rings such as seven-membered ones may facilitate incorporation of small-sized particles into the carbon cage. Besides, the attachment of addends to the common edges of pentagons gives significantly stronger bonds with the carbon cage. This fact can help to solve problems related to the instability of fullerene derivatives (for instance, to the susceptibility of fluorofullerenes to hydrolysis). Undoubtedly, the systematic studies in this field can be faced with substantial experimental difficulties, as isomerization processes take place under conditions that are by no means simple and easily controllable. Nevertheless, the chemistry of fullerene rearrangements can become a new interesting field not only in traditional chemistry dealing with various classes of compounds but particularly in the fullerene chemistry.

The authors express sincere gratitude to Ph.Ds. N B Tamm, A A Goryunkov and N S Ovchinnikova for fruitful discussions, including useful critisism, which stimulated this review.

The article was prepared with the financial support of the Russian Foundation for Basic Research (Projects Nos 09-03-00353, 09-03-01131, 09-03-00433 and 09-03-91337).

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