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Synthesis, properties and transformations of fullerene peroxides

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Methods of synthesis, properties and transformations of fullerene peroxides are considered and systematized for the first time. It is shown that the chemistry of fullerene peroxides is a new approach to functionalization of fullerenes, which has been intensively developing since 2002. Methods of synthesis, mechanisms of formation and reactions of C_{60} and C_{70} alkyl peroxides with or without epoxide moieties are discussed. Transformations of fullerene peroxides affording a wide range of fullerene derivatives containing, as addends, halogen or sulfur atoms; epoxide, dioxolane, thiirane, crown ether, aziridine and dioxetane rings, as well as hydroxyl, alkoxyl and carbonyl groups, are considered. Special attention is focused on reactions constituting the basis of a new approach — so-called molecular surgery, which enables the synthesis of open-cage fullerene derivatives. It has been demonstrated that such compounds are good candidates for designing photovoltaic cells and carriers of drugs and radionuclides (for radiopharmaceuticals).
The bibliography includes 130 references.

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I. Introduction

One of the most striking and impressive achievements in the field of oxidative functionalization of fullerenes is the development of methods of synthesis of fullerene peroxides, as well as study of their properties, pioneered by Gan *et al.*[1] and extended by various research groups.[2–34] Such compounds, which can fairly be called 'Gan's peroxides', are of interest as novel oxygen-containing fullerene derivatives. As multifunctional precursors, they are capable of further transformations well known in the chemistry of organic peroxides.

A considerable amount of studies on this topic have been devoted to the derivatives of general formula $C_{60}(O)_m(Bu^tOO)_n$ ($n = 2–6$, $m = 1–3$) containing one to three epoxide rings, in addition to peroxide groups and C═C bonds.† Under thermal or photochemical activation conditions, these compounds can react with Lewis acids and other reagents to give different fullerene derivatives, oxygen-containing fullerenes being of most interest among them. It should be noted that the result of the reaction depends on the nature of the Lewis acid: some reagents (for example, $FeCl_3$) selectively open the epoxide ring, while other reagents (for example, $AlCl_3$) lead to the fragmentation of the peroxide group.[4] Yet another advantage of these compounds is that the presence of peroxide groups is favourable for regioselective transformations of epoxide addends: reactions occur through channels with controlled localization of the added group.

Here, we give three most spectacular examples that demonstrate the value of fullerene peroxides as precursors. The first example is the use of them for synthesizing pure fullerenols.[8, 23, 32] The synthesis of fullerenols is often accompanied by the formation of adducts containing, in

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† As distinct from simple fullerene epoxides of general formula $C_{60}O_n$, reactions involving the epoxide moiety in such compounds have been studied in more detail (see Refs 1, 2, 4–10, 13, 15, 17, 20, 22, 23, 30–32, 34).

addition to hydroxyl groups, also acetal and hemiacetal groups and other addends.[35–40] Pure fullerenol $C_{60}(OH)_8$ has been synthesized from fullerene peroxide.[23]

The second example is the synthesis of $C_{60}(S)(OOBu^t)_4$, the first C_{60} derivative containing the sulfur atom and several peroxide groups covalently bound to the fullerene cage.[15] This compound has been synthesized by the reaction of $C_{60}(O)(OOBu^t)_4$ peroxide with aryl isocyanates ArNCS (Ar = Ph, Naph).[15] Before this publication,[15] only compounds in which the sulfur atom was located in different rings annulated to the [6,6]-bond of the C_{60} cage were known.[41–43] In addition, ESR detected alkylthiofullerenyl radicals $[RS-C_{60/70}]^{\bullet}$ generated by photolysis of RSSR disulfides in the presence of C_{60} or C_{70} in *tert*-butylbenzene.[44]

The third example is the synthesis of open-cage oxafulleroid derivatives.[11,12,16,26] As known, one of the most important ways of fullerene functionalization is creating fullerene capsules through C_{60} cage opening in a chemical reaction followed by encapsulation of a desired reagent into the cavity.[25,45] A brilliant solution to this problem has been recently suggested by Gan and co-workers,[34] who have managed to convert fullerene C_{60} into an open-cage fullerene derivative with a ketolactone moiety on the orifice limited by ten carbon atoms.

On the whole, the chemistry of fullerene peroxides, still mainly focusing on the transformations of alkyl peroxides, is at the early stage of its development both in the context of synthesis of new types of derivatives and in the context of their practical use. This review, covering the publications of the last decade (2002 to 2012 inclusive), is the first summary of advances in the chemistry of fullerene peroxide derivatives. This review does not cover fullerene derivatives in which the dioxetane ring is anneleated to the carbon atoms of an addend. Fullerene 1,2,4-trioxolanes are also not considered since similar compounds have been covered in depth in our review on ozonolysis of fullerenes.[46]

II. Synthesis of fullerene C_{60} and C_{70} alkyl peroxides

Fullerene peroxides result from the addition of peroxyl radicals to fullerene C_{60} or C_{70} in benzene. Most common for this purpose are $Bu^tOO^{\bullet}$ radicals generated in the known[47] reaction of decomposition of *tert*-butyl hydroperoxide initiated by metal (Fe^{3+}, Ru^{2+}, Ru^{3+}, Ce^{4+}) compounds or (diacetoxyiodo)benzene [$PhI(OAc)_2$, DIB].[1,2,5,6] The $Bu^tOO^{\bullet}$ radicals are selectively attached to C_{60} to give compounds **1**–**8** of general formula $C_{60}(O)_m(OOBu^t)_n$ through formation of intermediate radicals **A**–**D** (Scheme 1).

The reaction affords, in addition to epoxide **1** ($m = 1$, $n = 0$), adducts of two major types: simple fullerene peroxides (SFP) containing only peroxide groups [$m = 0$: $n = 2$ (**2**, **3**), 4 (**5**), 6 (**6**)], and complex fullerene peroxides (CFP) containing also oxirane rings [$m = 1$: $n = 2$ (**4**), 4 (**7**), 6 (**8**)]. Since reactions of alkenes with Bu^tOOH lead to both epoxides and peroxides, isolation of CFPs in the case of fullerenes is an expected result.[2] It should be noted that, in the absence of metal compounds or DIB, fullerene C_{60} does not react with Bu^tOOH at room temperature in the dark even within three days.[2] The use of cumene hydroperoxide, instead of Bu^tOOH, in combination with $Ru(PPh_3)_3Cl_2$ leads to the CFP $C_{60}(O)(OOC_6H_4Pr^i)_4$ (yield, 15%). The isolation of the latter is severely hindered by the presence of oily by-products.

The probability of formation of SFP or CFP in the reaction with fullerene C_{60} depends on the concentration of peroxyl radicals $Bu^tOO^{\bullet}$ in the reaction mixture and increases on exposure to visible light. Strong oxidants — lead tetraacetate and cerium(IV) ammonium nitrate (CAN), as well as DIB, — react almost instantaneously with Bu^tOOH, so that a high concentration of $Bu^tOO^{\bullet}$ is created. This leads to generation of the first key intermediate — fullerenyl radical $(Bu^tOO)C_{60}^{\bullet}$ (**A**), to which the next $Bu^tOO^{\bullet}$ radical is 1,2- and 1,4-added to form 1,2-bis(*tert*-butylperoxy)-1,2-dihydro[60]fullerene [1,2-$C_{60}(OOBu^t)_2$, **2**] and 1,4-bis(*tert*-butylperoxy)-1,4-dihydro[60]fullerene [1,4-$C_{60}(OOBu^t)_2$, **3**], respectively.

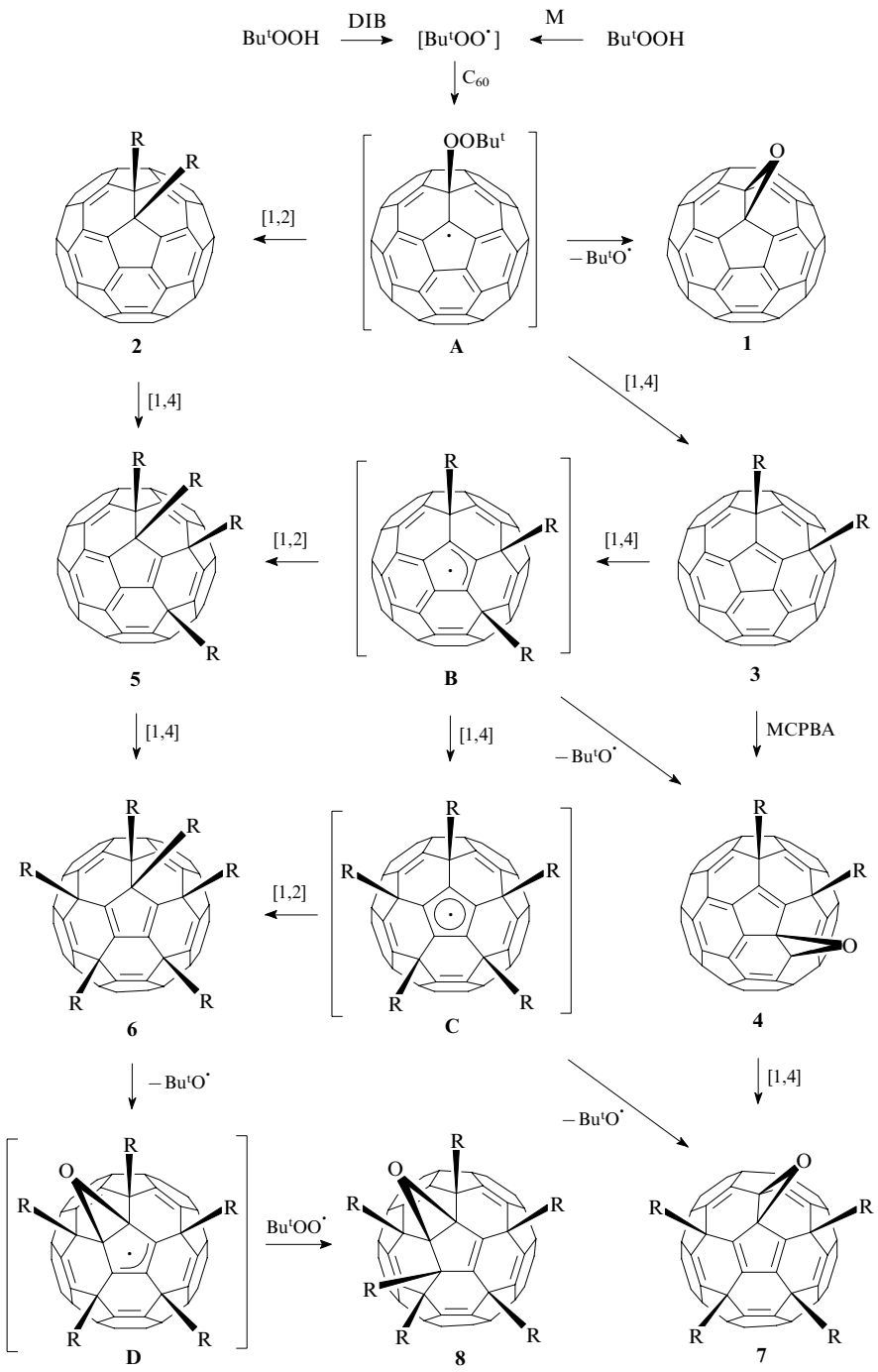
In an analogous reaction with ruthenium(II) or ruthenium(III) compounds, the $Bu^tOO^{\bullet}$ formation rate and concentration are considerably lower.[2] As a result, the peroxide moiety of intermediate **A** has time to undergo homolytic O–O bond cleavage accompanied by $Bu^tO^{\bullet}$ radical elimination to give 1,2-epoxydihydro[60]fullerene ($C_{60}O$, **1**), separated by high-performance liquid chromatography (HPLC). It turned out that the $Ru(PPh_3)_3Cl_2$ and $Ru(PPh_3)_4Cl_2$ complexes have similar catalytic activities. The reaction is carried out at room temperature, and decreasing temperature to 0° C does not change its selectivity. Monitoring the course of the reaction by HPLC shows that bisadducts **2** and **3** and monoepoxide **1** form first. Within two days, a major portion of C_{60} is converted into 4,11,15,30-tetrakis(*tert*-butylperoxy)-1,2-epoxy-1,2,4,11,15,30-hexahydro[60]fullerene [$C_{60}(O)(OOBu^t)_4$, **7**] and a minor one, into other products which are not eluted with a benzene–petroleum ether mixture. Elution of the column with benzene and its mixture with ethyl acetate leads to the appearance of two peaks on the chromatogram, which correspond to compounds with complicated ^1H NMR spectra.

The use of iron salts [$FeCl_3$, $Fe(NO_3)_3$, $(NH_4)_2Fe(SO_4)_2$] instead of the ruthenium catalyst at the ratio C_{60} : Bu^tOOH = 1 : 15 leads to analogous products, but at a lower rate.[2] At the same time, the reaction catalyzed by $Pb(OAc)_4$ or CAN yields, even within 30 min, 1,2,4,11,15,30-hexakis(*tert*-butylperoxy)-1,2,4,11,15,30-hexahydro[60]fullerene [$C_{60}(OOBu^t)_6$, **6**] as a major product, almost without admixture of epoxide **7**. This means that the limiting stage of catalysis by the ruthenium complex can be the oxidation of Ru^{II} to Ru^{III} by hydroperoxide. An analogous result has also been obtained using catalytic amounts of $Ru(PPh_3)_4Cl_2$ and an excess of $K_3Fe(CN)_6$. The use of another solvent (CS_2 rather than benzene) in the reaction with the ruthenium catalyst accelerates the formation of hexaperoxide **6**.

The reaction of C_{60} with *tert*-butyl hydroperoxide in the presence of CAN has been studied.[8] In the dark, the yield of compound **6** is 57%, and exposure to visible light leads to formation a CFP — 1,2,4,11,15,30-hexakis(*tert*-butylperoxy)-3,14-epoxy-1,2,3,4,11,14,15,30-octahydro[60]fullerene [$C_{60}(O)(OOBu^t)_6$, **8**] in 40% yield. Compound **8** is also the major product when the reaction mixture is irradiated with a luminescent lamp (16% yield in 15 min); in this case, a small amount of peroxide **6** is isolated as a by-product.[2]

In an analogous reaction, but in the presence of DIB as an initiator, the optimal C_{60} : DIB : Bu^tOOH ratio for synthesis of fullerene peroxides is 1 : 5 : 5.[8] Under such con-

Scheme 1



R = OOBu^t; M = Ru^{3+}, Ce^{4+}, Fe^{2+}, Pb^{4+}; symbols [1,2] and [1,4] mean the 1,2- and 1,4-addition of radicals R; hereinafter, only the bonds located on the 'front' side of the fullerene cage are shown for simplicity.

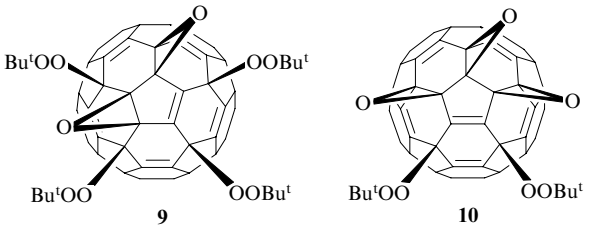
ditions, compounds **6**, **7** and **8** have been obtained in 57%, 45% and 40% yields, respectively. For isolation of minor products **2** and **5**, the Bu^{t}OO$^\bullet$ concentration should be decreased, while the reaction temperature should be increased. In particular, at 50 °C, the ratio C_{60} : DIB : Bu^{t}OOH = 1 : 0.8 : 2.4 and under normal lighting, the yields of fullerene peroxides **2** and **5** in 16 h become as high as 6% (as calculated for the isolated product). Under these conditions, epoxide **1** and 1,4-diperoxide **3** have been obtained in 6% and 24% yield, respectively (see Scheme 1).[2]

To prevent the addition to C_{60} of Bu^{t}O$^\bullet$ radicals, also forming in this redox system, hydroperoxide is taken in a large excess. As a result, 'undesirable' Bu^{t}O$^\bullet$ radicals are lost mainly in the reaction with Bu^{t}OOH to give an alcohol (Bu^{t}OH) and 'required' radicals (Bu^{t}OO$^\bullet$). However, Gan *et al.*[1] do not rule out that some unidentified reaction products can form through the addition of Bu^{t}O$^\bullet$ to C_{60}. Two pathways of formation of the epoxide group are suggested: elimination of Bu^{t}O$^\bullet$ from fullerene radical **C** (a precursor of CFP **6**) and oxidation of the $C_{60}(OOBu^t)_4$ tetraadduct (**5**) by dioxygen, which can form upon disproportionation of Bu^{t}O$^\bullet$ radicals. We believe that the first pathway is more realistic. Indeed, the oxidation of a C=C [6,6]-bond at the central pentagon in $C_{60}(OOBu^t)_4$ catalyzed

by metal compounds at room temperature without photoactivation is of low probability since, according to our data,[48] noticeable oxidation of C_{60} promoted by metal complexes occurs only at elevated temperatures (150 °C).

1,2-Adduct $C_{60}(OOBu^t)_2$ (**2**) synthesized at the ratio C_{60} : DIB : Bu^tOOH = 1 : 5 : 15 at room temperature in the dark is oxidized by DIB and Bu^tOOH to SFPs $C_{60}(OOBu^t)_4$ (**5**) and $C_{60}(OOBu^t)_6$ (**6**). The oxidation of CFP $C_{60}(O)(OOBu^t)_4$ (**7**) by *m*-chloroperoxybenzoic acid (MCPBA) leads to mixed diepoxide **9** (62% yield).[1,2,5,6] The reaction of compound **3** with MCPBA leads to CFP $C_{60}(O)(OOBu^t)_2$ (**4**) and mixed triepoxide **10** of symmetry C_S in small yields. Since compound **4** is oxidized in the reaction with DIB and Bu^tOOH to CFP $C_{60}(O)(OOBu^t)_4$ (**7**), this rules out symmetry C_S for its structure.

Structures 9, 10



Fullerene peroxides have been studied by various spectral methods. In the mass spectra of similar compounds, the molecular ion peaks are observed only for electrospray ionization (ESI): for example, CFP **7** is responsible for the peak at *m*/*z* 1115 ($[M + Na]^+$). The molecular ion peak is observed only for derivatives containing more than two peroxide groups, whereas for compounds less soluble in methanol [1,2- (**2**) and 1,4-isomers (**3**) $C_{60}(OOBu^t)_2$, $C_{60}(O)(OOBu^t)_2$ (**4**), $C_{60}(O)_3(OOBu^t)_2$ (**10**) and $C_{60}(O)(OMe)(OOBu^t)$], no molecular ion peaks are observed.[2] The matrix-assisted laser desorption/ionization mass spectra (MALDI TOF) of fullerene peroxides show only the peaks of epoxides $C_{60}(O)_n$ ($n \leqslant 12$) and $C_{70}(O)_m$ ($m \leqslant 9$), which form upon laser-induced decomposition of peroxides in a mass spectrometer. In particular, the mass spectrum of CFP $C_{60}(O)(OOBu^t)_4$ (**7**) shows only peaks for $C_{60}(O)_n$ with *n* being as large as 12, and the strongest peak is observed for the epoxide with $n = 4$.

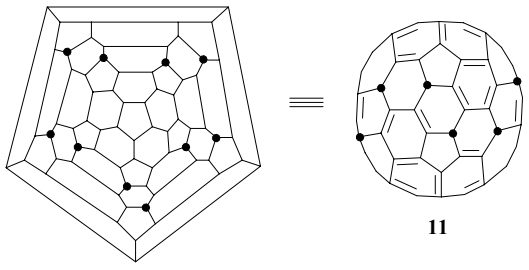
The ^{13}C NMR spectrum of compound **7** shows 32 signals of the carbon atoms of the fullerene cage: four of them are due to sp^3-hybridized carbon atoms (at 84.84, 80.98, 75.79 and 71.41 ppm) and the other signals arise from sp^2-hybridized atoms (in the range 149.56–140.80 ppm).[1,2] Four signals corresponding to two sp^2-hybridized and two sp^3-hybridized atoms are two times weaker than the other signals, which is evidence in favour of symmetry C_S of the $C_{60}(O)(OOBu^t)_4$ (**7**) structure. All the four tertiary carbon atoms of the Bu^t groups of compound **7** give rise to one signal at 81.90 ppm, which is split at 10 °C into two signals (81.92 and 81.94 ppm), which also points to symmetry C_S. The signals of the fullerene sp^2 carbon atoms bound to the epoxide oxygen atom are observed at 71.41 and 75.79 ppm.

Stoichiometric reactions of Bu^tOOH with fullerenes in the presence of CAN and DIB are faster than the catalytic decomposition of Bu^tOOH induced by ruthenium or iron complexes. The number of addends added to the fullerene can be regulated by the amount of the oxidant. For synthesis of fullerene peroxides, $Bu^tOO^{\bullet}$ radicals are preferred over their n-butyl analogues. The $OOBu^t$ group attached to the cage strongly affects the addition of the next group, creating steric hindrance and/or increasing the stability of the fullerene radical. The structures of peroxides formed in such radical reactions indicate that the carbon atoms of the fullerene cage in the 1- and 4-positions of the six-membered rings are most reactive with respect to peroxyl radicals. Therefore, *para*-addition of radicals to the six-membered ring to form 1,4-adducts is the dominating process. For C_{60}, these are the hexagons surrounding a five-membered ring; therefore, this addition mode is referred to as cyclopentadienyl addition mode[6] or cyclopentadienyl addition motif.[49]

According to Huang *et al.*,[2] 1,2-adduct **2** is a kinetic product, while 1,4-adduct **3** is a thermodynamic product, which accounts for the competition between the pathways of their formation. The authors explain this conclusion by the higher spin density of the 2-position in intermediate **A** and the higher stability (by 6 kcal mol^{-1}) of 1,4-adduct **3** as compared with 1,2-adduct **2**. Therefore, at elevated temperature (60 °C), the yield of compound **3** (31%) is considerably higher than that of 1,2-isomer **2** (5%).[2]

It should be noted that, under all experimental conditions studied (at different reactant concentrations and ratios and different temperatures), the reaction of C_{60} with *tert*-butyl hydroperoxide yields 1,4-adduct **3** as the major product. When a mixture of fullerenes C_{60} and C_{70} is introduced into the reaction, C_{60} is consumed faster than C_{70}; *i.e.*, the former is more reactive to the peroxyl radicals $Bu^tOO^{\bullet}$.[3] Unlike C_{60}, fullerene C_{70} reacts with *tert*-butyl hydroperoxide to give exclusively homoperoxo adducts $C_{70}(OOBu^t)_n$ ($n = 2, 4, 6, 8, 10$), which do not contain epoxide groups.[1,2] It is characteristic of fullerene C_{70} to form adducts containing a large number of identical addends: $C_{70}Cl_{10}$,[50] $C_{70}Br_{10}$,[51] $C_{70}Ph_{10}$ (Ref. 52) and $C_{70}[C_6H_4(CH_2)_nCO_2H\text{-}4]_8$ ($n = 2, 3$).[53] Under optimal conditions (0.75 mol C_{70}, 0.03 mol $Ru(PPh_3)_3Cl_2$, 25 ml Bu^tOOH), the major reaction product is 7,19,23,27,33,37,44,49,53,63-decakis(*tert*-butylperoxy)-7,19,23,27,33,37,44,49,53,63-decahydro[70]fullerene [$C_{70}(OOBu^t)_{10}$, **11**].[1]

Structure 11

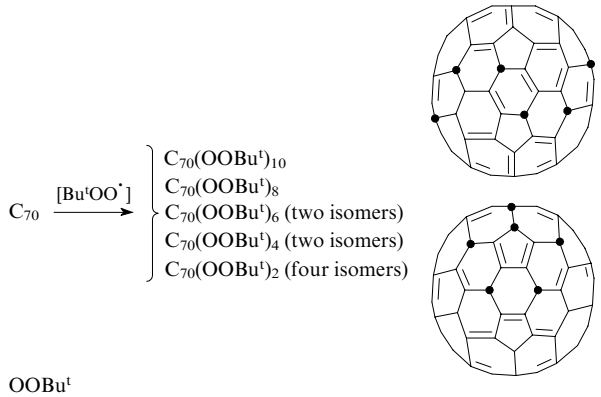


• = $OOBu^t$

The yields of $C_{60}(O)(OOBu^t)_4$ (**7**) and $C_{70}(OOBu^t)_{10}$ (**11**) when both fullerenes C_{60} and C_{70} are present in the reaction mixture are 30% and 8%, respectively; the conversion of the fullerenes reaches 100% (in 24 h in the presence of a ruthenium catalyst). The regiochemistry of the reaction with fullerene C_{70} is more complicated than that with C_{60}: $Bu^tOO^{\bullet}$ radicals are attached to C_{70} both along the equatorial belt of the cage and at the cyclopentadienyl moiety.

Two polar pentagons of fullerene C_{70} are passive in these reactions, presumably because the degree of pyramidalization of their carbon atoms is too high to form C=C bonds. The ^{13}C NMR spectra of peroxide **11** are evidence in favour of the C_2 symmetry of its structure. Ten $OOBu^t$ groups give rise to five separate signals of the tertiary carbon atom and four signals of methyl groups. Separation of a mixture of the $C_{70}(OOBu^t)_n$ (n = 2, 4, 6, 8, 10) products by column chromatography on silica gel has led to isolation of four $C_{70}(OOBu^t)_2$ isomers with the $OOBu^t$ groups located in the 1,2-, 5,6-, 7,23- and 2,5-positions, as well as two $C_{70}(OOBu^t)_4$ isomers with the $OOBu^t$ groups located along the equatorial belt (symmetry C_S) and at the side region (C_1) of the C_{70} cage (Scheme 2).[3] In addition, two $C_{70}(OOBu^t)_6$ isomers have been obtained with molecular symmetry C_2 and C_S (the upper and lower structures in Scheme 2, respectively).

Scheme 2



Isomers of fullerene C_{70} peroxides with n = 8 (symmetry C_S) and 10 (symmetry C_2) in which all $OOBu^t$ groups are located along the equatorial belt of the C_{70} cage have not been identified. The reaction catalyzed by Ru^{II}, Ru^{III} or Fe^{III} compounds is relatively slow and requires a large Bu^tOOH excess, and the yield of $C_{70}(OOBu^t)_{10}$ (**11**) is 8%. The CAN-catalyzed reaction requires smaller Bu^tOOH amounts and is rather selective. At the reactant ratio C_{70} : CAN : Bu^tOOH = 1 : 20 : 40, major product **11** forms in 30% yield (based on reacted fullerene), and at the 1 : 10 : 30 ratio, the reaction leads to peroxides with a smaller number of $OOBu^t$ groups. It is likely that this difference in the action of the above metal compounds is due to that, unlike the heterogeneous reactions with CAN or $Pb(OAc)_4$, the ruthenium and iron catalysts are soluble in the reaction medium.[5] It is also possible that these catalysts form a weak η^5-type coordination complex with the pentakis-adduct intermediate, effectively preventing further $Bu^tOO^•$ radical addition.

III. Transformations of fullerene alkyl peroxides

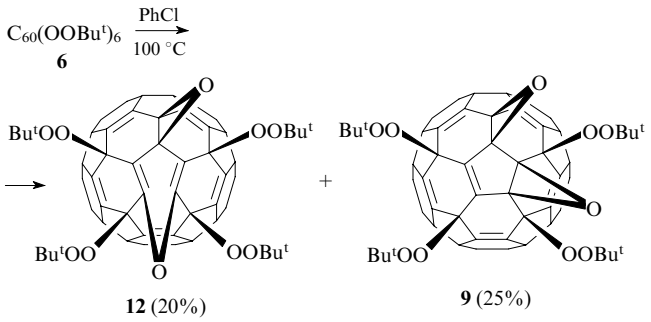
Transformations of fullerene peroxides can be conventionally divided into three basic types: opening of the epoxide ring of CFPs, homolysis or heterolysis of $OOBu^t$ group bonds in SFPs and CFPs, as well as fullerene cage opening. In some cases, several reaction pathways are realized at a time. It is accepted that CFP epoxide ring opening processes are more promising because of the possibility of using flash chromatography for isolation of peroxy-substituted fullerenes and products of their transformations, whereas the time-consuming HPLC method is applied for separation of $C_{60}O_n$ epoxides. In addition, CFPs and the products of their reactions are more soluble in common solvents, and transformations involving these compounds are usually regioselective owing to a definite position of the epoxide group. For this reason, Gan and coworkers [1, 2, 4–10, 13, 15, 17, 20, 22, 23, 30–32, 34] have suggested to use CFPs (rather than simple epoxide $C_{60}O$) — $C_{60}(O)_m(OOBu^t)_n$ containing peroxide and epoxide groups — as a precursor for further functionalization.

1. Thermo- and photostability of fullerene alkyl peroxides

All peroxide derivatives of C_{70} are very stable and decompose by 50% after two years of storage under conventional laboratory conditions. Among fullerene C_{60} peroxides, epoxy-containing compounds are most stable. In particular, CFP **7** withstands heating to 150 °C or irradiation with visible light in solution and decomposes by 50% upon storage at room temperature for one year.[2] The NMR spectra of readily soluble $C_{60}(O)(OOBu^t)_4$ (**7**) and $C_{70}(OOBu^t)_{10}$ (**11**) remain unaltered over a period of several weeks for solutions kept in the dark at room temperature and on heating to 50 °C.[1]

At the same time, a powder of SFP $C_{60}(OOBu^t)_6$ (**6**) slowly decomposes even at room temperature to give a mixture of products containing an open-cage fullerene derivative, its yield being as high as 1% within two months.[2] In chlorobenzene, compound **6** is thermolyzed at 100 °C through homolysis of the most reactive O–O bond at the vertex of the central pentagon to form two isomeric products **9** and **12** of general formula $C_{60}(O)_2(OOBu^t)_4$ (Scheme 3). Isomer **12** contains [5,6]-open ether and [6,6]-closed epoxide moieties and isomer **9**, two closed epoxide moieties.[20] Four $OOBu^t$ groups in each isomer persist. Diepoxide **9** is also formed from $C_{60}(O)(OOBu^t)_4$ upon oxidation by MCPBA.[2] The main pathway of fullerene peroxide decomposition is O–O bond cleavage; under irradiation or thermolysis, C–O bond cleavage is considerably less common.

Scheme 3

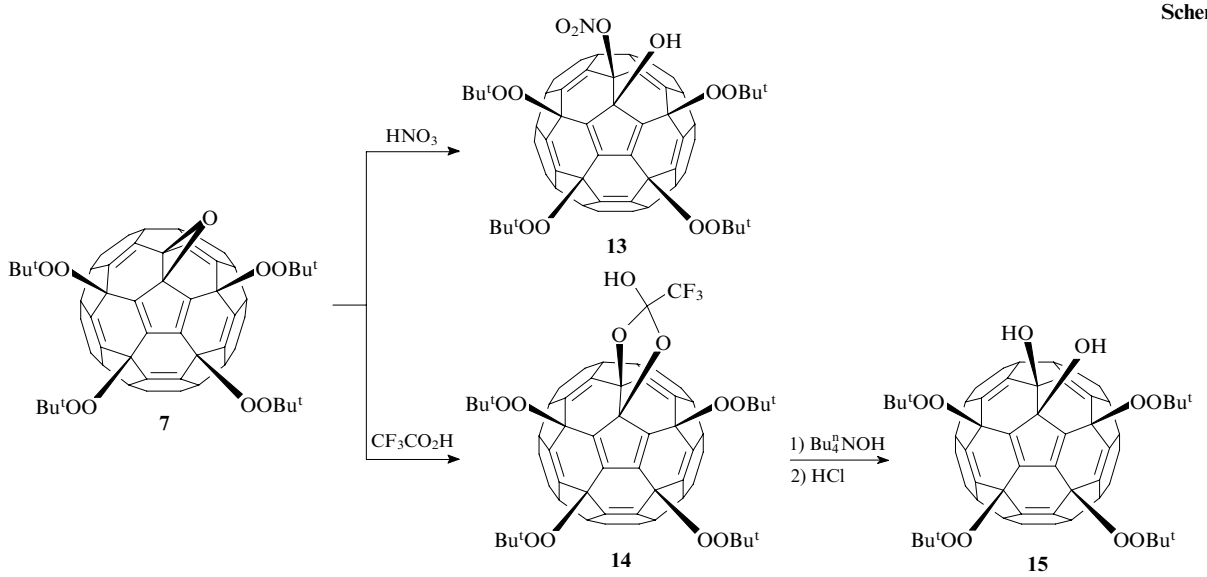


2. Epoxide ring opening in complex fullerene alkyl peroxides

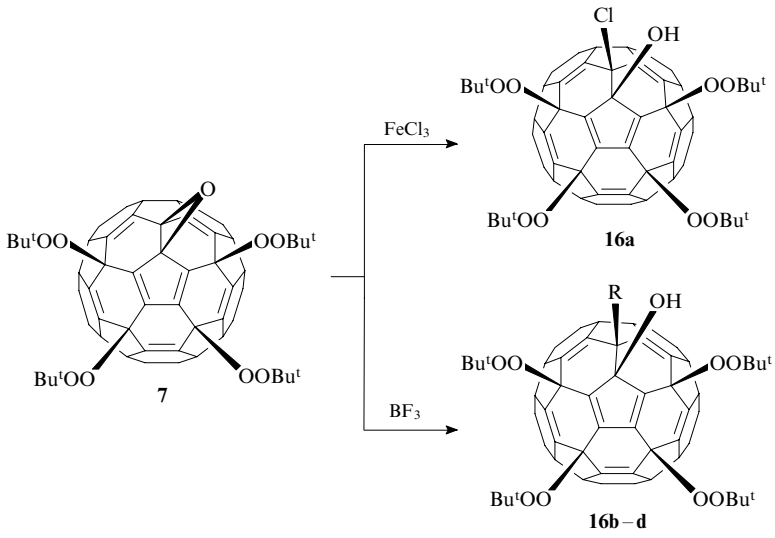
The first example of epoxide ring opening in CFPs induced by chemical reagents is the reaction of $C_{60}(O)(OOBu^t)_4$ (**7**) with nitric or trifluoroacetic acid yielding nitratofullerenol **13** (58% yield) or 1,3-dioxolane **14** containing OH and CF_3 groups (Scheme 4).[2]

Other acids (H_2SO_4 and HCl), as well as bases, are not capable of opening this epoxide ring like $(NH_4)_2Ce(NO_3)_6$, which readily decomposes organic epoxides. Upon treatment of adduct **14** with the base Bu^n_4NOH with subsequent

Scheme 4



Scheme 5



Compound **16**	R	Reagent	Yield (%)
a	Cl	$FeCl_3$	85
b	OMe	BF_3 in MeOH	61
c	$OOBu^t$	BF_3 in Bu^tOOH	23
d	OOH	H_2O_2 in BF_3	16
e	F	BF_3	27

hydrolysis in an acid medium (HCl), the 1,3-dioxolane moiety is cleaved and fullerenediol **15** is formed (see Scheme 4).

Lewis acids also effectively open the epoxide ring of CFP **7**. For example, the reaction with $FeCl_3$ leads to a vicinal chlorohydrin — 4,11,15,30-tetrakis(*tert*-butylperoxy)-2-hydroxy-1-chloro-1,2,4,11,15,30-hexahydro[60]fullerene $C_{60}(Cl)(OH)(OOBu^t)_4$ (**16a**) (Scheme 5).[4–6,32]

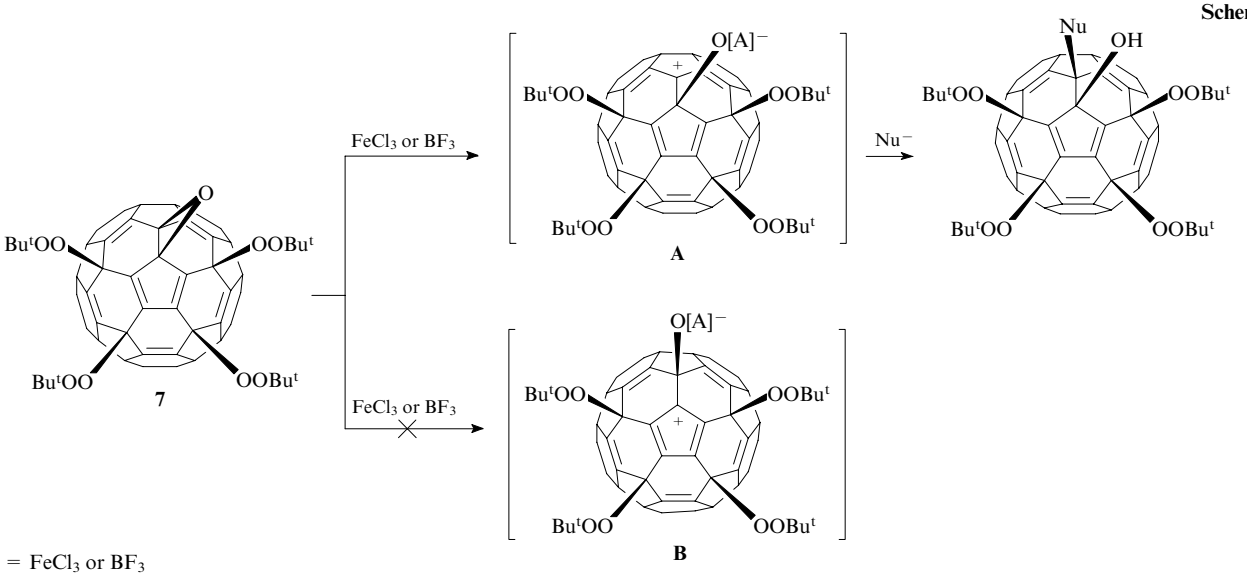
Using BF_3 in combination with another reagent (MeOH, Bu^tOOH, H_2O_2) affords adducts **16b–d**, respectively. In all cases, fluorinated fullerene **16e** is formed in small amounts as a by-product. It is assumed that the epoxide ring is opened after the attack of a Lewis acid ($FeCl_3$ or BF_3) on the oxygen atom of the epoxide addend, which leads to intermediate fullerene cation **A** (Scheme 6). Then, the attack of a nucleophile (Nu) on this intermediate results in formation of the OH group at the central pentagon. The alternative reaction pathway through the formation of cation **B** is less probable owing to its instability caused by the antiaromatic nature of the cyclopentadienyl cation.[4–6]

As distinct from an aqueous HCl solution reacting with fullerene peroxides to give a complex mixture of products,[2] treatment of CFP **17** with gaseous HCl or HBr effectively opens the epoxide ring to form adducts **18** (Scheme 7).[10]

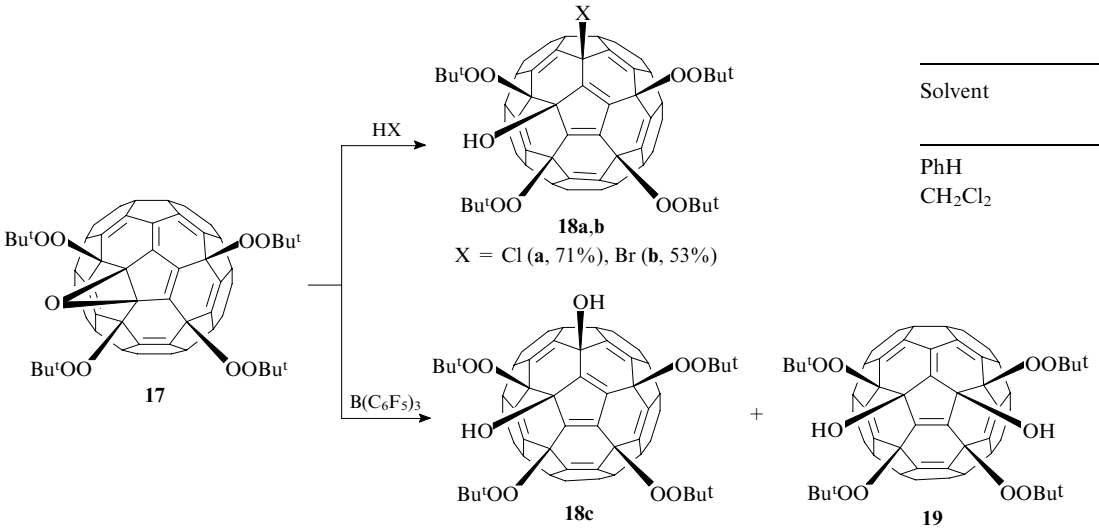
Among the known transformations of compounds **16**, the most interesting one is alkoxylation of bromohydrin **16f** through homo- or heterolytic cleavage of C–Br bond under visible light irradiation or in the presence of silver salts (for example, Ag_2CO_3; Scheme 8).[14] As follows from Table 1, the photochemical reaction is completed much faster. It is believed that the reaction starts with photolysis of the C–Br bond of adduct **16f**, generating intermediate fullerenyl radical **A**, which is oxidized by oxygen to cation **B**.

This mechanism is based on the known data[54] on the possibility of easy oxidation of azafullerene $C_{59}N^{\bullet}$ to the iminium cation $C_{59}N^{+}$ in the presence of *p*-toluenesulfonic acid and oxygen. The authors suggest that oxygen is in the singlet excited state since fullerene and its derivatives are good $^1O_2$ generators. This is a necessary condition since fullerenyl radicals $Bu^tO-C_{60}^{\bullet}$ react very slowly with unexcited oxygen in the triplet state ($^3O_2$).[55] It is also known that

Scheme 6

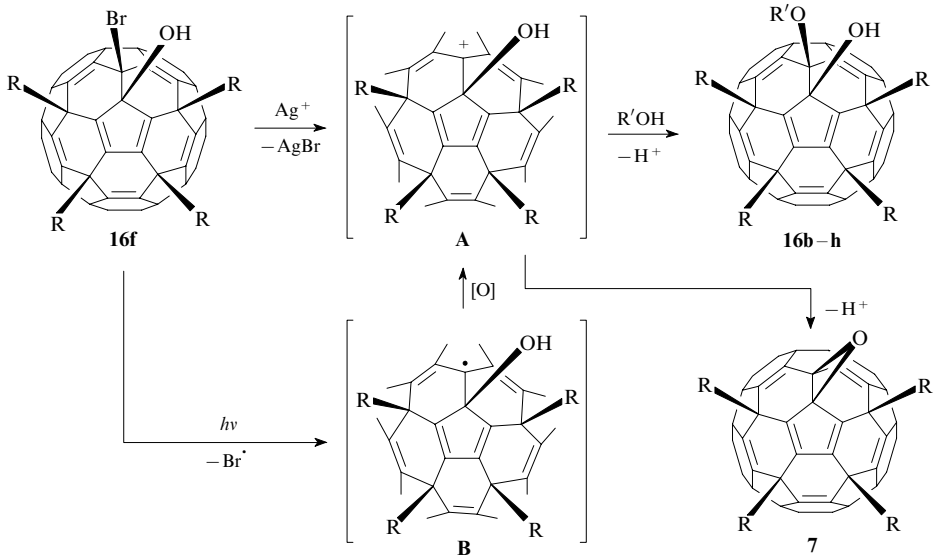


Scheme 7



Solvent	Yield (%)	
	18c	**19**
PhH	72	0
CH_2Cl_2	36	34

Scheme 8



R = $OOBu^t$; hereinafter, in some cases for intermediates only a fullerene moiety involved in reaction is shown for simplicity

Table 1. Effect of reaction conditions on the yield of **16b**,**g**,**h** (see Scheme 8).[14]

Product	R′	Reaction conditions	Time	Yield (%) [a]
16b	Me	*hv*	10 min	95 (72)
		Ag_2CO_3	3 h	98 (78)
16g	Et	*hv*	15 min	91 (60)
		Ag_2CO_3	8 h	94 (76)
16h	Bn	*hv*	20 min	41 (30)
		Ag_2CO_3	3.5 h	91 (72)

[a] The yield is based on converted adduct **16f** (the yield of the isolated product is parenthesized).

$Et-C_{60}^{\bullet}$ radical reacts with $^3O_2$ to form a complex, which manifests itself as broadening of its signal in the EPR spectrum.[56] In the chemical variant of this reaction, silver ions can initiate heterolytic cleavage of the C–Br bond with immediate formation of cation **A** (see Scheme 8).

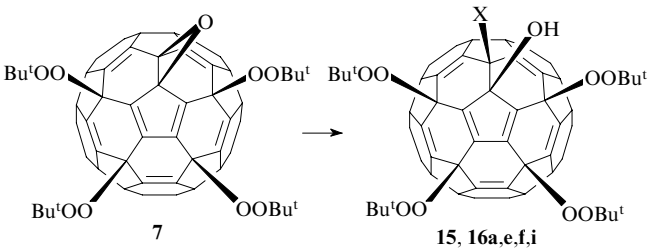
Iodofullerene derivatives with covalent I–C(fullerene) bond are treated as promising radioactive contrast agents. However, as distinct from other halofullerenes, such adducts have remained uncharacterized for a long time. Iodofullerenes were synthesized for the first time from a CFP as a precursor.[9] In particular, iodohydrin fullerene derivative **16i** has been synthesized by the reaction of compound **7** with a Ph_3P-I_2 mixture in dichloromethane at room temperature (Scheme 9).

The reaction products depend on the reactant ratio and reaction duration.

In the course of the reaction, all peroxide groups remain intact, being responsible for the high solubility of the adducts in organic solvents and the easiness of their isolation by HPLC. The highest yield of iodohydrin **16i** is achieved at an iodine excess, whereas at the equimolar reactant ratio, the major product is diol **15**.

Iodofullerene derivative **16i** is moderately stable; it decomposes in air to form diol **15**, and its reaction with MCPBA regenerates CFP **7**. Bromohydrin **16f** has been synthesized by the reaction with $FeBr_3$, and fluoro- (**16e**) and chloro-containing adducts (**16a**) have been prepared by the reaction with BF_3 and $FeCl_3$, respectively (as described by Gan and coworkers [4]).

Scheme 9



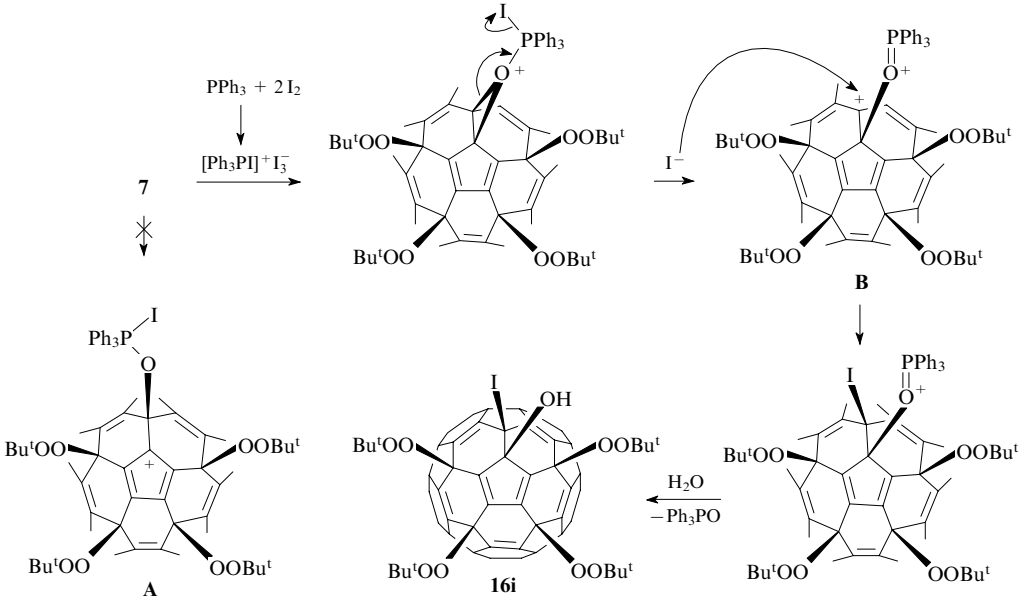
X = OH (**15**), Cl (**16a**), F (**16e**), Br (**16f**), I (**16i**)

7 : PPh_3 : I_2 ratio	Time /h	Yield (%)	
		16i	**15**
1 : 1 : 1	48	0	14
1 : 2 : 8	2	56	0

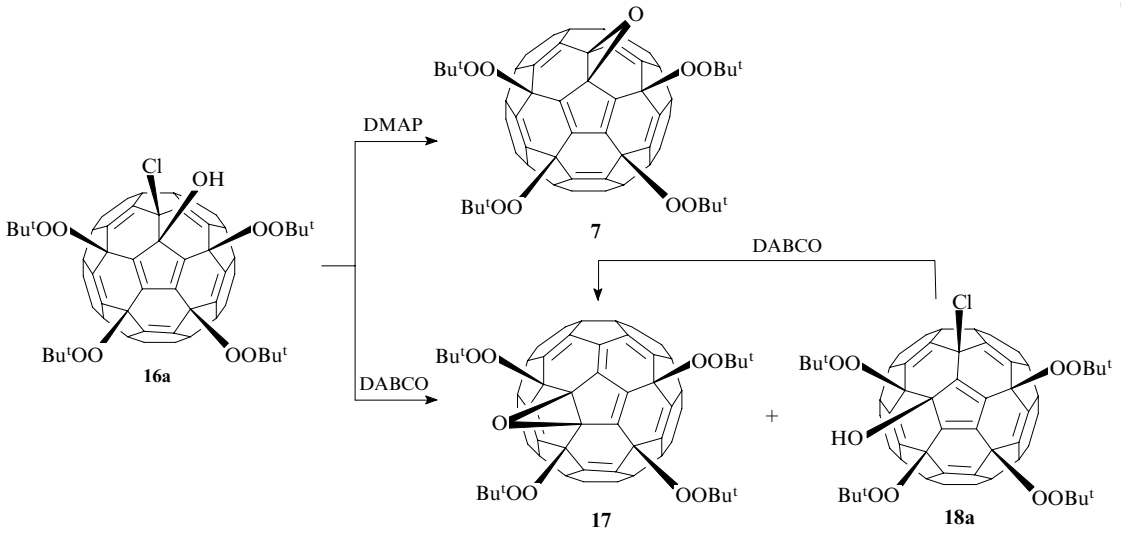
Scheme 10 shows a probable mechanism of the S_N1 reaction yielding iodohydrin **16i**. The regioselectivity of the reaction is caused by the antiaromatic nature of the central pentagon in intermediate **A**. In addition to intramolecular transfer of the I^- anion from the phosphine moiety $^+PPh_3-I$ in intermediate cation **B**, the nucleophilic attack of I_3^- anion on intermediate **B** is possible.

The epoxide group is regenerated in the reaction (named by the authors as 'boomerang-type') of chlorohydrin **16a** (symmetry group C_S) with 4-dimethylaminopyridine (DMAP) or 1,4-diazabicyclo[2.2.2]octane (DABCO) (Scheme 11).[10] Two isomers with the formula $C_{60}(O)(OOBu^t)_4$ are thereby formed — compounds **7** and **17** — with different location of the epoxy functionality. Epoxide **7**, obtained by the reaction with DMAP (50% yield), has symmetry C_S, and its isomer **17** (81% yield) has symmetry C_1 with the epoxy group on the central cyclopentadienyl moiety.

Scheme 10



Scheme 11

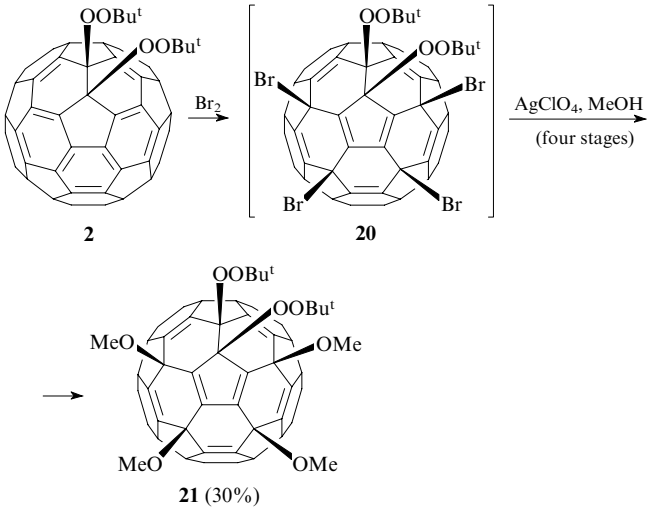


With bases other than DMAP and DABCO (for example pyridine and sodium acetate), this reaction does not occur. At the same time, compound **16a** reacts with Et_3N or NaOH to give epoxide **17** (12% and 59% yields, respectively) along with adduct **18a** (38% and 12% yields). The structures of these fullerenes have been determined by NMR and IR spectroscopy, single-crystal X-ray diffraction, and chemical correlation experiments. According to Jia *et al.*,[10] a combination of an oxygen-atom shift and S_N2 process (boomerang substitution) is responsible for the formation of the isomer in the reaction of compound **18a** with DACBO. However, the classical S_N2 mechanism is impossible in this case because of the spherical structure of the carbon cage; likewise, inversion of configuration is impossible. It is likely that the reaction proceeds through a concerted intramolecular S_N2'' mechanism in which the anionic moiety $C_{60}-O^-$ is a nucleophile and the chloride ion is a leaving group. A similar mechanism in the intermolecular version was described for the first time by Taylor[57] to explain the formation of trannulenes from the $C_{60}F_{18}$ fluorofullerene (see below).

To elucidate the mechanism of the above transformations, model reactions have also been carried out.[10] In particular, the reaction of 2,3-epoxide **17** with $B(C_6F_5)_3$ yields dihydroxy derivatives **18c** and **19** (see Scheme 7). The nature of the solvent plays a key role: in dichloromethane, adducts **18c** and **19** form in 36% and 34% yields, respectively, while the reaction in benzene leads only to product **18c**. A necessary condition for the formation of these compounds is the presence of water traces in the solvent. When epoxides **7** and **17** are treated with ICl and Br_2, the epoxide moiety persists, and only the [6,6] double bond of the fullerene cage is halogenated and halogen atoms are substituted for the peroxide groups.[10] Addition of bromine atoms at multiple bonds of the cage with the peroxide addends remaining intact has also been demonstrated for bromination of 1,2-bisadduct $C_{60}(OOBu^t)_2$ (**2**) leading to fullerene tetrabromoperoxide $C_{60}(OOBu^t)_2Br_4$ (**20**) (Scheme 12).[27]

Despite the nearly quantitative yield of product **20**, attempts to isolate it in the pure form are unsuccessful since it rapidly decomposes on a preparative silica gel column. However, it can be easily converted into alkoxyfullerene derivatives. In particular, in the presence of $AgClO_4$, the bromine atoms are replaced regioselectively by alkoxymethyl groups to form adduct **21**.

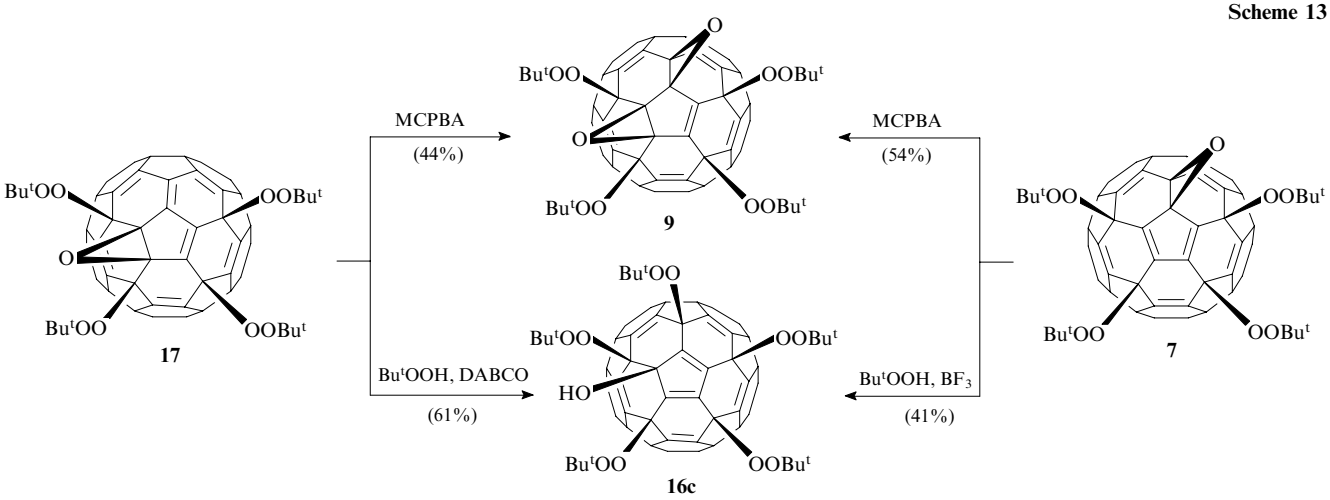
Scheme 12



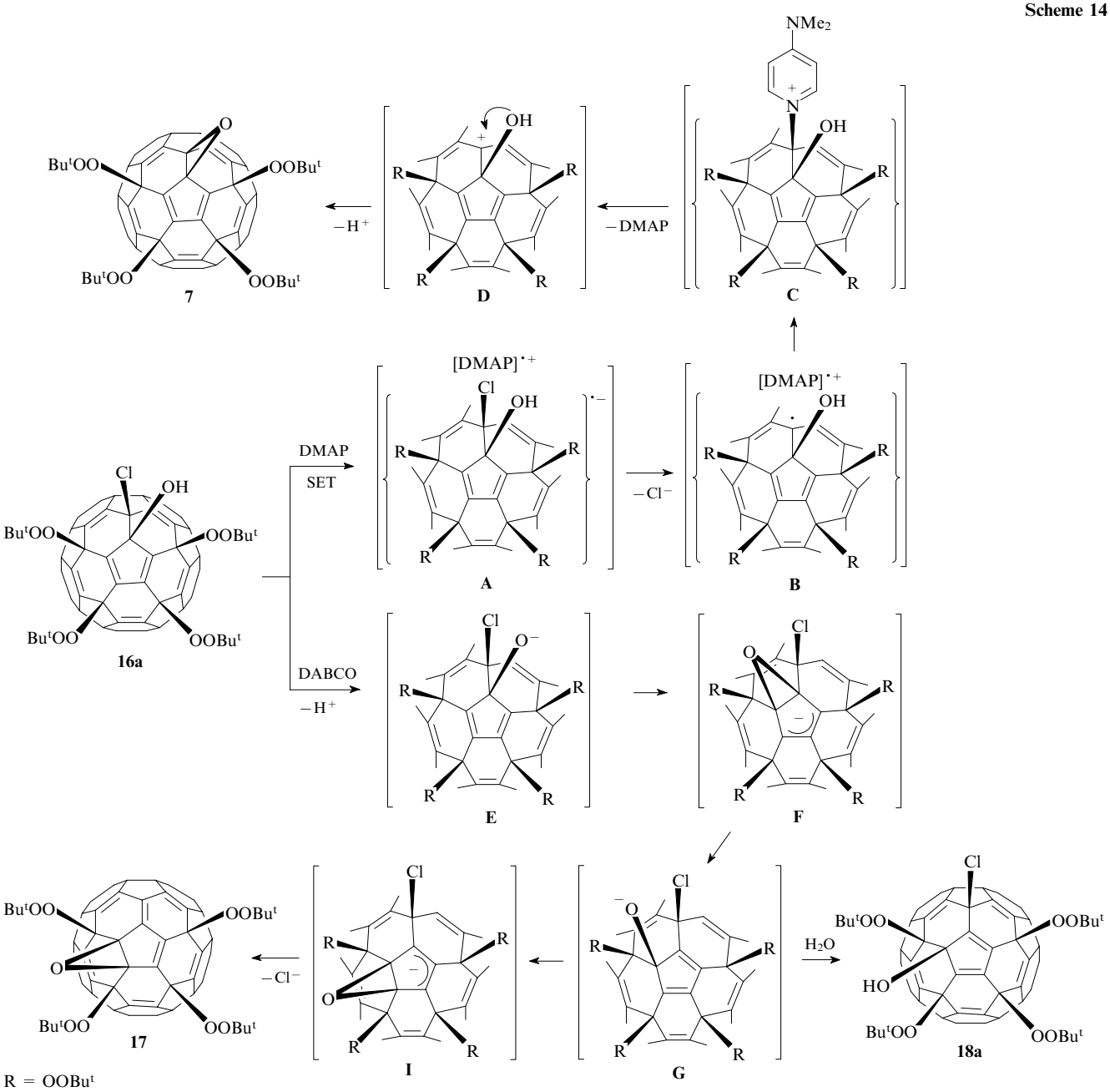
Isomeric epoxides **7** and **17** are oxidized by MCPBA to diepoxide **9** (Scheme 13). The treatment of epoxides **7** and **17** with *tert*-butyl hydroperoxide in combination with, respectively, BF_3 and DABCO leads to hydroxyl-containing adduct **16c**.[10] Isomer **17** is more reactive in these transformations than compound **7**, since the [6,6] double bond adjacent to the central pentagon is more active. For example, it takes 2 to 30 h for adduct **9** to form from epoxide **7** (54% yield), whereas a reaction time of 10 min is sufficient for the formation of the same adduct from isomer **17** (44% yield).

The ^{13}C NMR signals of the epoxide carbon atoms of isomer **17** (66.8 and 68.4 ppm) are observed at a higher field than those of C_S-symmetric epoxide **7** (71.4 and 75.8 ppm). This difference can be caused by the shielding effect of the OOBu^t groups in compound **17**. Two mechanisms are proposed to explain the formation of isomers **7** and **17**, which differ only in the location of the epoxy functionality (Scheme 14).

Scheme 13



Scheme 14



The first mechanism involves single-electron transfer (SET) from DMAP to fullerene peroxide to generate the corresponding radical cations and anions forming ion pair **A**.

Elimination of the chloride ion from intermediate **A** leads to fullerenyl radical **B**, which reacts with radical cation $DMAP^{\bullet+}$ to produce cation **C**. Removal of the DMAP molecule from this cation gives fullerene cation **D**, and its deprotonation leads to isomer **7**. In this case, DMAP acts simultaneously as an SET initiator and as a base neutralizing hydrochloride. Stabilization of $DMAP^{\bullet+}$ as intermediate structures **A**, **B** and **C** is due to the existence of several resonance forms of this radical cation.

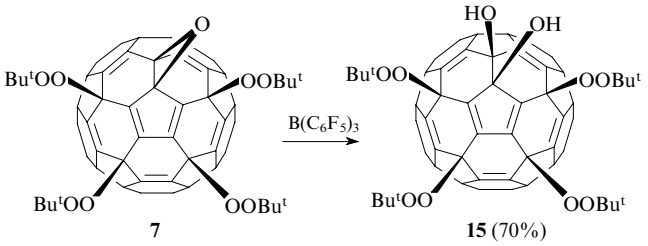
Unlike DMAP, DABCO is not able to form resonance structures; therefore, it reacts only as a base responsible for the deprotonation of the HO^- group at the first stage. Before considering the mechanism of the addition reaction of compound **16a** with DABCO, it should be noted that the nucleophilic substitution of halohydrins under the action of bases (in the absence of Lewis acids) leading to an epoxide ring usually proceeds through the S_N2 mechanism since a nucleophile attacks the back of the substrate with respect to a leaving group. However, the spherical structure of the fullerene cage prevents the nucleophilic backside attack, which rules out the S_N2 mechanism.

The authors [10] suggest another variant of reaction mechanism (see Scheme 14). First, the deprotonation of compound **16a** gives fullerene oxide intermediate **E**; then, the oxygen-centred anion adds to a neighbouring double bond C=C to form fullerene-centred allyl anion **F**. The opening of the epoxide ring in anion **F** generates another oxygen-centred anion **G**; the existence of the latter is supported by the isolation of adduct **18a**.

In a similar way, *i.e.*, through the formation of intermediate **G**, anion **I** is formed. Loss of a chloride ion completes the boomerang-type substitution and formation of epoxide **17**. The formation of compound **17** from intermediate **G** is a typical S_N2'' process, which is similar to the fluorine substitution in fluorofullerenes described by Taylor and co-workers.[58, 59] Quantum chemical calculations are required to determine the most probable mechanism of transformation of chlorohydrin **16a** in the presence of DABCO.

Hydrolysis of 1,9-epoxide **7** promoted by $B(C_6F_5)_3$ gives vicinal 1,9-fullerenediol **15** in good yield (Scheme 15).[7]

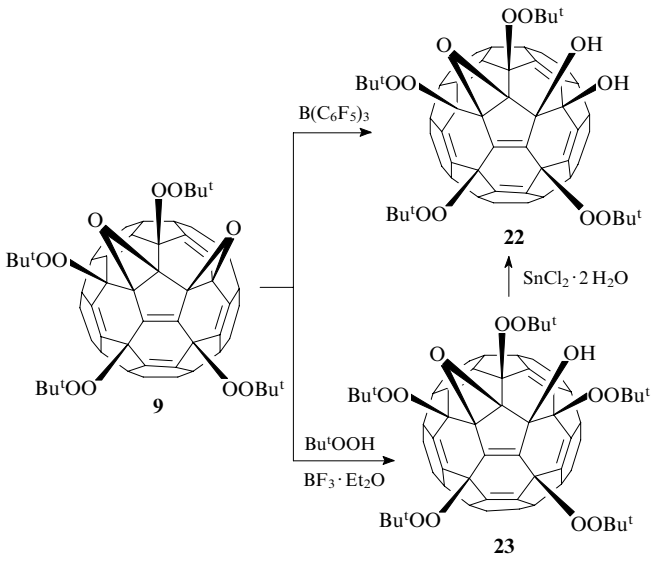
Scheme 15



7 **15** (70%)

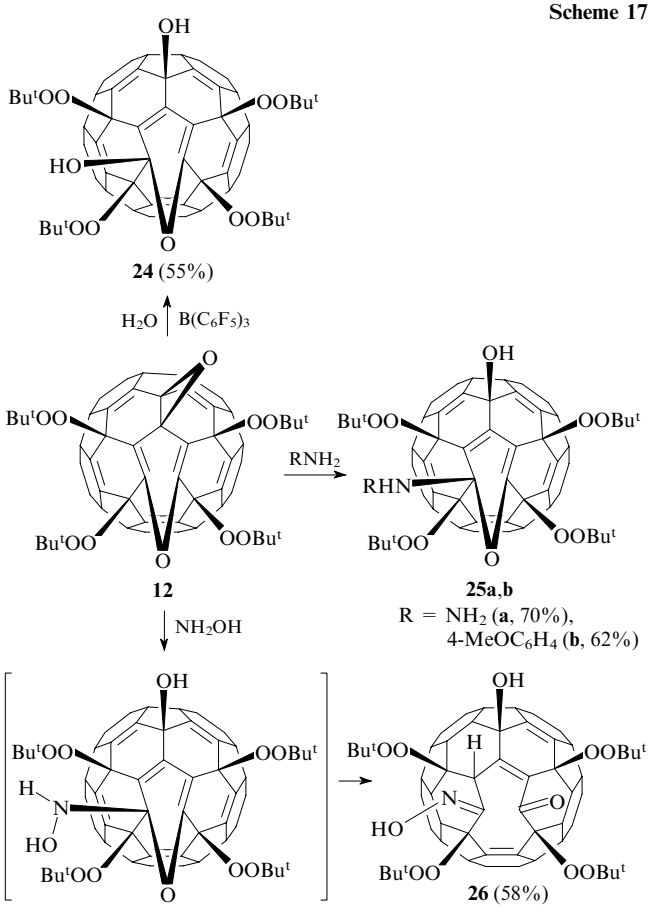
In bis(epoxy) derivative $C_{60}(O)_2(OOBu^t)_4$ (**9**), most reactive is the epoxide ring annelated to the [6,6] bond; it is opened under the action of $B(C_6F_5)_3$ to form vicinal diol **22** (70% yield) (Scheme 16).[8] In the reaction of compound **9** with a $BF_3 \cdot Et_2O$–Bu^tOOH mixture, the same epoxide ring is opened to produce, however, adduct **23**, containing vicinal hydroxyl and peroxide groups. When treated with $SnCl_2 \cdot H_2O$, compound **23** is readily converted into diol **22**.

Scheme 16

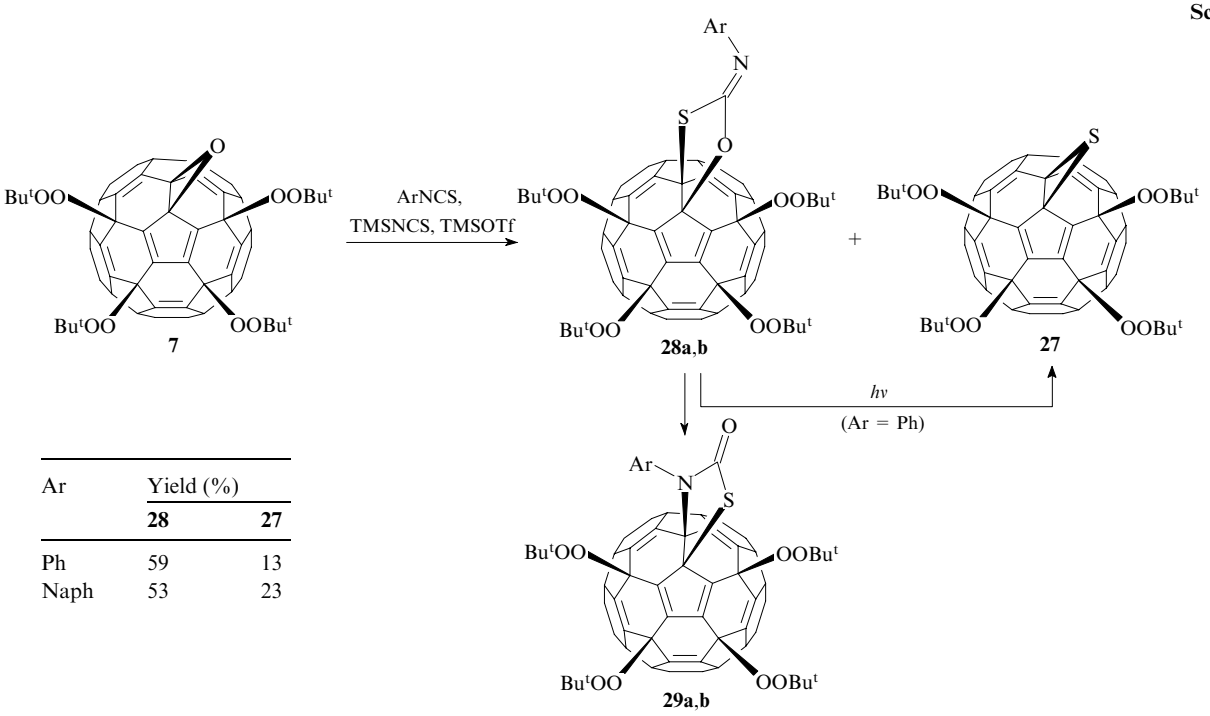


The existence of both [6,6]-closed epoxide and [5,6]-open ether moieties in CFP $C_{60}(O)_2(OOBu^t)_4$ (**12**) noticeably affects the reactivity of the former.[20] The reaction of bisepoxide **12** with $B(C_6F_5)_3$ in the presence of water gives hemiacetal **24**, while the reaction with nucleophilic hydrazine and *p*-anisidine leads to hemiaminals **25a**,**b**

Scheme 17



Scheme 18



Ar	Yield (%)	
	28	**27**
Ph	59	13
Naph	53	23

Ar = Ph (**a**), Naph (**b**); TMS is trimethylsilyl, Tf is trifluoromethanesulfonate

(Scheme 17). Addition of hydroxylamine to adduct **12** opens both the epoxide and ether rings and rapidly gives, after a rearrangement, an open-cage keto-ketoxime derivative **26**.

The acetal groups in adducts **24**, **25a** and **25b** give rise to the ^{13}C NMR signals at 105.8, 103.1 and 97.4 ppm, respectively. The signal of the carbonyl carbon atom of ketoxime **26** is observed at 190.4 ppm.

The fullerene derivative $C_{60}(S)(OOBu^t)_4$ (**27**), containing *tert*-butyl peroxide groups and sulfur atom covalently bound to carbon atoms of the fullerene cage, has been synthesized by the reaction of epoxide **7** with phenyl isothiocyanate.[15] The epoxide group in CFP **7** easily reacts with aryl isothiocyanates ArNCS [Ar = Ph, 1-naphthyl (Naph)] in the presence of trimethylsilyl trifluoromethanesulfonate and trimethylsilyl isothiocyanate to form adducts **28a**,**b** and **27** (Scheme 18).[15] On exposure to visible light, compound **28a** is converted into thiirane adduct **27**, whereas heating in a CH_2Cl_2–toluene mixture gives compound **29a** as the major product. X-Ray crystallography has shown that the sulfur atom in adduct **29a** is bound to the central pentagon and has no bond to the nitrogen atom. The benzene ring of adduct **29a** is perpendicular to the thiazolidine moiety, and the thiazolidine ring is perpendicular to the cyclopentadienyl moiety of C_{60}. X-Ray crystallographic data show insignificant conjugation of the 1,4-diene of the central pentagon.

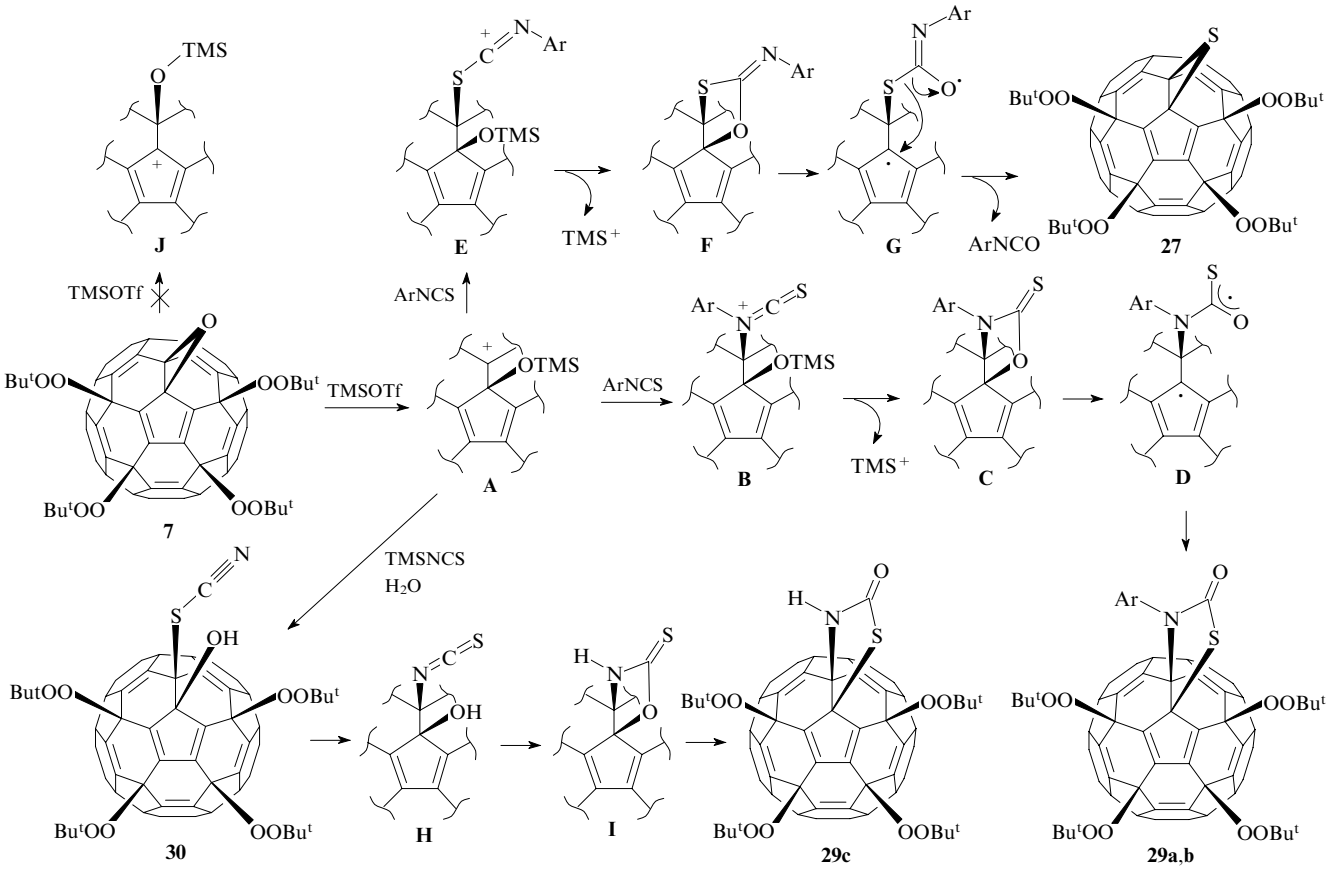
All operations for isolation of adduct **28** are carried out in the dark, which ensures its stability for several hours; then, it is slowly converted into adducts **27** and **29**. The reaction of compound **28a** with TMSOTf gives a complex product $C_{60}(SCN)(OH)(OO^tBu)_4$ (**30**), and its isothiocyanate and hydroxyl moieties are involved in conversion under the action of Al_2O_3 to quantitatively give the fullerene adduct with tetrahydrothiazol-2-one (compound **29**) (Scheme 19).

The proposed mechanism of formation of thiirane derivative **27** and thiazolidine adduct **29** involving intermediate **A**–**I** is shown in Scheme 19. At the first stage, an acidic reagent (TMSOTf) attacks the epoxide moiety of compound **7** to regioselectively form carbocationic intermediate **A**. Depending on the nature of the attacking atom (nitrogen or sulfur), addition of ArNCS to cation **A** gives intermediate **B** or **E**, and elimination of the TMS^+ cation from intermediates **B** or **E** gives neutral product **C** or F. Homolysis of the C–O bond leads to formation of stable cyclopentadienyl radical **D**. This process is more probable than heterolytic C–O bond cleavage at the first stage initiated by a Lewis acid since alternative intermediate **J**, which has a positive charge in the central pentagon, is antiaromatic.

Intramolecular interaction of free spins localized on the five-membered ring and the sulfur atom of intermediate **D** ends with the formation of thiazolidinone **29**. The C–O bond cleavage in intermediate **F** to give structure **G** is also possible; removal of the ArNCO fragment from **G** leads to thiirane derivative **27**. The product of photolysis is compound **27**, and those of thermolysis are compounds **29a**,**b**.

As the reaction mixture of CFP **7** with TMSOTf is run through a silica gel column, red thioisocyanate derivative **30** is formed owing to the easier elimination of the TMS group as compared with the aryl one. The use of a column with another stationary phase (Al_2O_3) affords adduct **29c** (Scheme 20). The same adduct is formed upon the treatment of thiocyanate **30** with neutral Al_2O_3. It is suggested that the reaction proceeds through isomerization of thiocyanate **30** into isothiocyanate intermediate **H**, which is then converted into intermediate oxazolidinethione **I** (see Scheme 19). This process is similar to the synthesis of adducts **29a**,**b** through formation of intermediate **B**. The reaction of compound **29c** with benzoyl chloride yields adduct **31** (see Scheme 20).

Scheme 19

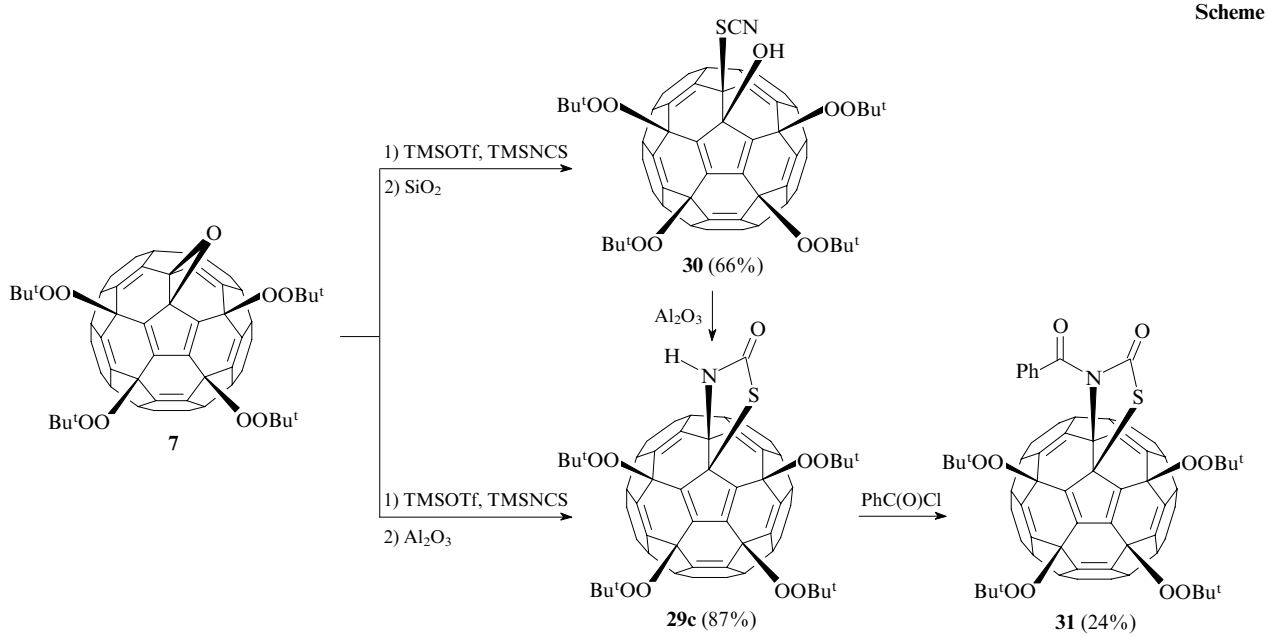


The reaction of $C_{60}(O)(OOBu^t)_4$ (**7**) with another Lewis acid — $BF_3 \cdot Et_2O$ — involves the epoxide group and leads to the fullerene adduct with 1,3,2-dioxoborolane $C_{60}(O_2BOH)(OOBu^t)_4$ (**32**) (Scheme 21).[15]

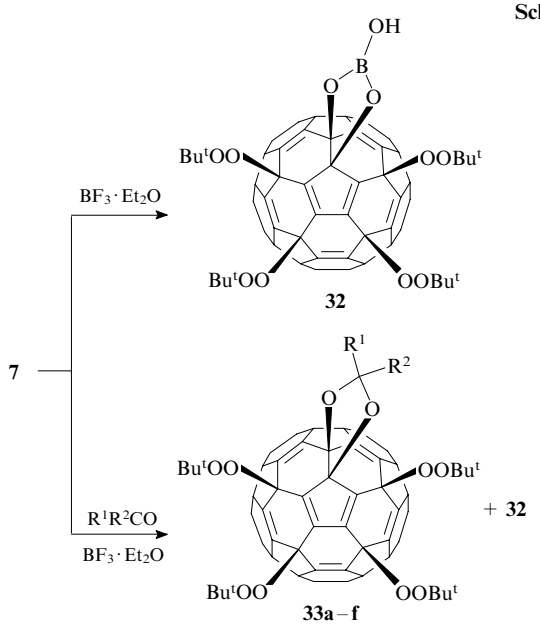
In combination with aldehyde or acetone, boron trifluoride diethyl ether complex catalyzes the transformation of CFP **7** into fullerene adducts with 1,3-dioxolane (**33a**–**f**). Compounds **33a**,**d**,**e** are formed in higher yields in the reactions with aromatic aldehydes containing electron-donating groups and with aliphatic aldehyde (about 50%).

Adduct $C_{60}(O_2BOH)(OOBu^t)_4$ (**32**) has also been obtained by esterification of vicinal diol **15** with (het)arylboronic acids (Scheme 22).[33] The reaction proceeds through the formation of dioxaborolanes **34a**–**e**.

Scheme 20

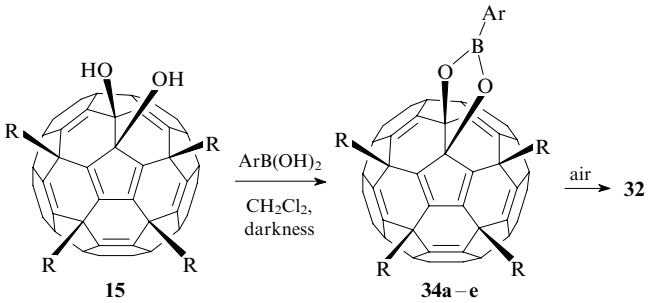


Scheme 21



R^1 = H: R^2 = 4-HOC_6H_4 (**a**), 4-$O_2NC_6H_4$ (**b**), 3-$O_2NC_6H_4$ (**c**), 4-$MeOC_6H_4$ (**d**), Me (**e**); R^1 = R^2 = Me (**f**)

Scheme 22



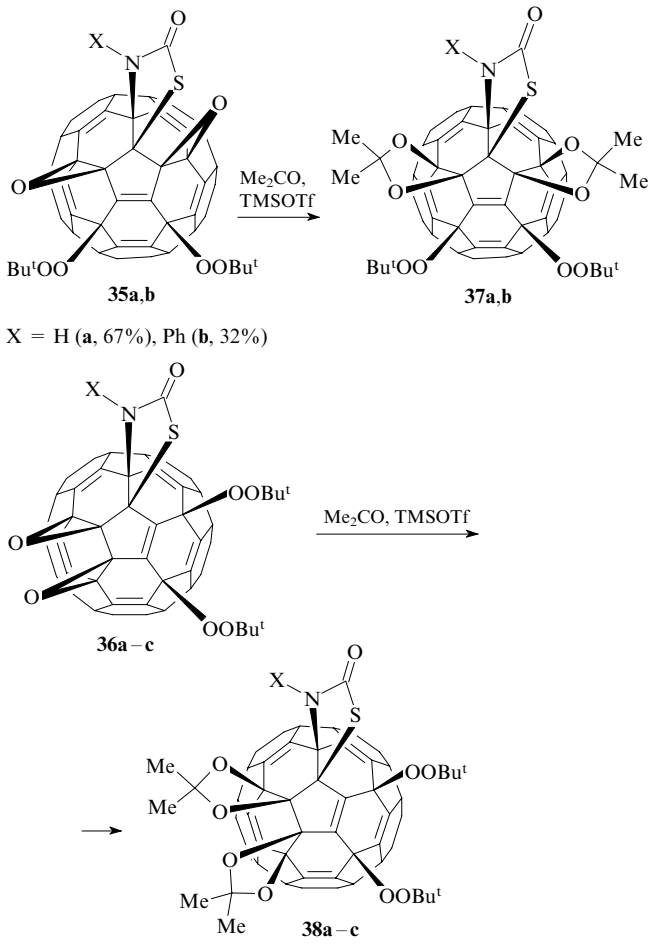
R = $OOBu^t$; **34**: Ar = Ph (**a**, 94%), 2-Fu (**b**, 86%), 2-BFu (**c**, 95%), 2-Th (**d**, 25%), Fc (**e**, 69%);
Fu is furyl, BFu is benzofuryl, Th is thienyl, Fc is ferrocenyl

The epoxide ring in isomeric bisepoxides **35a**,**b** and **36a**–**c** is readily acetalized with an aldehyde or ketone in combination with a Lewis acid to form the 1,3-dioxolane moiety, the reaction being faster in CH_2Cl_2 than in benzene (Scheme 23). The reaction results in isopropylidene derivatives **37a**,**b** and **38a**–**c**. It is worth noting that analogous naphthyl-substituted adduct **35c** (X = Naph) does not react under these conditions.

3. Reactions of fullerene alkyl peroxides with O–O bond cleavage

Unlike $FeCl_3$ opening the epoxide ring, $AlCl_3$ in the reaction with chlorohydrin **16a** leads to heterolysis of the peroxide O–O bond so that regioisomers **39** and **40** are formed. In these compounds, hemiacetal moieties are located at the [5,6] and [6,6] junctions (Scheme 24).[4] The regioselectivity of the process can be controlled by varying the solvent. In dichloromethane, the major product is [5,6] hemiacetal **39**, with a trace of [6,6] adduct **40**. However,

Scheme 23



X = H (**a**, 67%), Ph (**b**, 32%)

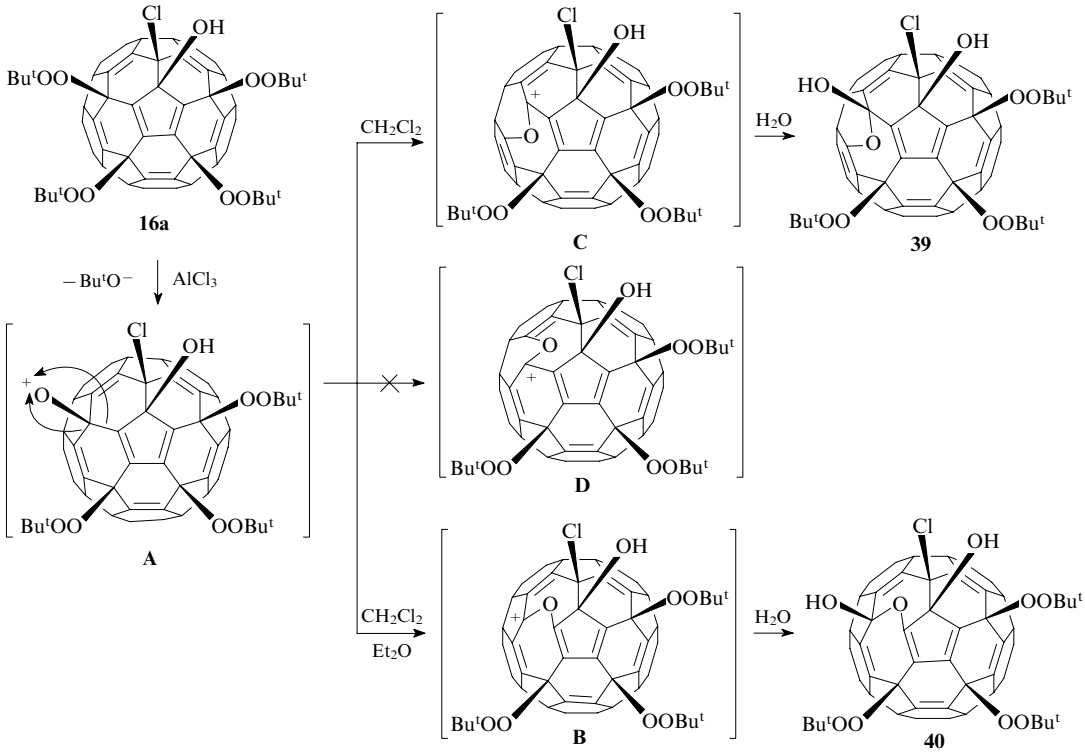
X = H (**a**, 45%), Ph (**b**, 45%), Naph (**c**, 23%)

addition of Et_2O, MeCN or Me_2S as a cosolvent reverses the product ratio and affords hemiacetal **40** as the major product. The key stage is proposed to be heterolysis of the O–O bond with elimination of the Bu^tO^- anion, leading to oxonium cation **A**, which then rearranges (through the known Hock-type rearrangement) to carbocation **B** ([5,6] junction cleavage) or **C** ([6,6] junction cleavage). In the absence of Et_2O, ether **C** is the favoured species. The adjacent OH group probably stabilizes carbocation **C**. When diethyl ether is added, cation **B** is the favoured species, since the positive charge on this cation is located farther from the central pentagon than in cation **C**. Thus, Et_2O can stabilize cation **B** more effectively for steric reasons. Cleavage of the [5,6] junction would form carbocation **D**, but no corresponding hemiacetal was detected.

The reaction of $FeCl_3$ with chlorohydrin **16a** in dichloromethane leads to the replacement of the chlorine atom by a hydroxyl group to form mixed diol **15** (Scheme 25).[4]

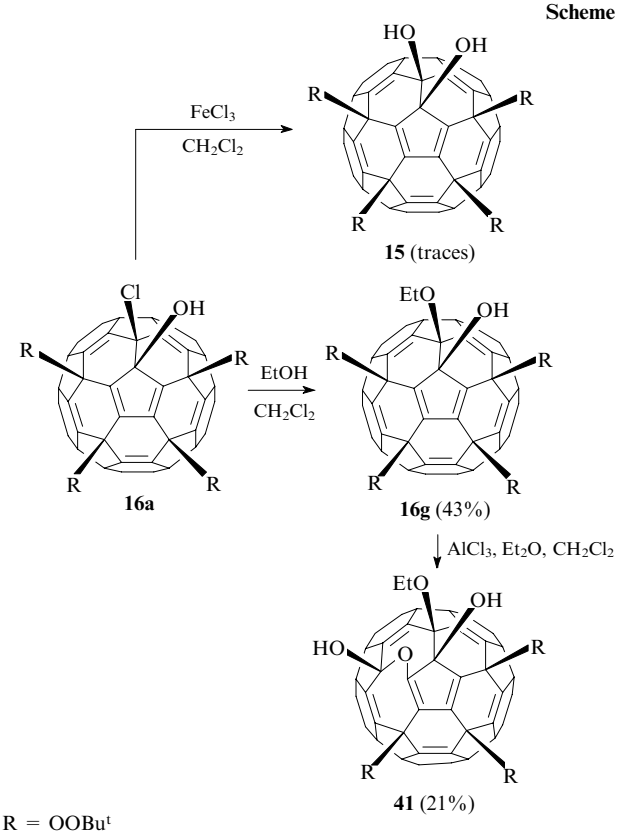
When dichloromethane contains EtOH, the chlorine atom is replaced by an EtO group to form adduct **16g**, which then reacts with $FeCl_3$ (or $AlCl_3$ in a CH_2Cl_2–Et_2O mixture) to convert into hemiacetal **41**. Hemiacetals **39**, **40** and **41** isomerize on addition of Lewis acids or irradiation with visible light (Scheme 26). In particular, hemiacetal **39** is converted into adduct **40** and hemiacetal **42** when treated

Scheme 24



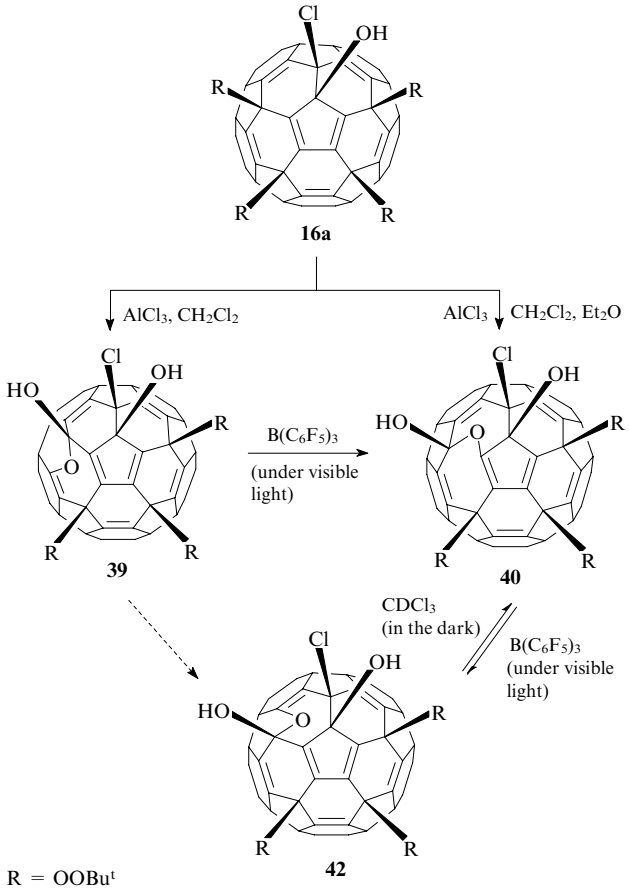
with $La(NO_3)_3$ or $B(C_6F_5)_3$ or exposed to light. It is still unclear whether compound **42** forms directly from hemiacetal **39** or by further isomerization of hemiacetal **40**, which also gives product **42** under the same conditions. The structure of adduct **16g**, in which the shortest two C=C bonds belong to the central pentagon, has been determined by single-crystal X-ray diffraction.

Scheme 25



R = OOBu^t

Scheme 26



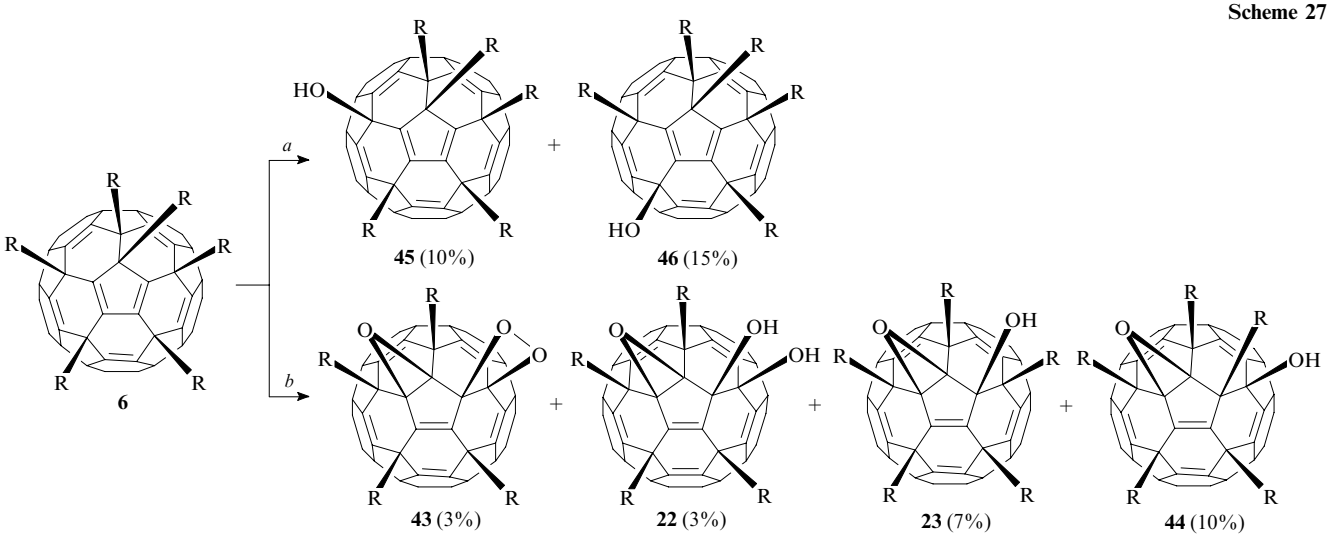
R = OOBu^t

4. Synthesis of fullerene alcohols from fullerene alkyl peroxides

The development of efficient methods of synthesis of fullerenols faced two major problems. One of them is related to the fact that these reactions often yield complex mixtures of compounds with an unknown number and location of OH groups on the fullerene cage. In particular, the fullerenols synthesized by oxidation of fullerene C_{60} by acids contain hemiacetal moieties,[38] and the adducts formed upon treatment of C_{60} with an aqueous NaOH solution are radical anions with a complex structure.[40] For these reason, characterization of the synthesized fullerenols has often been incomplete. However, it should be noted that reactions leading to isomerically pure fullerenols containing extra addends of different nature have been reported in the literature. Among such compounds for which the structure has been reliably determined are monool $C_{70}Ph_9(OH)$ obtained by the reaction of $C_{70}Cl_{10}$ with $FeCl_3$ in benzene,[60] bis(epoxy)fullerenol $C_{60}Me_5O_2OH$ synthesized by the reaction of $C_{60}Cl_6$ with methyllithium,[61] diol $C_{70}Ph_8(OH)_2$ isolated after UV irradiation of an oxygen-saturated solution of $C_{70}Ph_8$ in CH_2Cl_2,[62] fluorofullerenol $C_{60}F_{35}OH$ formed upon hydrolysis of $C_{60}F_{35}$ (Ref. 58), and the first oxahomofluorofullerenol $C_{60}F_{17}(O)OH$ obtained by UV irradiation of a toluene solution of $C_{60}F_{18}$ in air.[63]

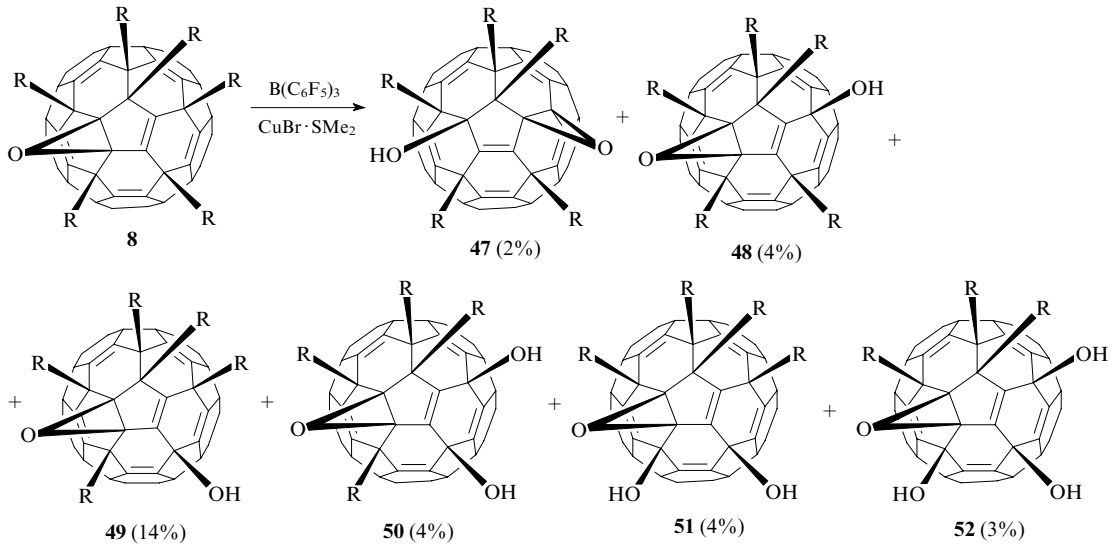
The second problem is related to the synthesis of 'pure' alcohols free of the addends other than hydroxyl groups. Indeed, as mentioned above, the synthesized fullerenols often contain hemiacetal moieties and a carbonyl group[38] or are saltlike compounds.[64,65] Successful syntheses of fullerenols containing only hydroxyl groups have been reported. The first compounds of this series — alcohols $C_{60}(OH)_{18-20}$ — have been synthesized by Chiang with coworkers in the 1990s through the reaction of a C_{60} solution in CH_2Cl_2 with the nitronium salt NO_2BF_4 in sulfolane,[66] as well as by bubbling NO_2 through a C_{60} solution in benzene or toluene.[67] Later, the $C_{60}(OH)_2$ and $C_{70}(OH)_2$ diols have been synthesized by oxidation of the corresponding fullerenes by ruthenium oxide RuO_4.[68]

Scheme 27



R = $OOBu^t$; (*a*) $B(C_6F_5)_3$, $CuBr \cdot SMe_2$; (*b*) $B(C_6F_5)_3$

Scheme 28



R = $OOBu^t$

Gan and co-workers [8] have suggested to solve the problem of synthesis of isomerically pure fullerenols with different addends by using transformations of isomerically pure fullerene peroxides. In particular, $C_{60}(OOBu^t)_6$ (**6**) reacts with the Lewis acid $B(C_6F_5)_3$ to form (as a result of partial fragmentation of $OOBu^t$ groups) dioxetane **43**, diol **22** and two $C_{60}(O)(OH)(Bu^tOO)_5$ isomers — compounds **23** and **44**; under other conditions, the reaction leads to two $C_{60}(OH)(Bu^tOO)_5$ isomers — compounds **45** and **46** (Scheme 27).

The regioisomers in the pairs of compounds **23**, **44** and **45**, **46** differ only in location of OH groups. Further treatment of these fullerenols affords di- and trihydroxyl-containing fullerene peroxides. Two monohydroxyperoxides (**45** and **46**) have been characterized by single-crystal X-ray diffraction and the other products shown in Scheme 27, by chemical correlation experiments and NMR.

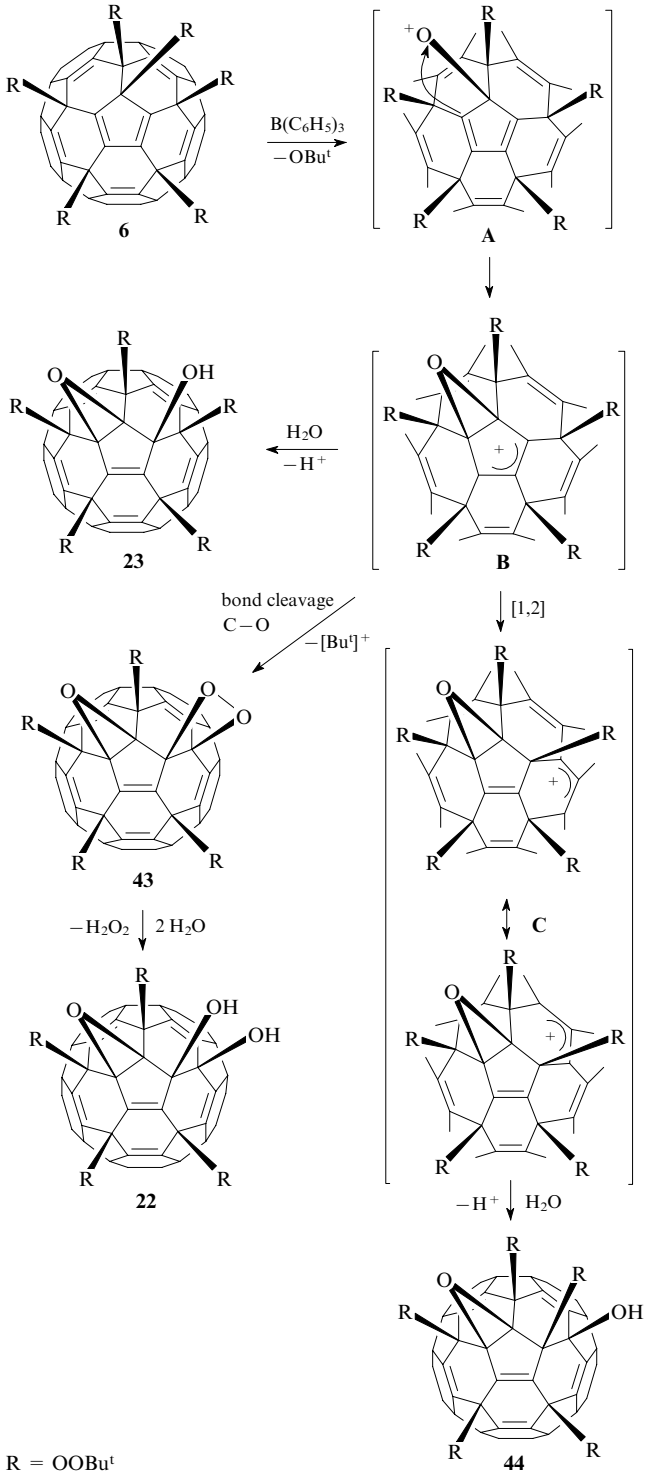
The CuBr salt can protect the most reactive $OOBu^t$ groups from the attack of strong Lewis acids.[8] The proposed mechanism involves heterolysis of the peroxide O–O bond. Upon the joint action of the $CuBr \cdot SMe_2$ complex and $B(C_6F_5)_3$ on peroxide **6**, the number of isomeric products decreases to two monohydroxy derivatives **45** and **46**. The treatment of $C_{60}(O)(OOBu^t)_6$ (**8**) with $CuBr \cdot SMe_2$ and $B(C_6F_5)_3$ leads to three isomers of monohydroxy derivatives (**47**–**49**), two dihydroxy isomers (**50**, **51**) and trihydroxyfullerene **52** (Scheme 28).

The reaction of CFP **8** only with $B(C_6F_5)_3$ yields a complex mixture of products. In addition, compounds **6** and **8** are inert to $CuBr \cdot SMe_2$. Reactions should be stopped long before complete conversion of peroxides **6** and **8** to prevent the formation of a complex product mixture. The following mechanism of the reaction of SFP **6** with $B(C_6F_5)_3$ has been proposed (Scheme 29). The first stage is heterolysis of the peroxide bond located at the vertex of a five-membered ring with abstraction of the Bu^tO^- anion and formation of oxonium cation **A**; then the positively charged oxygen atom is added to the neighbouring C=C bond in the cyclopentadienyl moiety so that cation **A** converts to allyl cation **B**. Addition of a water molecule to cation **B** gives diol **22**. It is likely that diol **22** can be formed by hydrolysis of dioxetane **43** or monohydroxyl derivative **23**, and isomer **44** is produced upon conversion of intermediate **B** to cation **C** through 1,2-shift. Hydrolysis of intermediate allyl cation **C** is regioselective and gives only alcohol **44**.

When an excess of a copper(I) salt is added to CFP **8**, the $OOBu^t$ group attached to the central pentagon is coordinated to the copper ion to give complex **A**, in which some of the $OOBu^t$ groups are sterically inaccessible to the attack of $B(C_6F_5)_3$ (Scheme 30).[8] The reaction of intermediate **A** with $B(C_6F_5)_3$ leads to heterolysis of $OOBu^t$ groups and generation of oxonium ions **B** and **C**. These ions are reduced by copper(I) bromide, which is a weak Lewis acid, to form complexes **D** and **E**. Hydrolysis of these complexes gives fullerenols **48** and **49**, respectively. The oxonium group can also add to the neighbouring C=C bond of the central cyclopentadienyl moiety with opening of the epoxide ring to form new oxonium intermediate **F**, which is hydrolyzed to adduct **47**.

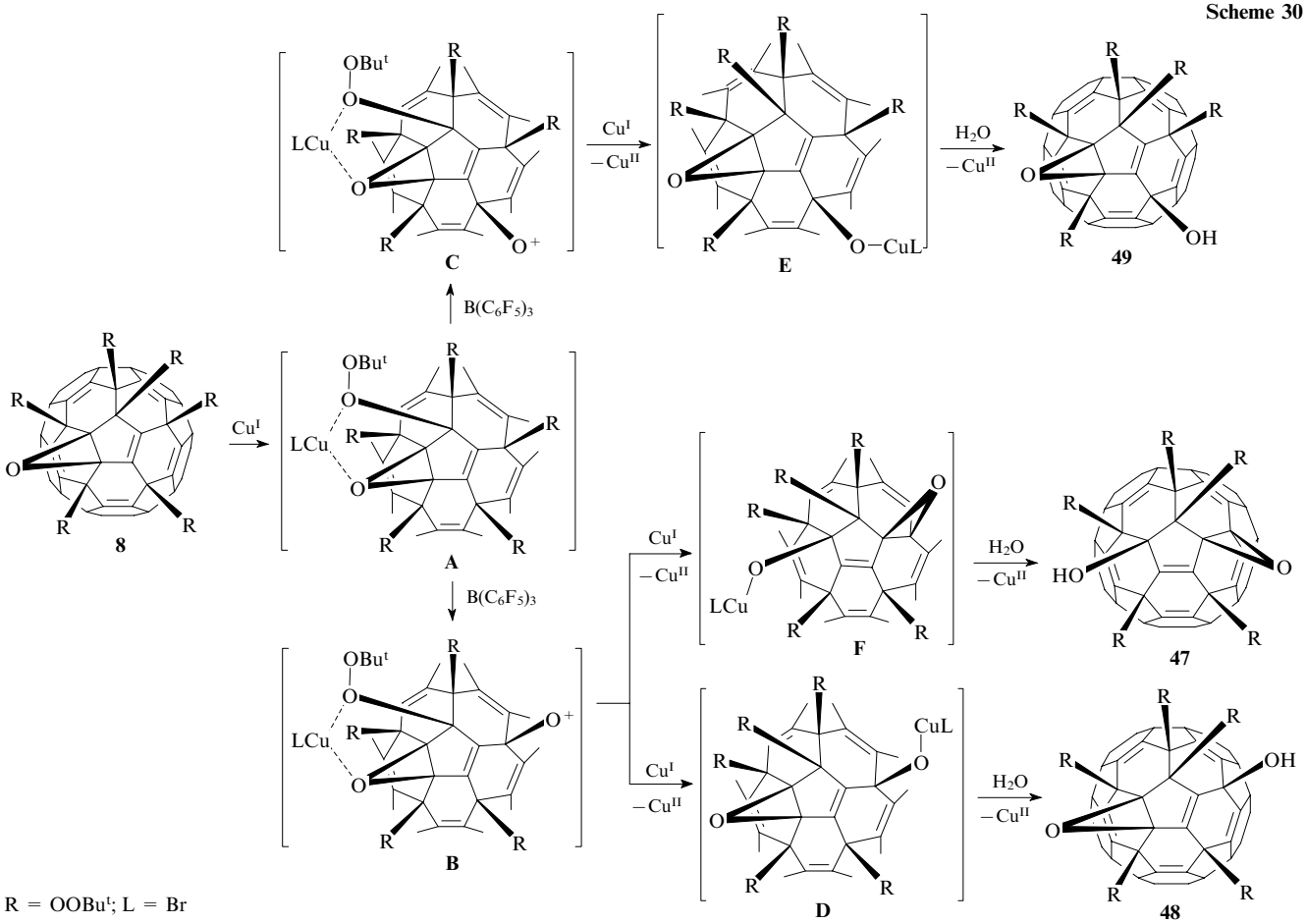
To obtain fullerenols containing only hydroxyl groups, a scheme of synthesis from peroxides has been developed.[8, 23] The peroxide groups in SFP **6** were successively reduced to epoxide and then to hydroxyl groups. This approach afforded the synthesis of fullerenols containing from two

Scheme 29



to eight OH groups. However, only the adduct with eight hydroxyl groups turned out to be a pure fullerenol. The sequence of reactions used for its preparation is shown in Scheme 31. In particular, $C_{60}(OOBu^t)_6$ (**6**) is first converted into vicinal diol $C_{60}(OH)_2(OOBu^t)_4$ (**15**), and its thermolysis leads to bis(epoxy)diols $C_{60}(O)_2(OH)_2(OOBu^t)_2$ (**53**, **54**). The addition of iodine increases the yield of compounds **53** and **54** owing to its reaction with radical thermolysis products.[23] These are most likely alkoxyl radicals $Bu^tO^{\bullet}$, the products of homolysis of the peroxide bond; addition of

Scheme 30

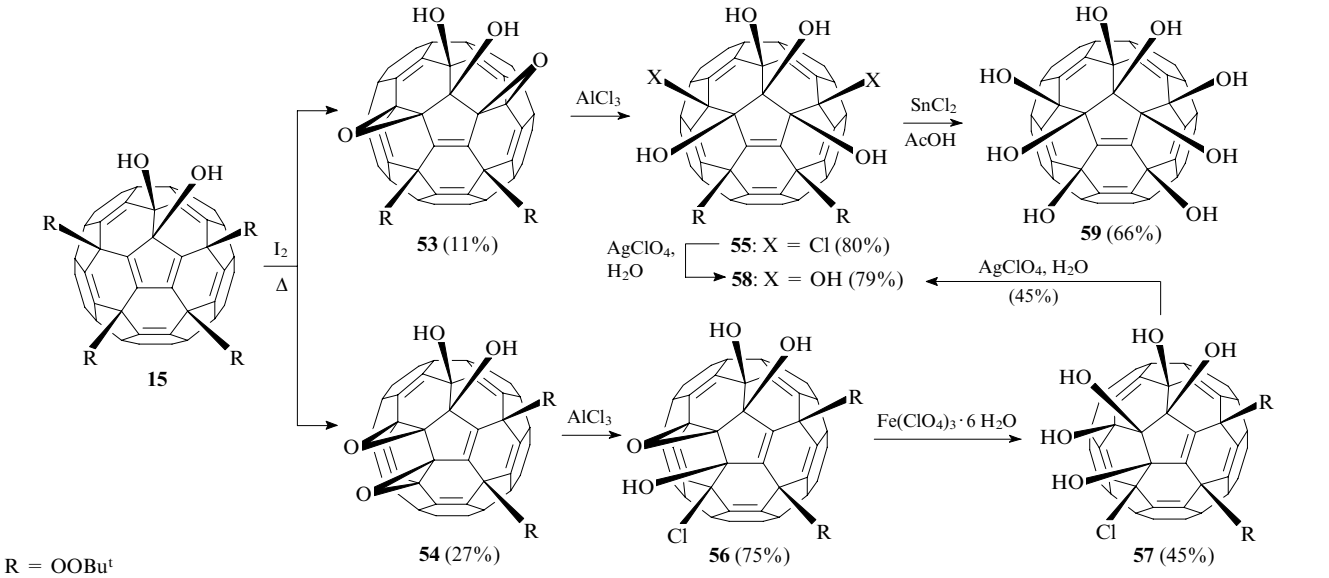


R = OOBu^t; L = Br

these radicals to the fullerene cage gives by-products. Then, $AlCl_3$ opens two epoxide rings in compound **53** to give adduct **55**, containing vicinal Cl atom and OH group. The same reaction of compound **54** leads to the opening of only one epoxide ring to give adduct **56**; the latter reacts with $Fe(ClO_4)_3 \cdot 6\,H_2O$ to form vicinal polyol **57**. Adducts **55** and **57** react with $AgClO_4$ in the presence of water to give hexahydroxy derivative **58**.

Finally, the two last OOBu^t addends are reduced to hydroxyl groups by tin(II) chloride, which gives the target product — octahydroxyfullerene $C_{60}(OH)_8$ (**59**). The authors state that neither thermolysis nor photolysis is

Scheme 31

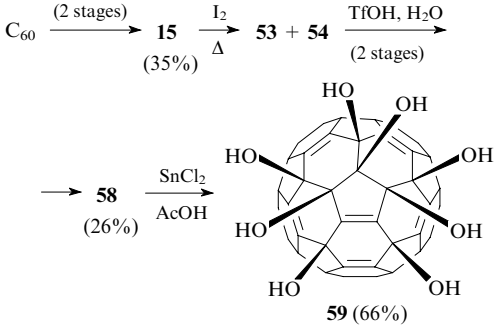


R = OOBu^t

effective for conversion of two $OOBu^t$ addends in adducts **53** and **58** into epoxide rings.

Since fullerenol **59** is a promising candidate for practical use, an optimal scheme of its synthesis has been developed (Scheme 32). According to this scheme, a mixture of isomers **53** and **54** is treated with trifluoromethanesulfonic acid to obtain compound **58**. Then, CFP **58** is converted into product **59** with the use of $SnCl_2$ as a reducing agent. The yield of compound **59** in this case is 6% based on the initial fullerene C_{60}.

Scheme 32

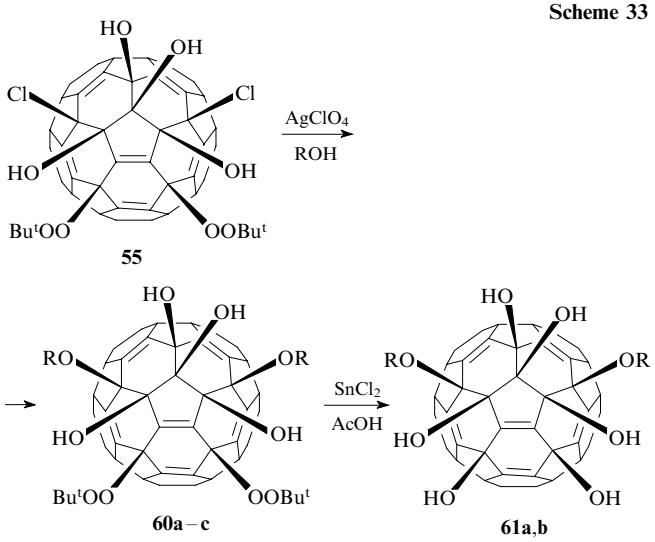


Since all OH groups in fullerenol **59** are located on the same hemisphere of the fullerene cage, it is amphiphilic and forms spherical aggregates in water with a hydrodynamic radius (R_h) of 100 nm (at a concentration of 10^{-5} mol litre^{-1}). The size of dried aggregates is much smaller (8 nm); aggregation presumably occurs in solutions with low density. Aggregates consisting of several $C_{60}(OH)_8$ molecules have polydomains, *i.e.*, regions enriched in hydrophobic (fullerene cages) or hydrophilic (OH groups) moieties, which can be used to deliver hydrophobic and hydrophilic drugs to the body.

As noted above, adduct **55** reacts with $AgClO_4$ in the presence of water to form fullerenol **58** (see Scheme 31). The use of acetylene alcohols rather than water leads to formation of intermediate adducts **60a**,**b**, which contain three different functional groups and, being reduced, give complex fullerenols **61a**,**b** (Scheme 33).[32] The reaction also gives homologue **60c** in low yield.

The triple bond in the alkoxyl addend of adduct **61b** enables the selective azide–alkyne cycloaddition of benzyl azide to give adduct **62** (Scheme 34). Diyne **63** has been synthesized by copper-catalyzed intramolecular cyclization of **61b** under Gllaser–Hay conditions. The high yield of the product is achieved by selecting the substrate concentration (1 mg per 3 ml CH_2Cl_2) that rules out the undesired intermolecular coupling reaction. Compounds **62** and **63** have been characterized by NMR. Their molecules have symmetry C_S.

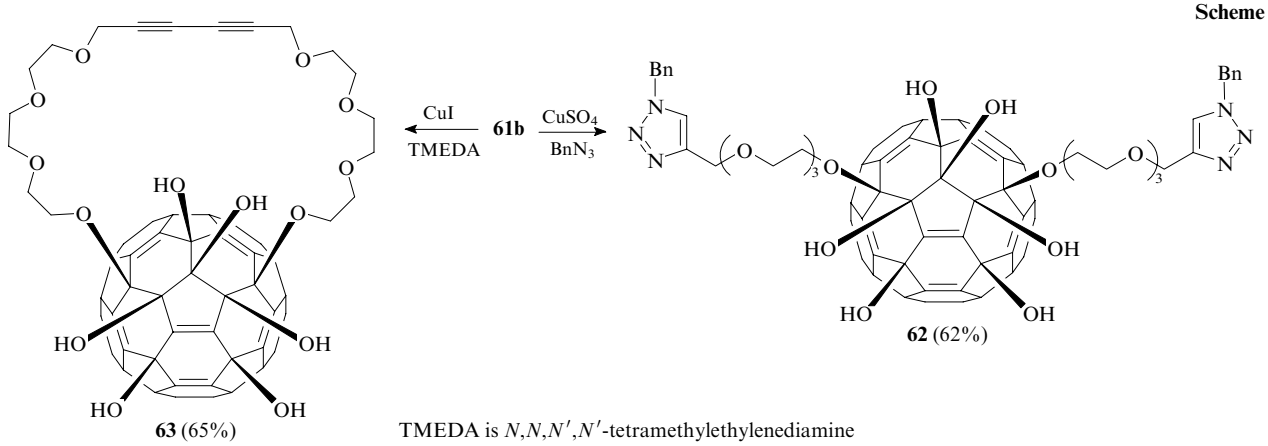
Scheme 33



Compounds **60**, **61**	R	Yield (%)	
		60	**61**
a	$(CH_2)_3C{\equiv}CH$	62	32
b	$(CH_2CH_2O)_3CH_2C{\equiv}CH$	77	45
c	$(CH_2CH_2O)_4CH_2C{\equiv}CH$	12	0

Fullerene peroxide $C_{60}(O)(OOBu^t)_4$ (**7**) readily reacts with primary and secondary aliphatic amines with O–O and C–O bond cleavage to form amino adducts, including simple hydroamination products, and aminoketo derivatives.[13] The observed chemo- and regioselectivities of such reactions are explained in terms of SET and steric hindrances. The $OOBu^t$ groups in these compounds effectively protect the central pentagon, thus stabilizing unstable products. With the aim of synthesizing C_{60} derivatives with addends containing nitrogen and oxygen atoms, reactions of peroxide **7** with ammonia and primary and secondary aliphatic amines have been studied.[13] Both ammonia and amines add to the cyclopentadienyl moiety (1,4-conjugate addition). Unlike C_{60}, CFP **7** readily reacts with

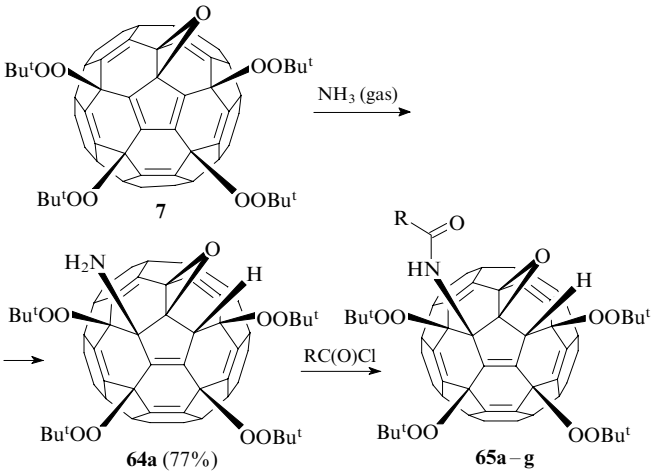
Scheme 34



TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

gaseous ammonia to give, even in the presence of a reagent excess, only monoadduct **64a** in which the epoxide and peroxide groups are retained (Scheme 35). The reaction with an aqueous ammonia solution is much slower. Amide derivatives **65a–g** have been synthesized in the reaction of adduct **64a** with acyl chlorides.

Scheme 35



65: R = Ph (**a**, 61%), 4-$O_2NC_6H_4$ (**b**, 65%), 2-$HO_2CC_6H_4$ (**c**, 29%), 3-$ClC(O)C_6H_4$ (**d**, 41%), 4-$ClC(O)C_6H_4$ (**e**, 52%), 4-$MeOC(O)C_6H_4$ (**f**, 52%), $(CH_2)_8CO_2H$ (**g**, 48%)

CFP **7** reacts with primary amines (methylamine and benzylamine) to form, respectively, adducts **64b** and **64c** (Scheme 36). The opening of the epoxide ring in the reaction with 2,2-diethoxyethylamine gives monoadduct **66f** (of symmetry C_S), which is isolated in the pure form. However, other amines lead to a mixture of isomers with the intact (**64d**,**e**) and opened (**66d**,**e**) epoxide ring. Because of low selectivity, the yield of compounds **64b–f** is rather low. Compound **66** is formed by the conjugate addition mechanism with nucleophilic opening of the oxirane ring (S_N2''). The reaction with butylamine yields a difficult to separate mixture of two isomers.

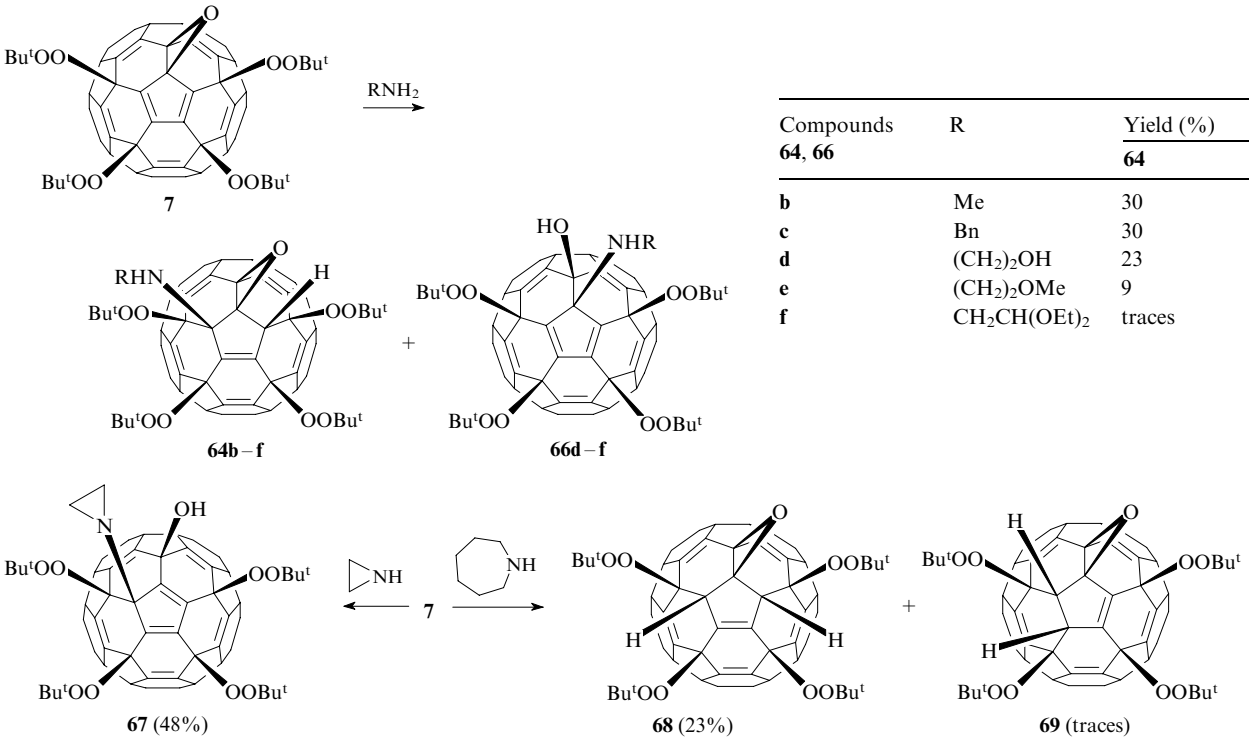
Secondary cyclic amines show different reaction patterns with $C_{60}(O)(OOBu^t)_4$ (**7**). The nucleophilic attack of aziridine on epoxide **7** leads to epoxide ring opening and conjugate addition to form compound **67**, which contains the OH group (see Scheme 36). Meanwhile, bulky hexahydroazepine is not added to the fullerene cage; rather, it acts only as a hydrogenating agent to give isomeric hydrogenated derivatives **68** and **69**.

In the reaction of vicinal bromohydroxy derivative $C_{60}(OH)(Br)(OOBu^t)_4$ (**16f**) with bulky cyclic amines (pyrrolidine, piperidine, hexahydroazepine and morpholine), two $OOBu^t$ groups are converted into two aminoacetal moieties in products **70a–d**, and one HBr molecule is eliminated from the vicinal bromohydroxy moiety to give the epoxide ring (Scheme 37). In the reaction with aziridine, only an aziridine ring is substituted for the bromine atom. The structures of compounds **65a**, **66e** and **70a** have been proved by X-ray crystallography.

The mechanism of reactions of compound **7** with amines is not exactly understood. However, it has been noted that the key factor determining the direction of addition is the size of an amine molecule. This is caused by two facts. First, the C=C bond in the cyclopentadienyl moiety of CFP **7** is most reactive as compared with the other bonds; second, this bond is sterically hindered by the four peroxide addends surrounding the pentagon.

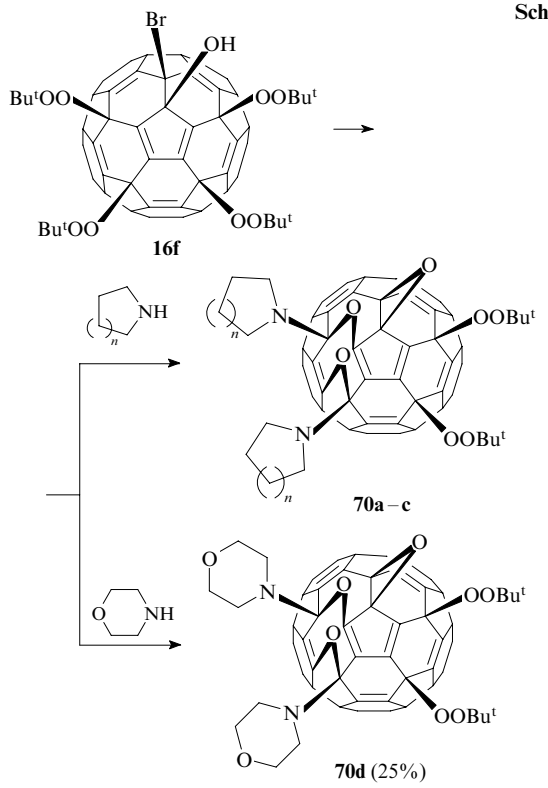
Generally, nucleophiles react with fullerene peroxides by the S_N1 or S_N2' and S_N2'' mechanisms. In particular, the addition of NaOMe to 1,4-bisadduct $C_{60}(OOBu^t)_2$ (**3**) leads to the elimination of the OBu^t group to give the $C_{60}(O)(OMe)(OOBu^t)$ epoxide (**71**) (44% yield)

Scheme 36



Compounds **64**, **66**	R	Yield (%)	
		64	**66**
b	Me	30	0
c	Bn	30	0
d	$(CH_2)_2OH$	23	16
e	$(CH_2)_2OMe$	9	23
f	$CH_2CH(OEt)_2$	traces	36

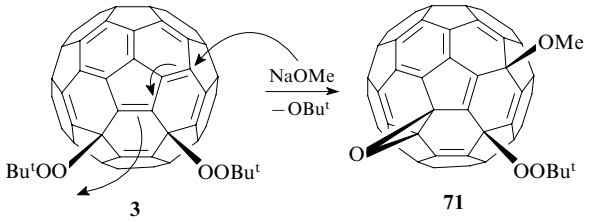
Scheme 37



n = 1 (**a**, 12%), 2 (**b**, 21%), 3 (**c**, 9%)

(Scheme 38).[2,6] With CFP **7**, the reaction is more complicated: polyaddition of four methoxy groups gives four products, including $C_{60}(O)(OH)_2(OMe)_4(OOBu^t)_2$ (**72**) (Scheme 39). At the first stage, methoxy anion attacks the carbon atom of the epoxide ring. The latter is opened to form the positively charged carbon atom of the fullerene cage, to which the first OMe group is added. Formation of the fullerene alkoxide anion upon the epoxide ring opening promotes the elimination of the OBu^t group (by the S_N2' mechanism) to produce the primary intermediate $C_{60}(O)_2(OMe)(OOBu^t)_3$, its structure being proved by single-crystal X-ray diffraction. Then, its reaction with

Scheme 38



NaOMe and MeOH yields product **72**, which has also been characterized by X-ray crystallography.

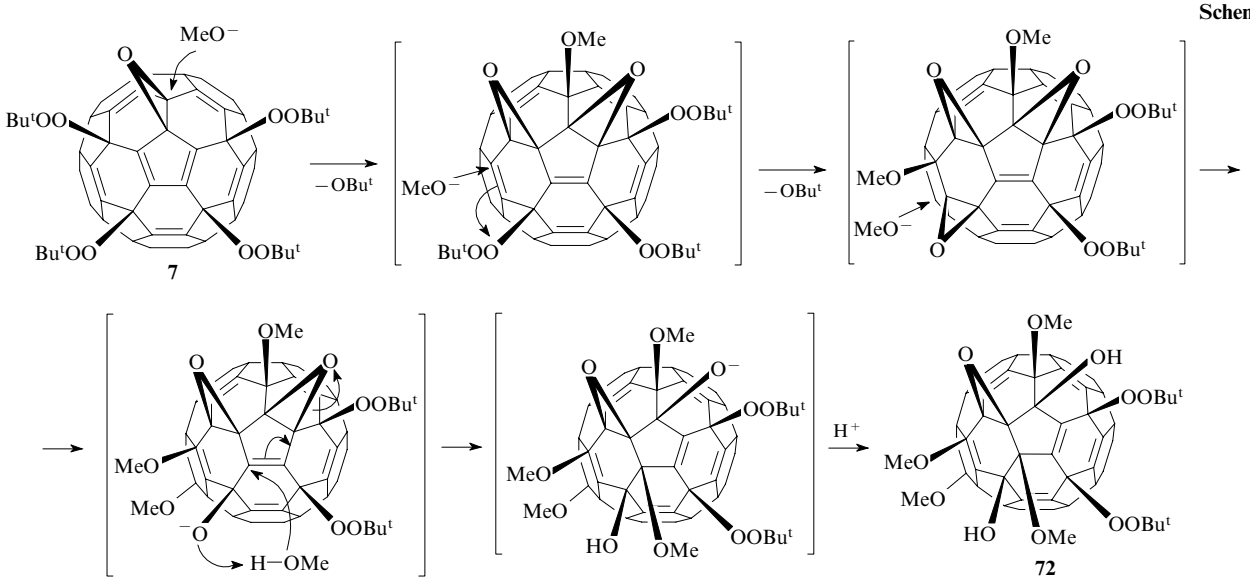
The authors have suggested that, at the first stage, the coordination of the sodium cation to the epoxide oxygen atom can ininitate epoxide ring opening with appearance of a positive charge on the carbon atom, which adds the methoxide anion. However, no evidence of such an alternative reaction path has been reported.

5. Alkyl peroxides in fullerene cage opening reactions

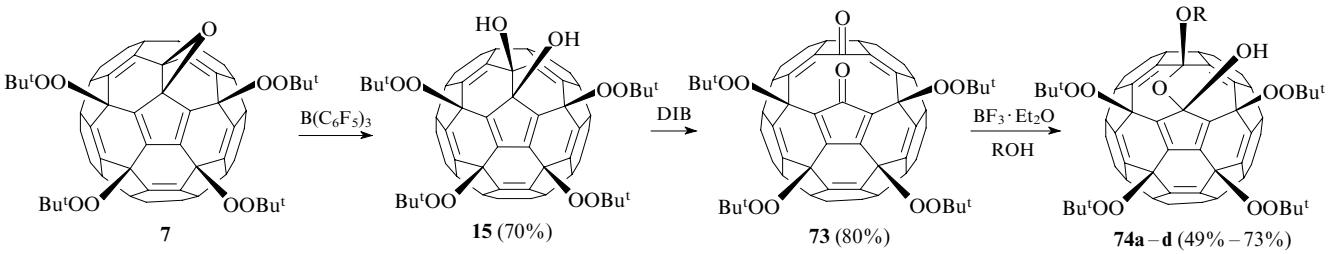
Fullerene alkyl peroxides turned out to be valuable precursors in synthesis of open-cage fullerene derivatives, *i.e.*, in the field referred to as molecular surgery.[69] These compounds are of interest as capsules promising for use in molecular electronics,[70] pharmacology and medicine.[7,12,16,21,23,25] For example, fullerene cage opening considerably changes physicochemical properties of a compound (in particular, redox potentials), which makes it possible to increase the idle voltage in solar cells fabricated on the basis of open-cage adducts.[71] Such derivatives can be used as contrast agents in magnetic resonance imaging[7,72] and as carriers of encapsulated tritium-labelled water in diagnostic radiopharmacology.

It should be noted that, as distinct from the well-developed chemistry of exohedral fullerenes, fullerene cage opening reactions have been much less studied. In particular, it is known that the oxidation of organic vicinal diols is a classical example of C–C bond cleavage leading to carbonyl groups. A similar approach has been suggested for synthesis of open-cage fullerene derivatives. For example, vicinal fullerenediol **15** turned out to be a good precursor for synthesis of open-cage keto derivatives **73**

Scheme 39



Scheme 40



7 **15** (70%) **73** (80%) **74a–d** (49%–73%)

R = H (**a**), Me (**b**), OH (**c**), OBu^t (**d**)

with the use of DIB as an oxidant. Diol **15** was obtained in 70% yield by epoxide ring opening in compound **7** upon hydrolysis promoted by $BF_3 \cdot Et_2O$ (Scheme 40).[7, 25]

Other oxidants [for example, $Pb(OAc)_4$ and $NaIO_4$] do not induce this reaction. Treatment of diketone **73** with $BF_3 \cdot Et_2O$ in the presence of water gives adduct **74a** through coupling of the two carbonyl groups, which contain oxygen-bridged hemiacetal and acetal moieties. Analogously, the reactions with MeOH, H_2O_2 and Bu^{t}OOH yield products **74b–d**, respectively. Compounds **73** and **74** are readily soluble in organic solvents, and they can be easily purified by column chromatography over silica gel. These coupling processes are regioselective since they lead to the only isomer with the side OR group and the OH functionality on the central pentagon. It is believed that product **74** forms from the cation in which the positive charge is localized on the carbon atom bound to the sp^3-hybridized carbon atom of the cyclopentadienyl moiety through an oxygen bridge (Scheme 41).

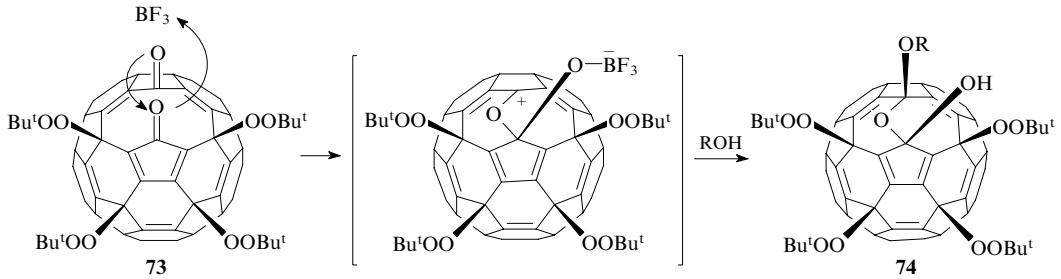
The ^{13}C NMR spectra of diketone **73** show the signals of two carbonyl carbon atoms at 196.88 and 196.64 ppm, and the mass spectrum (ESI) shows the molecular ion peak at m/z = 1126 ($M + NH_4$). The ^{13}C NMR spectra of alkoxyfullerene **74b** show four well-defined signals in the range 100–110 ppm corresponding to two carbon atoms of the hemiacetal and acetal groups. It has been reported[7] that the location of the OH and OR groups (R = Me, OH, OBu^t) of adducts **74b–d** has been confirmed by X-ray crystallography, although single crystals were obtained only for compound **74d**.

To produce fullerene capsules for insertion of water molecules, the possibility of synthesis of open-cage derivatives from fullerene peroxides through C–C bond cleavage and elimination of one carbon atom from the cage has been studied.[12] As a result, fulleroids containing 59 carbon atoms have been prepared starting from SFP $C_{60}(OOBu^t)_6$ (**6**). Such derivatives have a 17-membered-ring orifice. One of the variants of cage opening is visible light irradiation of compound **6**, obtained by the reaction of C_{60} with Bu^{t}OOH under the action of DIB or CAN, in the presence of an I_2 excess. Irradiation leads to diketone **75** in 40 h.[2, 12] Upon exposure to blue light (λ_{max} = 470 nm), the reaction is completed in only 1.5 h and requires only 1 equiv. of I_2, although the yield of product **75** in both cases is the same (25%).[12] In addition to compound **75**, this reaction gives CFP **7** and bisepoxide **9** in low yield.[2] The existence of the open cage in the structure of diketone **75** is supported by strong signals of carbonyl carbon atoms at 193.11 and 192.08 ppm in the ^{13}C NMR spectrum.[2] Initially, based on the observation that the absorption band at 1748 cm^{-1} in the IR spectrum of **75** is close to the absorption band of cyclopentanone (1743 cm^{-1}), a structure in which the C=O groups are attached to the five-membered ring has been suggested for this product.[2] However, single-crystal X-ray diffraction analysis of the adduct obtained by amination of diketone **75** has later shown that the carbonyl groups are located at the six-membered ring.[12] The proposed mechanism of the photoreaction is presented in Scheme 42.

The first stage involves elimination of the *tert*-butyl radical through homolysis of the O–Bu^t bond in the substituent at the central pentagon. This leads to generation of fullerene peroxyl radical **A**, in which intramolecular addition of the O–O$^\bullet$ group to the C=C bond leads to formation of 1,2-dioxetane intermediate **B** containing allyl radical. Subsequent homolytic abstraction of the Bu^{t}O$^\bullet$ radical from the OOBu^t group attached to a hexagon leads to epoxide-containing intermediate **C**; the latter, after rearrangement of the 1,2-dioxetane adduct, gives diketone **75**. A similar rearrangement of a 1,2-dioxetane intermediate has also been proposed for the reaction of C_{60} cage opening leading to ketolactam.[73]

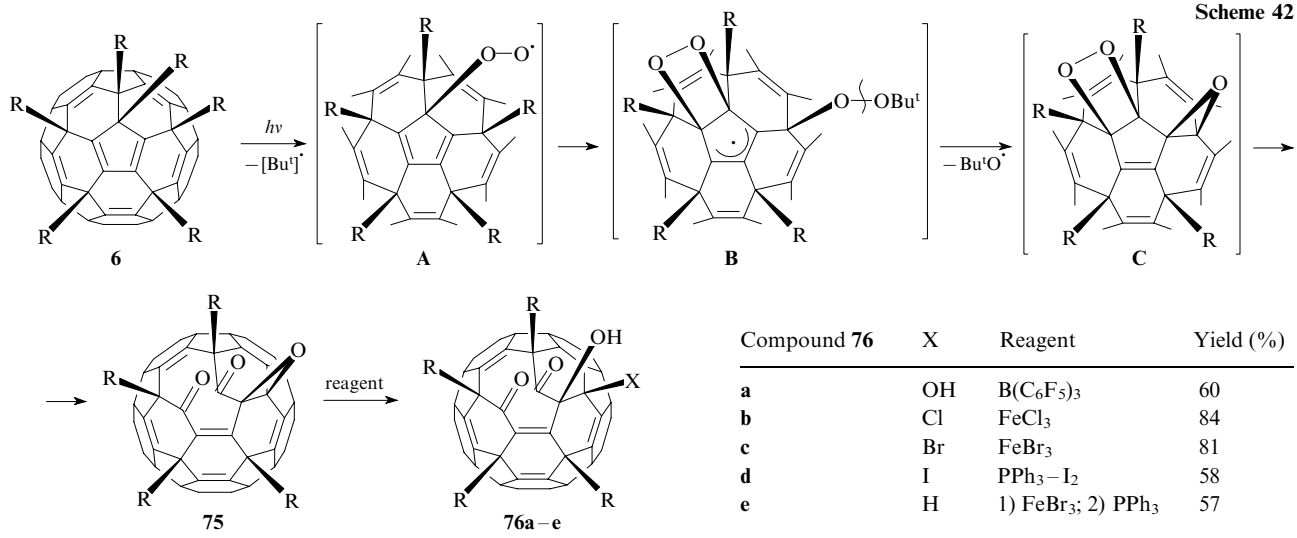
In the absence of iodine, photolysis is inefficient and leads to a complex mixture of products. Inasmuch as iodine does not react with $C_{60}(OOBu^t)_6$ (**6**) in benzene, it presumably acts as a trap of *tert*-butyl radicals, which can add to diketone **75**. Opening of the epoxide ring in the latter is yet another way of expansion of the orifice in the fullerene cage.

Scheme 41



73 **74**

Scheme 42



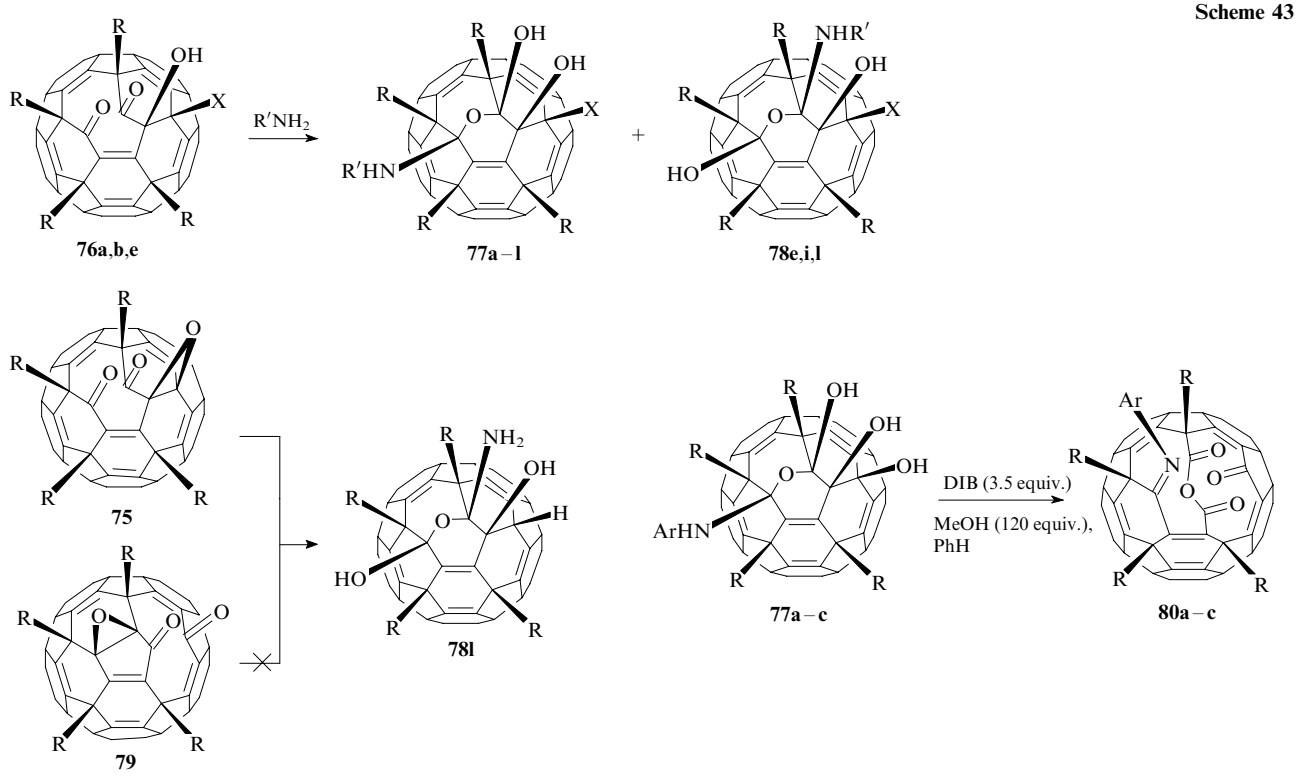
Compound **76**	X	Reagent	Yield (%)
a	OH	$B(C_6F_5)_3$	60
b	Cl	$FeCl_3$	84
c	Br	$FeBr_3$	81
d	I	PPh_3-I_2	58
e	H	1) $FeBr_3$; 2) PPh_3	57

R = $OOBu^t$

The reaction of diketone **75** with $B(C_6F_5)_3$ gives vicinal fullerenediol **76a** in good yield. The reactions of **75** with $FeCl_3$, $FeBr_3$ and the PPh_3-I_2 system are accompanied by epoxide ring opening to form chloro- (**76b**), bromo- (**76c**) and iodohydrins (**76d**) (see Scheme 42), and successive treatment of compound **75** with $FeBr_3$ and PPh_3 reagents leads to hydride **76e**. The high regioselectivity of these reactions corresponds to the cationic mechanism at the first stage. Unsuccessful attempts to oxidize the vicinal fullerenediol moiety of compound **76a** were associated with the steric shielding by the diketone moiety, which the authors have tried to eliminate through conversion of diketone **76a** into the corresponding hemiacetal.

An analogous transformation of diketone to hemiacetal/acetal has been achieved in the reaction with O-nucleophiles in the presence of Lewis acids as catalysts.[7] The attempt to realize this transformation for compounds **76a**,**b**,**e** was unsuccessful, but the problem has been solved by using an N-nucleophile instead of an O-nucleophile, *i.e.*, by amination of diketones **76a**,**b**,**e** to adducts **77a**–**l** (Scheme 43, Table 2).[12] The efficiency and regioselectivity of this reaction depend on steric factors. In particular, with gaseous NH_3, it is completed in a few seconds at room temperature, whereas with aromatic amines, the reaction comes to the end in several hours at elevated temperatures. Bulky amines form only less sterically crowded isomers **77**. Ammonia

Scheme 43



R = $OOBu^t$; **80**: Ar = Ph (**a**, 60%), 4-$MeOC_6H_4$ (**b**, 50%), 4-BrC_6H_4 (**c**, 59%)

Table 2. Yields of the products of reaction of diketones **76** with amines (see Scheme 43).[12]

Substrate **76**	X	R′	Products **77**, **78**	Yield (%)	
				77	**78**
a	OH	Ph	**a**	85	0
	OH	4-$MeOC_6H_4$	**b**	85	0
	OH	4-BrC_6H_4	**c**	79	0
	OH	TsNH	**d**	74	0
	OH	H	**e**	43	43
	OH	$(MeO)_2CHCH_2$	**f**	78	0
b	Cl	4-$MeOC_6H_4$	**g**	65	0
	Cl	$(MeO)_2CHCH_2$	**h**	85	0
	Cl	H	**i**	18	64
e	H	$(MeO)_2CHCH_2$	**j**	81	0
	H	$(EtO)_2CHCH_2$	**k**	89	0
	H	H	**l**	27	67

gives both regioisomers **77e**,**i**,**l** and **78e**,**i**,**l**. The higher yield of products **78** points to higher electron density on the C=O group owing to partial conjugation with isolated double bond.

The ^{13}C spectra of compounds **77** do not show the signals of carbonyl carbon atoms; rather, they show signals of sp^3-hybridized C atoms in the range 90–100 ppm (of two carbon atoms of aminoketal/hemiketal groups). The IR spectra of derivatives **77** have no band corresponding to the carbonyl group and observed in the spectrum of diketones **76**. Both isomers **77** and **78**, which have nearly the same spectral characteristics, have been identified by single-crystal X-ray diffraction analysis.

The structure of compound **78l**, determined by X-ray crystallography, demonstrates that its precursor is compound **75** rather than its isomer **79**.[12] After conversion of the ketone groups into aminoketal/hemiketal, arylamine derivatives **77a–c** are oxidized by DIB in the presence of MeOH to open-cage derivatives **80a–c** (see Scheme 43). One of the three OH groups in compound **77** is oxidized to the ketone group, and the other two OH groups are oxidized to give anhydride; the amino group is oxidized to the imino group. The loss of four protons upon the oxidation of adducts **77a–c** to **80a–c** is clearly monitored by the decrease of the corresponding peaks in the ESI mass spectra. In the IR spectrum of compounds **77**, the ketone group absorption is lacking, and the anhydride group is responsible for the strong and weak bands at 1860 and 1800 cm^{-1}, respectively. The mechanism of oxidation reactions is shown in Scheme 44.

The more reactive amino group is oxidized first to the imine one, which leads to opening of the cage in the aminoketal moiety to form oxonium intermediate **A**. The latter is rearranged to carbocation **B**. Abstraction of proton from this carbocation gives intermediate **C**. Another DIB molecule oxidizes the vicinal diol moiety to two carbonyl groups. As compared with 'open' diketone **75**, compounds **80a–c** have two orifices on the fullerene surface separated by the anhydride moiety. The size of these orifices can be increased by the reaction of the anhydride group with primary amines giving products **81a–f** and **82a–f** with similar structures: compounds **81** have three $OOBu^t$ groups, and compounds **82** contain two $OOBu^t$ groups and one OH group (Scheme 45, Table 3). Treatment of products **81** with copper(I) bromide gives compounds **82** in 90% yield. The structures of adducts **81** and **82** have one large 17-membered-ring orifice. The amide proton of adduct **81a** gives rise to the signal at 8.93 ppm in the ^1H NMR spectrum. The ^{13}C NMR spectrum shows the signals of carbonyl carbon atoms at 185.56 and 184.20 ppm and the signals of the amide and lactone moieties at 160.97 and 162.52 ppm, respectively.

The C=O absorption band of the anhydride moiety, which is observed in the IR spectrum of adduct **80a**, is absent in the spectra of compounds **81**. Instead of this band, strong absorption bands appear at 1802, 1748 and 1699 cm^{-1} corresponding to the lactone, ketone and amide groups, respectively. Single-crystal X-ray analysis of these adducts has shown that one of the carbon atoms is removed from the five-membered ring to form amide functionality. As a result, cyclopentadiene converts into an

Scheme 44

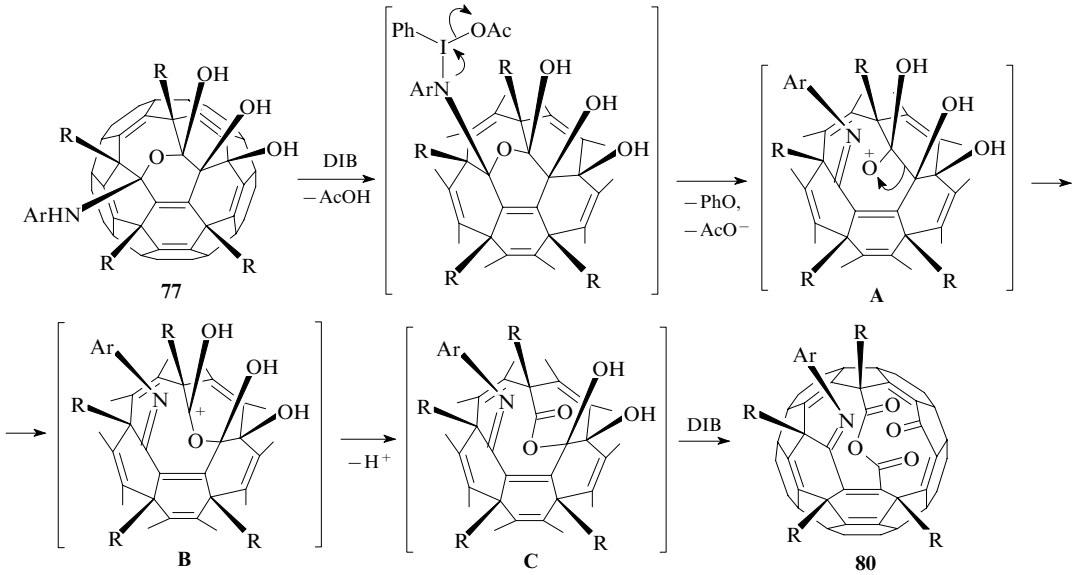
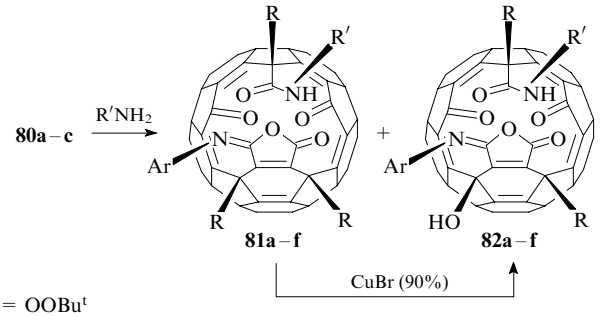


Table 3. Yields of the products of reaction of triketone **80** with amines (see Scheme 45).[12]

Substrate **80**	Ar	Products **81**, **82**	R′	Yield (%)	
				81	**82**
a	Ph	**a**	Ph	21	19
	Ph	**b**	4-$MeOC_6H_4$	30	24
	Ph	**c**	NH_2	30	30
	Ph	**d**	H	30	31
b	4-$MeOC_6H_4$	**e**	4-$MeOC_6H_4$	34	15
c	4-BrC_6H_4	**f**	4-$MeOC_6H_4$	23	24

isomaleic moiety and, as a whole, somewhat lifts above the carbon cage surface.

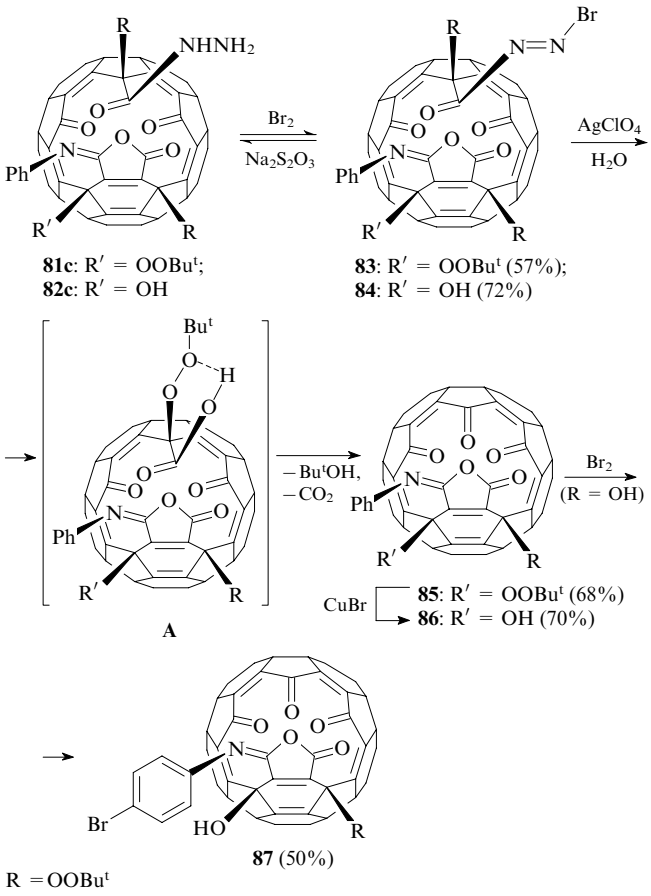
Scheme 45



The following mechanism of these transformations has been suggested [12] (Scheme 46). At the first stage, the nucleophilic attack of an amine on the most electron-deficient C=O group of the anhydride moiety breaks the bridge, generating the amide and carboxyl groups of intermediate **A**. Then, the carboxylate adds to the imine group to form aminolactone intermediate **B**. Although the orifices in the structures of **81** and **82** are rather large, they are blocked by the amide group (as probed by X-ray diffraction).

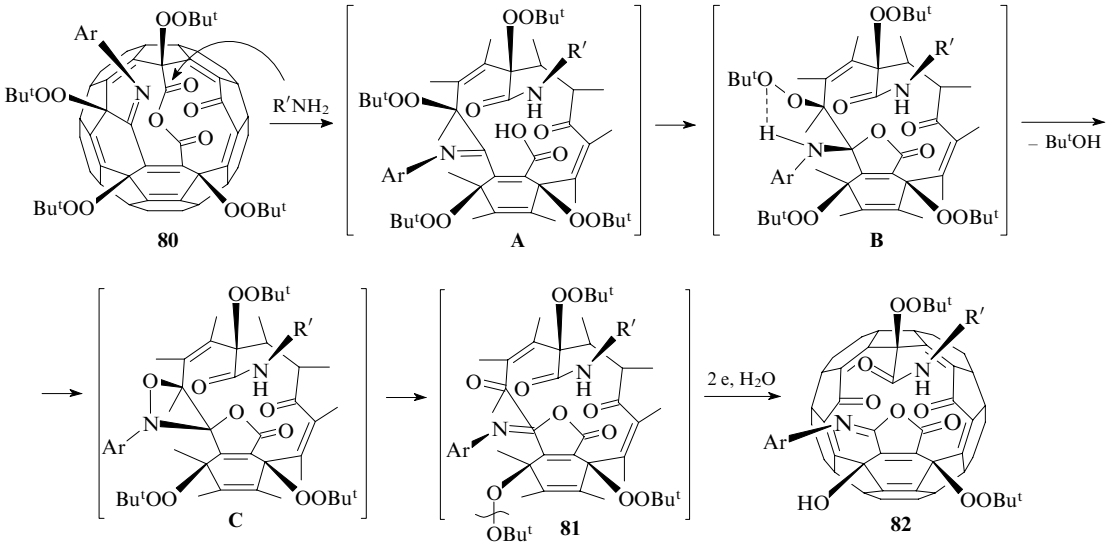
To remove this hindrance, adducts **81c** and **82c** are brominated with a bromine excess to give products **83** and **84**, respectively (Scheme 47). These products are readily reduced to the initial compounds by treatment with

Scheme 47



$Na_2S_2O_3$, and the reaction with $AgClO_4$ releases the acyl group to generate (presumably) polar unstable intermediate **A**, which decomposes into less polar adducts **85** and **86**. Decarboxylation can also occur through the formation of a six-centre transition state in intermediate **A**. The elimination of the amide carbon atom leads to C_{59} triketones **85** and **86**, which is supported by NMR, IR spectroscopy and mass spectrometry. For crystal growth, bromo derivative **87** is most suitable. The ^1H NMR spectra of adducts **85**, **86** and

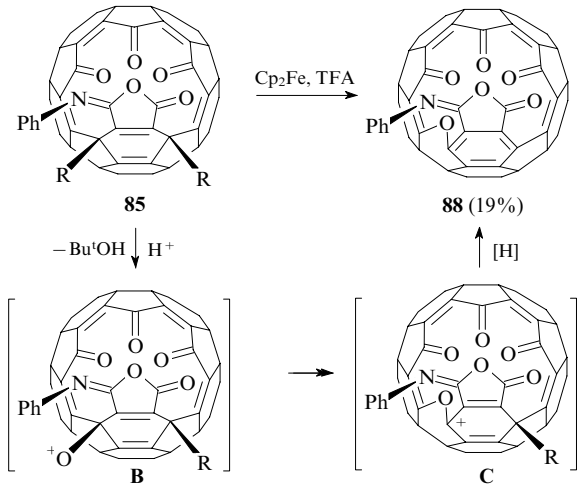
Scheme 46



87 show signals at −13.07, 13.11 and −13.13 ppm, assigned to the protons of water molecules encapsulated into the fullerene cage through the 17-membered-ring 'inlets.' The degree of filling of molecules **87** with water can be increased to 78% by heating a solution of compound **87** in a toluene–water mixture (80 °C, 5 h).

To enhance water encapsulation by enlarging the orifices on the cage surface, adduct **85** was made to react with ferrocene in the presence of trifluoroacetic acid (TFA) (Scheme 48). The reaction involved the elimination of two $OOBu^t$ groups and homoannelation of the oxygen atom to C atoms to form an orifice bounded by 17 carbon atoms in the cage of intermediate **B**. The subsequent rearrangement of intermediate oxonium cation **B** leads to insertion of the oxygen atom into the rim of the orifice. Reduction or removal of the second $OOBu^t$ group from structure **C** gives adduct **88** with an aromatic benzene ring. As expected, adduct **88** accommodates a larger amount of encapsulated water, which gives rise to the ^1H NMR signal at −12.8 ppm. Cooling from room temperature to −20 °C increases the water content from 57% to 88%.

Scheme 48

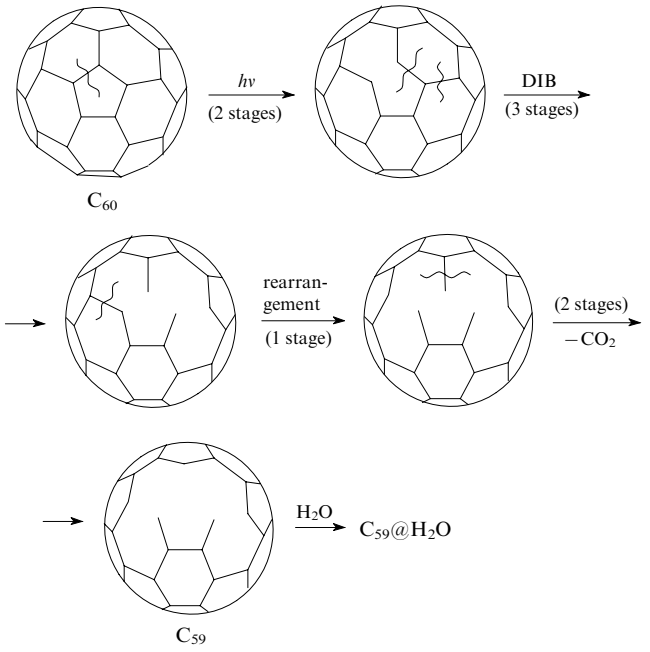


R = $OOBu^t$

The overall cleavage of five carbon–carbon bonds and elimination of one C atom from the fullerene C_{60} cage have been achieved through a series of transformations comprising eight stages (Scheme 49). First, homoinduced homolysis of the Bu^t–O bond leads to formation of a dioxetane intermediate. A key step of the fullerene cage opening reactions is the oxidation of the vicinal fullerenediol moiety by DIB. The strain in the structure is a driving force of the domino-type rearrangement involving the cleavage of four carbon–carbon bonds of the fullerene.

The possibility of mild decarboxylation at the last stage of this scheme characterizes fullerene *tert*-butyl peroxides as multifunctional precursors promising for modifying the fullerene cage. The yield of the product at the second stage of photolysis is relatively small (25%) as compared with most of the next stages (60%). The overall yield of the end product — C_{59} tetraketone **86** — is 1.12%. All reactions occur under mild conditions (<40 °C, in air). The most efficient purification of the products is achieved by flash chromatography. The cage-opened [59]fullerenone is a suitable host for encapsulation of water molecules. X-Ray crystallographic data prove the existence of endohedral

Scheme 49



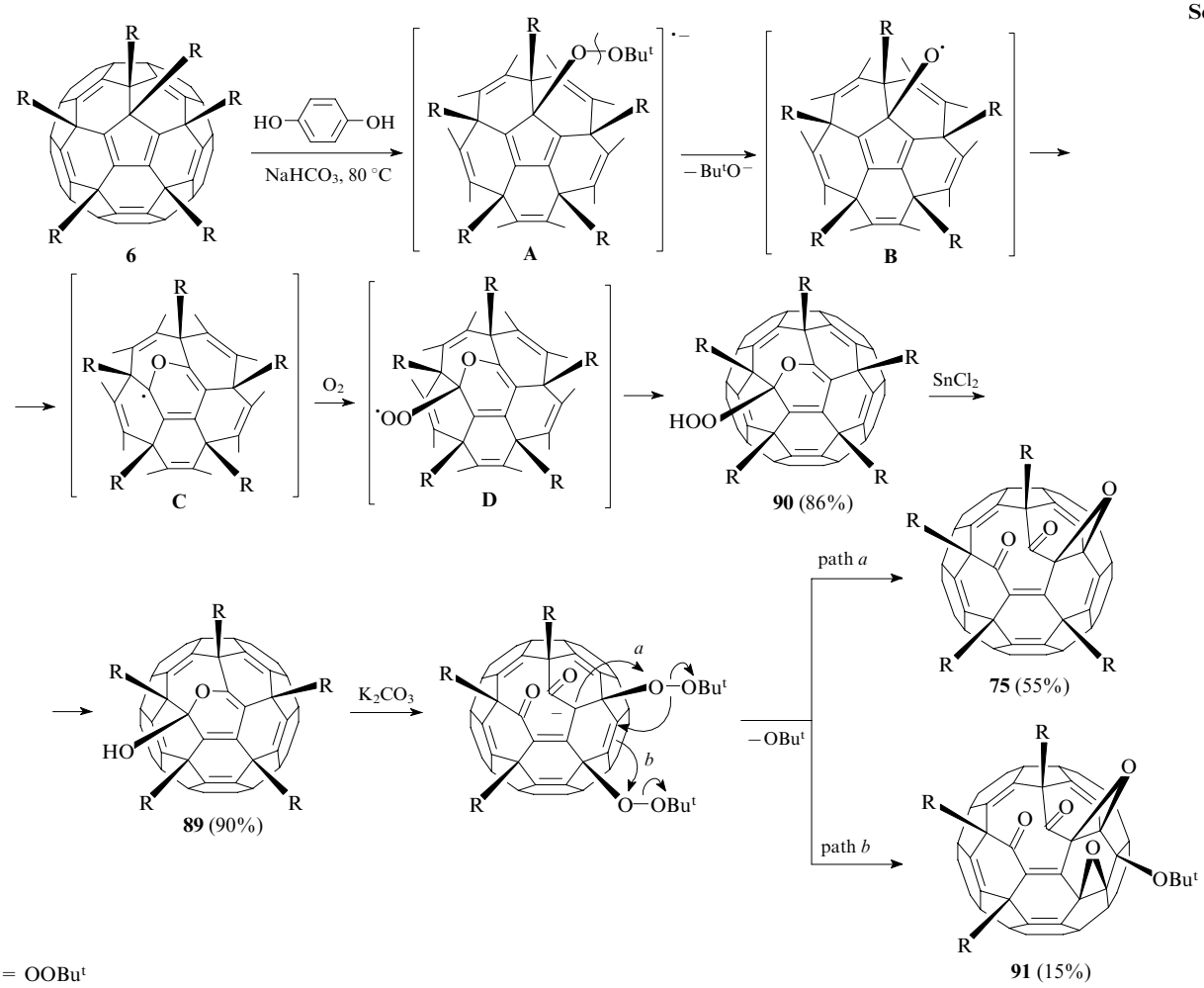
complexes H_2O@**87** and H_2O@**88**, which demonstrates that this approach is promising for synthesis of other similar complexes.

The joint action of hydroquinone and $NaHCO_3$ leads to homolytic bond cleavage in the $OOBu^t$ group to form fullerene derivative **89** with two moieties: hydroperoxide and 2*H*-pyran.[26] To avoid the photochemical decomposition of this adduct, all experiments were run in the dark. The hydroperoxide group is readily reduced by tin chloride to the hydroxyl one.

The proposed mechanism of transformation is shown in Scheme 50. First, compound **6** reacts with hydroquinone to form radical anion intermediate **A**, and the elimination of the Bu^tO^- anion from this intermediate gives oxygen-centred radical **B**. Hydrogen sodium carbonate enhances the reductive ability of hydroquinone. The rearrangement in intermediate **B** leads to pyran-type carbon-centred radical **C**. The rearrangement of radical **C** at the [5,6]-junction is preferred over that at the [6,6]-junction, since the latter rearrangement would lead to formation of a nonplanar unstable radical structure of the cyclopentadienyl (CPD) moiety. Then, intermediate **C** adds an O_2 molecule to give oxygen-centred radical **D**, which abstracts the mobile hydrogen atom from hydroquinone to form pyran derivative **89**. The use of pure oxygen instead of air has no essential effect on the yield and formation rate of product **89**; hence, this stage is not rate-limiting. At the same time, the presence of oxygen is crucial for the successful implementation of the process: in a nitrogen atmosphere, product **89** has not been identified.

In addition, the authors[26] have not ruled out the direct addition of the hydroperoxyl radical to intermediate **C**, relying on the ability of hydroquinone to reduce molecular oxygen to hydrogen peroxide. To verify this assumption, a model reaction of compound **6** with hydrogen peroxide has been carried out at 80 °C in the presence of $NaHCO_3$.[26] It has been demonstrated that product **89** is formed under these conditions as well, however, very slowly and in low yield (<10%).

Scheme 50



To produce an open-cage adduct, compounds **89** and **90** have been hydrolyzed under different conditions. A difficult-to-separate mixture is formed in an acidic medium. Under alkaline conditions in the presence of K_2CO_3, compound **90** gives adducts **75** and **91** with a nine-membered orifice (see Scheme 50). Under the same conditions, adduct **89** is hydrolyzed to form a complex mixture. It is worth noting that open-cage fullerene derivative **75** has been previously obtained (25% yield) in one stage by photolysis of compound **6**.[12] However, photochemical synthesis is complicated by the formation of by-products that are difficult to separate by column chromatography. At the same time, the three-stage synthesis through the formation of an intermediate pyran derivative is characterized by relative ease and high yield of diketone **75** (43%). The mechanism of formation of diketones **75** and **91** involves, as the first stage, deprotonation of the hydroxyl group of adduct **89** under the action of K_2CO_3 leading to the opening of the pyran ring and formation of two carbonyl groups. Product **91** is formed through heterolysis of the OOBu^t bond (see Scheme 50, path *b*).

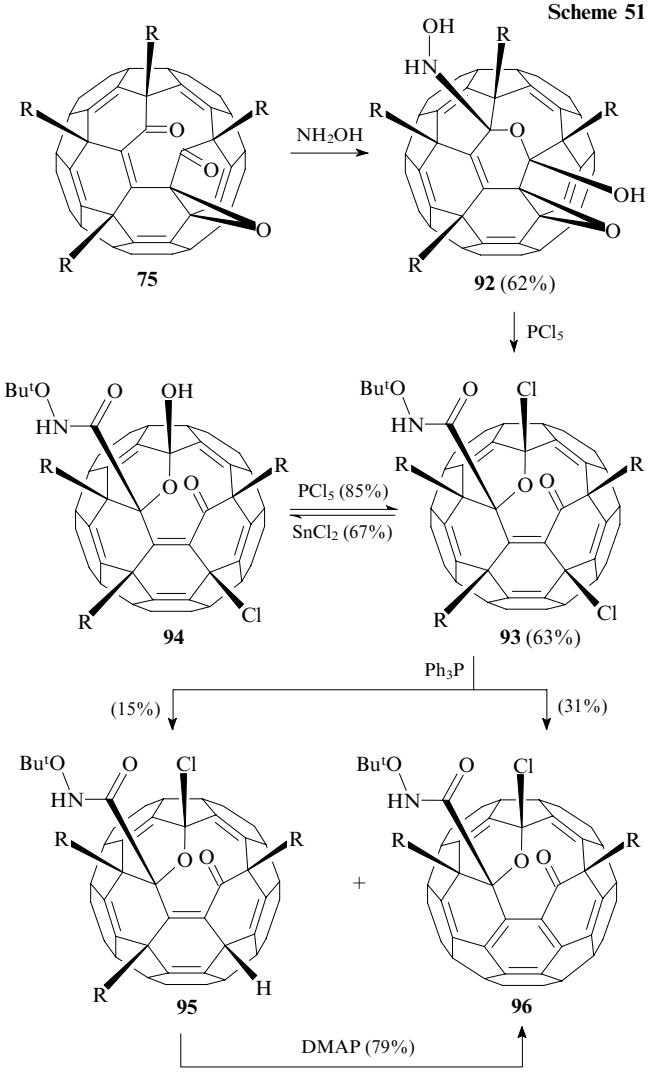
Compounds **89**–**91** have symmetry C_1; however, the NMR spectra do not enable the unambiguous interpetation of their structures. The ^{13}C NMR spectra of derivatives **89** and **90** are very similar to each other: the signals of the hemiacetal carbon atoms are observed at 113.0 and 106.0 ppm, respectively. The ^{1}H NMR spectra show the signal of the hydroperoxide group of adduct **90** at 9.83 ppm and the signal of the OH group proton of compound **89** at 5.78 ppm.

From diketone **75**, obtained previously,[12] triketones have been synthesized containing 59 carbon atoms and a different number of peroxide groups and Cl or Br atoms (Scheme 51).[16] First, the reaction of diketone **75** with hydroxylamine affords oxahomofullerene **92**, containing a hydroxylaminoketal moiety. In the reaction of adduct **92** with PCl_5, the migration of one OOBu^t group onto the nitrogen atom leads to compound **93**, containing 59 carbon atoms. The attempt to grow single crystals of this product failed. However, the substitution of a hydroxyl group for the chlorine atom in compound **93** and subsequent evaporation of a solvent (a CS_2–EtOH mixture) have given crystals, and the structure of **94** has been determined by X-ray crystallography. The reverse reaction readily occurs when compound **94** is treated with phosphorus pentachloride. Compound **93** is reduced by triphenylphosphine to a mixture of adducts **95** and **96**; the latter forms as the major product and can also be isolated upon the treatment of byproduct **95** with *N*,*N*-dimethylaminopyridine (DMAP).

To remove the amide group from the cage, a series of transformations (Scheme 52) has been carried out giving triketones (**97**, **98** and **99a**,**b**) of different structure.[16] Key reactions in this series are hydrolysis and decarboxylation.

Another variant of synthesis of an open-cage [59]fullerene derivative with 59 carbon atoms involves three stages (Scheme 53).[11] The initial peroxide $C_{60}(O)(OOBu^t)_6$ (**8**) has

Scheme 51



R = $OOBu^t$

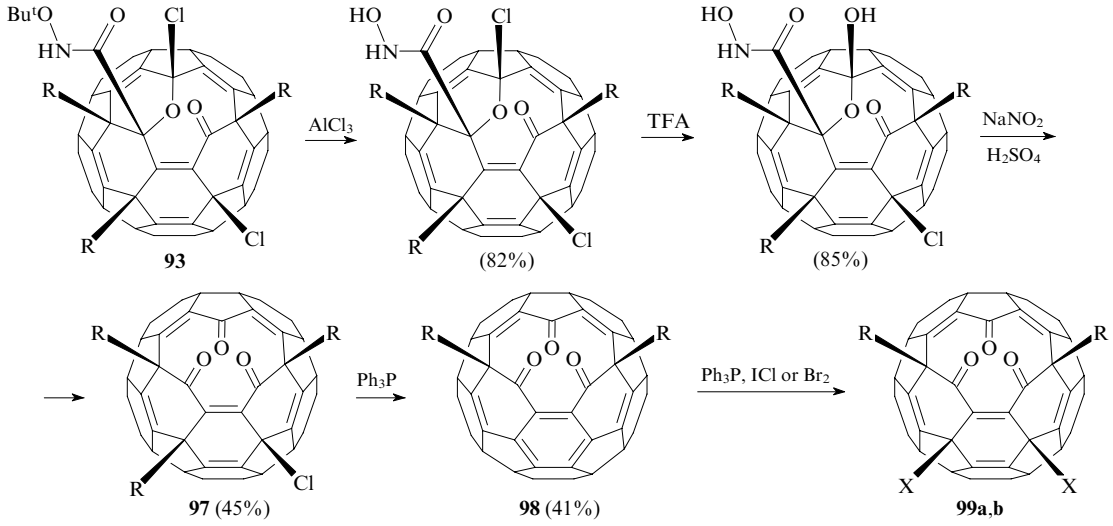
been obtained by oxidation of C_{60} by the Bu^tOOH–CAN system under irradiation with light. The reaction of compound **8** with $BF_3 \cdot Et_2O$ in dichloromethane yields oxahomofullerene **100**, which converts on heating (75 °C, 8h) into oxafulleroid **101**. The ^{13}C NMR spectrum of compound **100** shows two signals of ketone and lactone carbon atoms at 189.5 and 159.1 ppm, respectively, which are consistent with the presence of absorption bands at 1798 and 1743 cm^{-1} in the IR spectrum. One of the OH groups of oxafulleroid **101** converts into the alkoxy group of adducts **102a**,**b** in the HCl-catalyzed reaction with alcohols.

Slow evaporation of a CS_2–EtOH mixture has resulted in single crystals of adduct **102a**. X-ray diffraction data point to the presence of the furan moiety separated from the other C=C bonds by $OOBu^t$, OH and MeO addends, as well as to that the oxygen atoms of the furan ring and the lactone moiety are in close proximity to each other. This adduct has an open fullerene cage with a 11-membered-ring orifice. According to the suggested mechanism (see Scheme 53), the Lewis acid (BF_3) induces the heterolysis of the O–O bond to form oxonium intermediate **A**, which rearranges (through cleavage of the [5,6]-junction) to carbon-centred cation **B**. The latter transforms to neutral intermediate **C**, containing a dioxetane moiety, the product of heterolysis of the O–Bu^t bond of the adjacent *tert*-butyl peroxide group. The subsequent opening of the dioxetane ring gives ketolactone **100**. The latter, after the elimination of the C=O molecule from intermediate **D** and conversion of two $OOBu^t$ groups into hydroxyl one, gives oxafulleroid **101**.

Oxahomo[60]fullerene **40** (synthesized by Huang *et al.*[4]), in which the hemiacetal moiety is located at the [5,6]-junction, has been used as a precursor for synthesis of compounds containing four C=O groups.[21] First, the reaction of compound **40** with $AgClO_4$ and water leads to the substitution of a hydroxyl group for the chlorine atom (Scheme 54). Then, the hemiacetal OH group in adduct **103** is acylated with acetic anhydride to give diol **104**, which is oxidized by DIB to form diketone derivative **105**.[21,29]

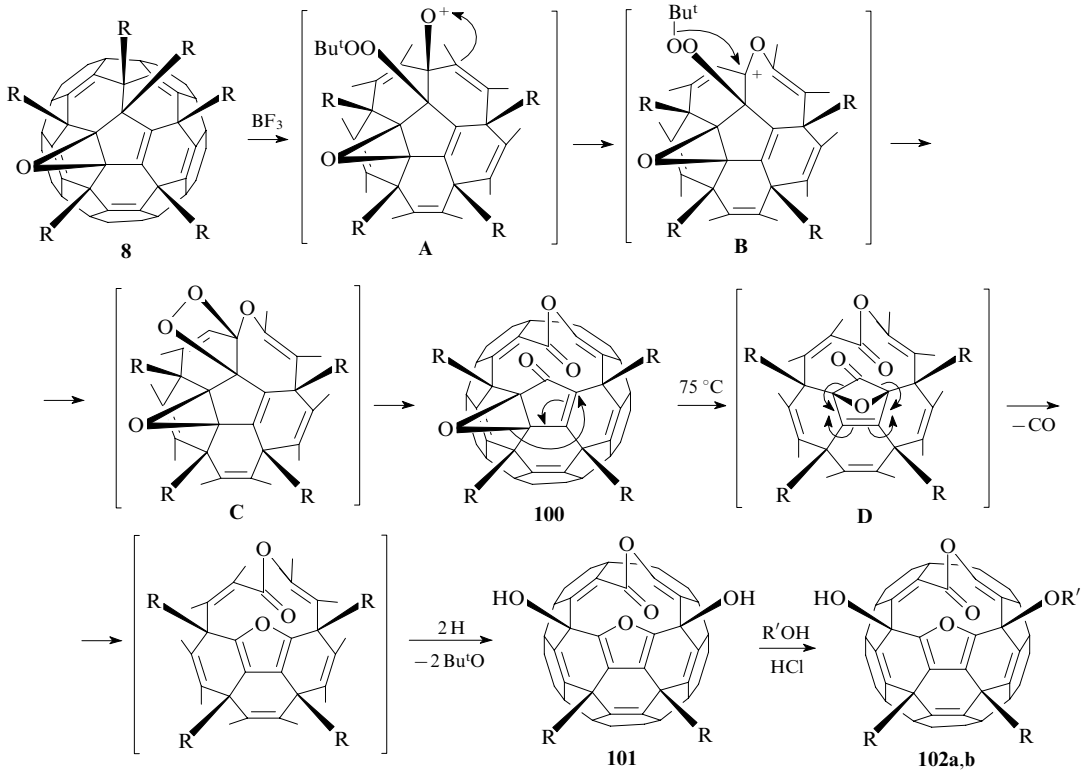
The hemiacetal should be protected since direct oxidation of compound **103** under these conditions gives a complex product mixture. The ^{13}C NMR spectrum of diketone **105** shows the signals of the C=O groups at 194.6 and 192 ppm and the signal of the cage carbon atom of the hemiacetal moiety at 110.2 ppm.

Scheme 52



R = $OOBu^t$; X = Cl (**a**, 60%), Br (**b**, 85%)

Scheme 53



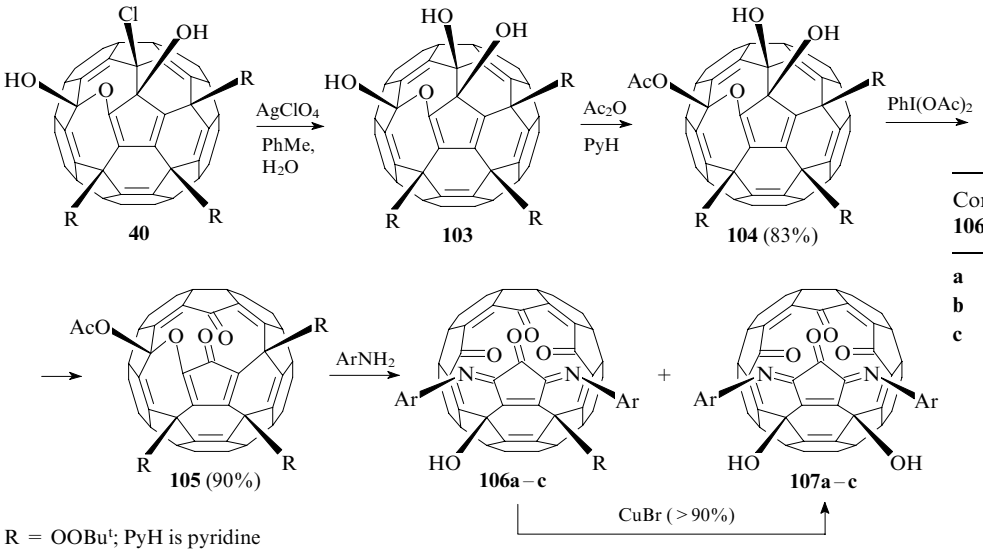
R = OOBu^t; R′ = Me (**a**, 47%), Et (**b**, 50%)

Then, diketone **105** without isolation is introduced into the reaction with aniline, which leads to compounds **106a** and **107a** (54% overall yield) with orifices on the fullerene cage. The OOBu^t group retained in adduct **106a** is readily reduced by CuBr to the OH group. The reactions with 4-bromo- and 4-isopropylanilines lead to similar results. Compounds **106a–c** and **107a–c** have 18-membered-ring orifices on the fullerene cage and are suitable for encapsulation of water molecules.

The proposed mechanism [21] of the aniline-initiated fullerene cage opening (Scheme 55) involves, as the first stage, the aminolysis of hemiacetal ester to form allyl anion **A**, containing four C=O groups. The elimination of the OBu^t group from anion **A** gives adduct **B**, in which the epoxide ring is opened under the action of another amine molecule by the S_N2' mechanism to form intermediate **C**. Then, a [3,3]-sigma rearrangement results in the cleavage of the cage C–C bond in adduct **C**; according to X-ray diffraction analysis for tetraketone **107a**, this bond cleavage causes a rise of the central pentagon over the cage sphere and formation of intermediate **D**.

At the final stage, a third amine molecule reacts with the least protected C=O group at the pentagon to give product **106**. A key step of the observed selective aminolysis is the activation of the C=O group to form an intramolecular bond to the hydrogen atom of the neighbouring OH group.

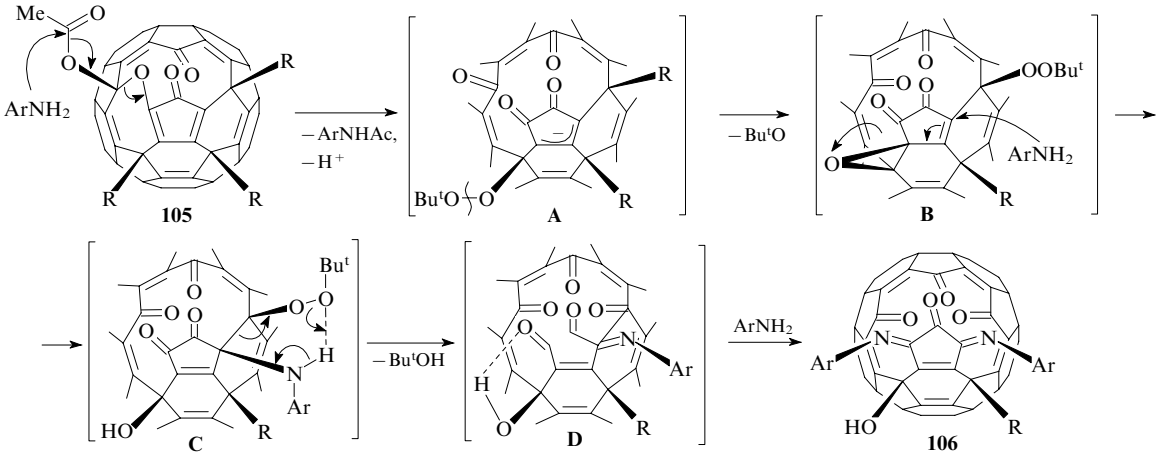
Scheme 54



Compounds **106**, **107**	Ar	Yield (%)	
		106	**107**
a	Ph	59	7
b	4-BrC$_6$H$_4$	61	6
c	4-Pr^{i}C$_6$H$_4$	57	12

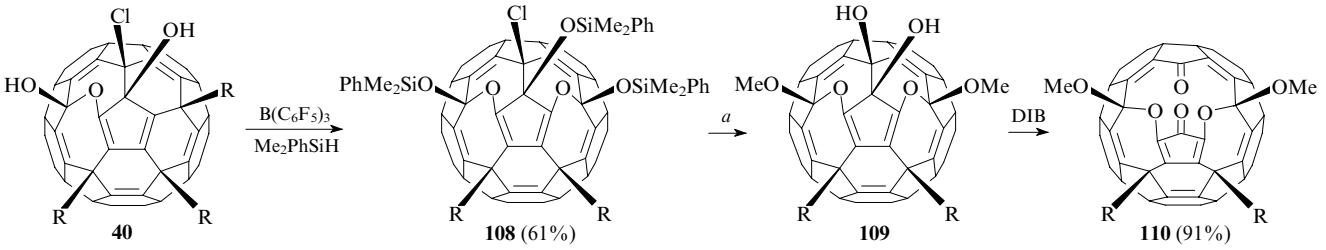
R = OOBu^t; PyH is pyridine

Scheme 55



R = $OOBu^t$

Scheme 56



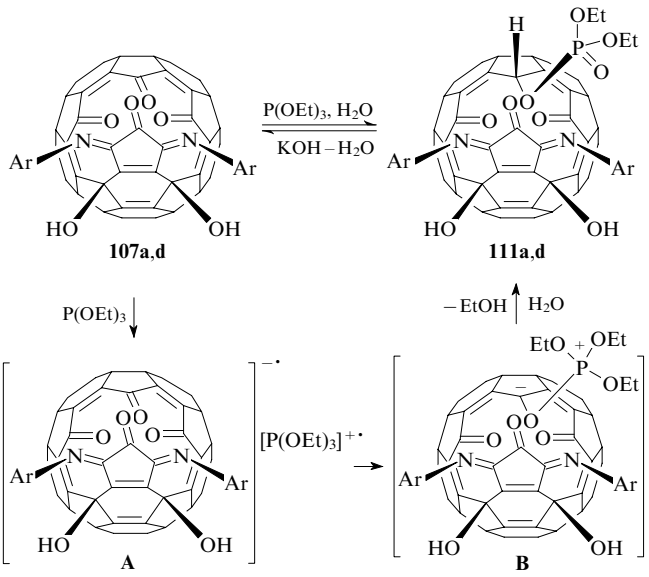
R = $OOBu^t$; (*a*) 1) TBAF, AcOH (83%); 2) Ag_2O, MeI (57%); 3) TBAF, AcOH (75%); 4) $AgClO_4$, H_2O (69%)

X-Ray crystallographic data on compounds **107** and H_2O@**107a** confirm the existence of such an O–HN bond with a length of 2.71 to 2.78 Å and an angle of 131 to 133°. Water encapsulation has no noticeable effect on the cage structure. After heating of adduct **107a** for 5 h in a toluene–water mixture, the degree of filling of the cage with encapsulated water is 40%, and upon further heating for 24h, it becomes as high as 87%.

Hemiacetal **40** has also been used as a precursor for synthesis of fulleroid.[28] First, it reacts with dimethylphenylsilane and a Lewis acid to give silylated derivative **108** (Scheme 56). Stepwise deprotection and methylation lead to vicinal diol **109**, which is oxidized by DIB to diketone **110** with two ketal groups. Compound **110** has a 10-membered-ring orifice, which has been proved by single-crystal X-ray analysis. It should be noted that all ketal and hemiacetal moieties give rise to characteristic ^{13}C NMR signals in the range from 107.5 to 112.5 ppm.

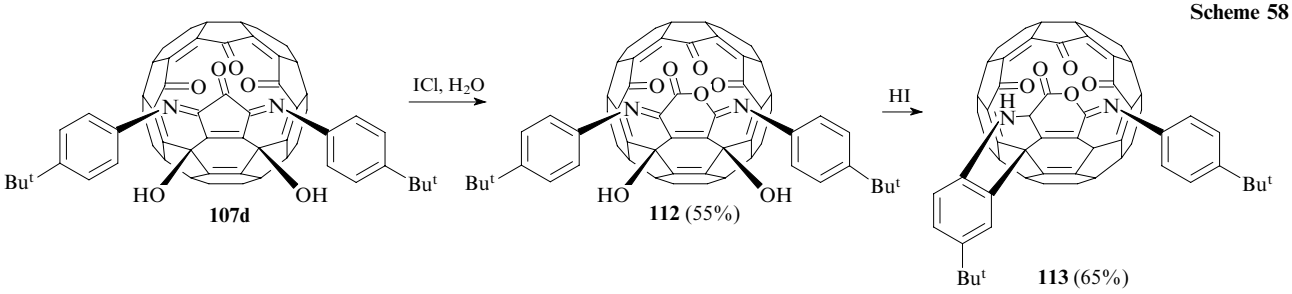
An adduct with an orifice on the fullerene cage ('host') can have a kind of 'chemical stopper' as a readily added and removed addend that blocks this orifice and prevents release of the guest molecule.[24] In particular, the reaction of tetracarbonyl derivative **107a**, described in Ref. 21, as a precursor with triethyl phosphite affords compound **111a**, in which the orifice on the fullerene cage is closed by the phosphate group (Scheme 57).[24] In the presence of bases, the phosphate group can be removed by hydrolysis to regenerate initial fulleroid **107a**. The direct reaction is completed in 10 min, whereas the reverse reaction is finished in 2 h. Derivative **107d** reacts analogously. The proposed mechanism of reaction involves, as the first stage, electron transfer from the phosphite molecule to the fullerene cage; the resulting radical ion pair **A** transforms into intermediate zwitterion **B** upon of formation of the O–P bond (see Scheme 57). Then, the protonation of the carboanion and hydrolysis afford the adduct with a 'chemical stopper', namely, host **111**. An alternative mechanism of formation of zwitterion **B** through the attack of the

Scheme 57



Ar = Ph (**a**, 64%), 4-$Bu^tC_6H_4$ (**d**, 65%)

Scheme 58



phosphonic group on the carbonyl carbon atom and subsequent migration of the phosphate group similar to the Brook rearrangement is not ruled out.

The existence of the phosphate stopper is confirmed by the expriments on heating H_2O@**107a** and H_2O@**111a** samples to 60 °C. In the first case, heating leads to a decrease in the intensity of the ^{1}H NMR signal at 7.37 ppm due to the protons of encapsulated water, whereas in the second case, there are no such changes.

Heating of complex tetraketone **107d** with iodine monochloride leads to compound **112**, which reacts with HI to give a bright green product— compound **113** (Scheme 58).[31] Such a bright colour is rather rare for fullerene derivatives. Among so-called 'green' fullerenes, trannulenes $C_{60}F_{15}[C(CO_2R^1)_{3x}R^2_x]_3$ (R^1 = H, Alk; R^2 = Ar, Fc, *etc.*; x = 0, 1, 2)[74–78] and $C_{60}[CMe(CO_2Alk)_2]$[79,80] should be noted. The electronic absorption spectrum of compound **113** shows a strong band in the range 600–800 nm with a maximum at 709 nm (Fig. 1). These spectral features make compound **113** a good candidate for design of new materials that can be used as photosensitizers for photosensors and in photodynamic therapy.

Diketone **73** turned out to be an excellent precursor for synthesis of new C_{60} derivatives — fullerene adducts with isothiocyanate group, azafullerenes and oxahomofullerenes. The presence of two keto groups, along with the peroxide ones, in CFP **73** plays a key role predetermining specific features of the peroxide reactivity. Indeed, buckminsterfullerene C_{60} does not react with (trimethylsilyl)isothiocyanate under common conditions, but the latter readily opens the epoxide ring of peroxide **7** to form compound **30** (see Scheme 20).[18] The reaction of diketone **73** with TMSNCS occurs more slowly; it is somewhat promoted by the addition of silica gel (Scheme 59). In particular, compound **114** has been obtained in 86% yield after keeping the reaction mixture at 0 °C for two days; in addition to this compound, the reaction yields a minor amount of C_S-symmetric thiocyanate **115** (4%). The introduction of a Lewis acid — $Al(OTf)_3$ or $BF_3 \cdot Et_2O$ — rather than silica gel into the reaction mixture decreases the reaction duration to 4 h and leads to the formation of thiocyanate **115** as a major product in 63% or 53% yield, respectively. The use of zinc chloride leads mainly to the formation of isothiocyanate **116**. Similar isomerization is known in organic chemistry and is described well in terms of Pearson's concept of hard and soft acids and bases.

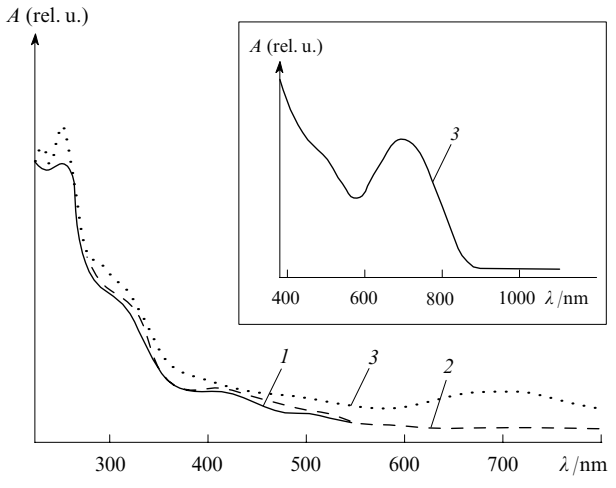
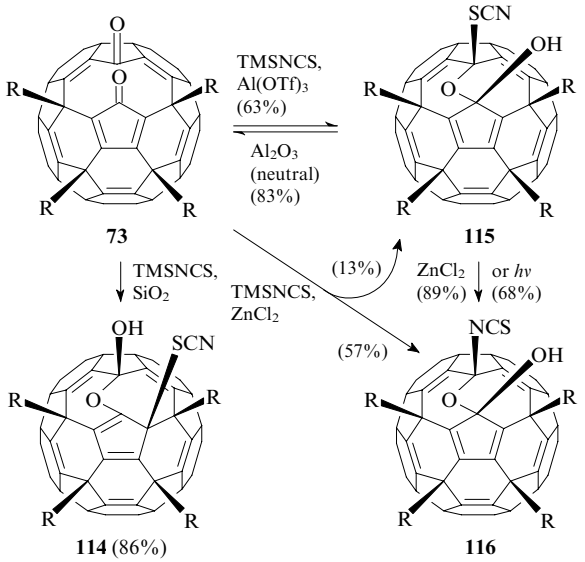


Figure 1. UV-Vis absorption spectra of compounds **107d** (*1*), **112** (*2*) and **113** (*3*) in CH_2Cl_2.[31]
Concentrations are 6×10^{-6}, 5.9×10^{-6} and 4.7×10^{-6} mol litre^{-1}, respectively (for the spectrum in the inset, concentration is 3×10^{-4} mol litre^{-1})

Scheme 59

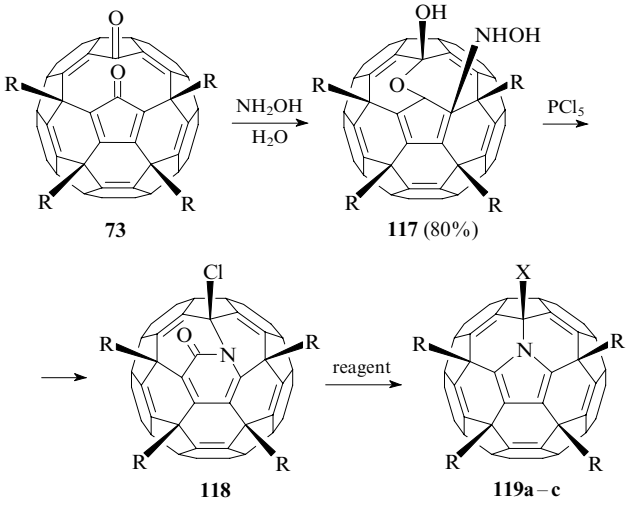


The reaction of diketone **73** with hydroxylamine in water leads to adduct **117**, which reacts with PCl_5 under anhydrous conditions to give compound **118** containing the lactam ring (Scheme 60).[19]

The purity of the reagent has a strong effect on the yield of compound **118**: freshly prepared PCl_5 is too reactive, and a by-product is formed. Preparative purification of adduct **118** on a column packed with SiO_2 or Al_2O_3 leads to azafullerene **119a**, in which the hydrogen atom can be

replaced by a bromine atom or a hydroxyl group (compounds **119b**,**c**). The mechanism of formation of adduct **118** through a rearrangement of the hemiacetal and hydroxylamine moieties in structure **117** is still unclear. Compounds **117**, **118** and **119b** have been characterized by spectral methods. For example, the ^{1}H NMR spectrum of azafullerene **119a** shows a singlet signal at 6.59 ppm, which corresponds to the hydrogen atom bound to the fullerene cage.

Scheme 60



R = OOBu^t

Compound **119**	X	Reagent	Yield (%)
a	H	Al_2O_3	33
b	Br	1)Al_2O_3; 2)Br_2	67
c	OH	$BnNH_2$, H_2O	18

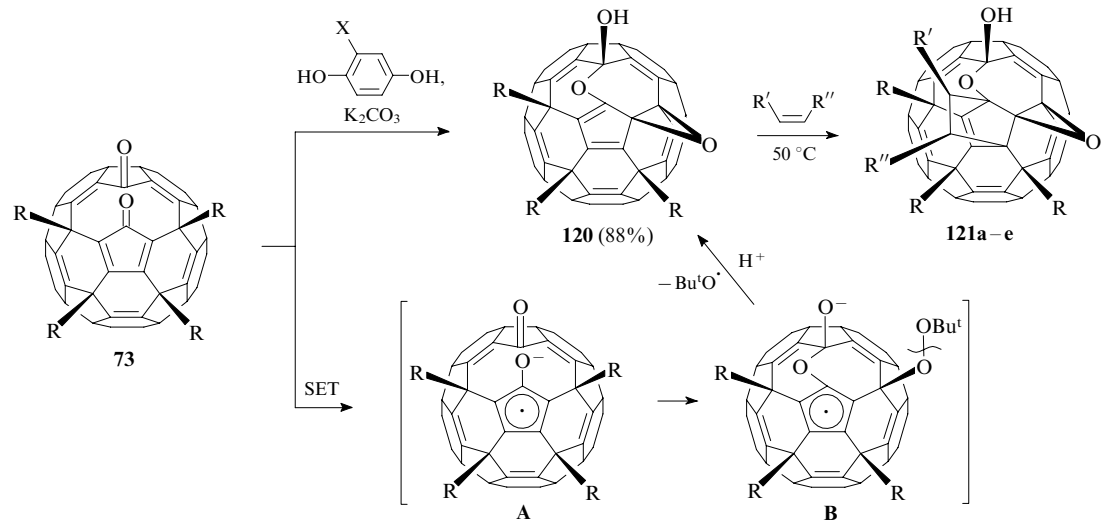
The cycloaddition reaction seems to be the most popular method of functionalization of fullerenes and their derivatives.[81–85] The synthesis and properties of functionally substituted fullerenes obtained by this method have been addressed in numerous studies. It has turned out that the isolated CPD moiety of complex fullerene peroxides is also able to react with dienophiles to form [4 + 2]-cycloaddition products. For example, heat treatment of diketone **73** with *p*-hydroquinone (Scheme 61) gives oxahomofullerene **120** in high yield (monitored by HPLC). However, after removal of the solvent at 60 °C, the residue is adduct **121a**, which is oxahomofullerene with oxidized hydroquinone as the addend.

Later, targeted synthesis of new fullerene derivatives **121b–e**, the products of addition of different dienophiles to oxahomofullerene **120**, has been carried out (see Scheme 61).[22]

To synthesize adduct **120**, *p*-hydroquinone has been replaced by 2-*tert*-butyl-1,4-hydroquinone (X = Bu^t), which does not lead to [4 + 2]-cycloaddition by-products under the reaction conditions. This has made it possible to increase the yield of target oxahomofullerene to 88%. The mechanism of formation of hemiacetal **120** involves the stage of electron transfer from hydroquinone deprotonated in an alkaline medium to form intermediate **A**, in which a negative charge is on the oxygen atom, while a free spin is localized in the CDP moiety. The oxygen-centred anion and the neighbouring carbonyl carbon atom form the hemiacetal group of intermediate **B**. The epoxide group of adduct **120** is the product of homolytic cleavage of the peroxide O–O bond. This example demonstrates how the electrophilic fullerene molecule can also act as a nucleophilic agent owing to functional modification of the fullerene core.

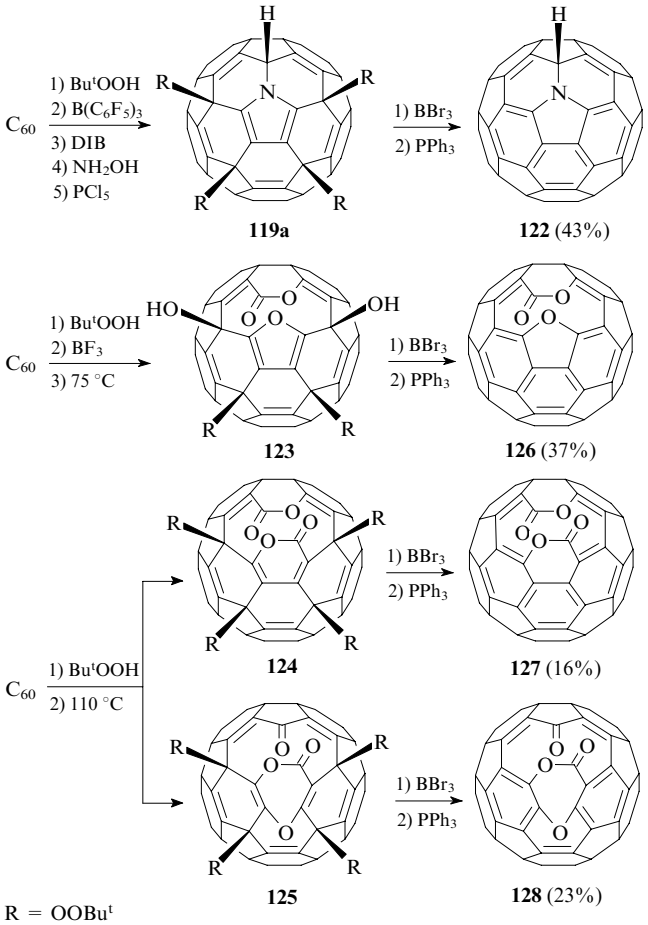
Yet another interesting application of peroxides as precursors is presented in studies aimed to extend a series of fulleroid structures through substitution of a heteroatom for a cage carbon atom.[30] For example, when successively treated with BBr_3, water and PPh_3, azafullerene **119a** loses all OOBu^t groups to form azafulleroid **122**. Peroxides **123–125** have been transformed into oxafulleroids **126–128** by similar procedures (Scheme 62).

Scheme 61



R = OOBu^t; X = H, Bu^t; R′, R″ = O=⟨⟩=O (**a**, 70%), Ph-N(O)=O (**b**, 21%), O=O(O)=O (**c**, 70%), Ph (**d**, 87%), CO_2Me (**e**, 58%)

Scheme 62



Noteworthy is the insignificant difference between the spectral characteristics of the initial complex fullerene peroxides and the products of their transformation — the corresponding fulleroid compounds. For example, characteristic absorption bands of carbonyl groups in the IR spectra of compounds **123** and **126** have maxima at 1775 and 1781 cm^{-1}, respectively. The signals of the carbon atoms of the C=O groups in the ^{13}C NMR spectra of product **128** and initial compound **125** are also close to each other: 196.1 and 193.5 ppm, respectively. At the same time, in the ^{13}C NMR spectra of fulleroids **122**, **126**–**128**, signals characteristic of sp^3-hybridized carbon atoms disappear. The signals of the C(sp) and C(sp^2) atoms of the fullerene cage change insignificantly.[30]

The mechanism of reduction of peroxides to fulleroids is rather simple: boron tribromide reacts with OOBu^t or OH groups to form products of homo- (C–OBBr$_3$ or COOBBr$_3$) or heterolytic (C–Br) cleavage of the peroxide or hydroxyl bond. A large excess of BBr_3 makes it possible to replace all OOBu^t or OH groups by bromine atoms. A large amount of forming Br_2 is removed by treatment with sodium thiosulfate. Then, the resulting halofullerene derivatives are subjected to dehalogenation with the use of PPh_3 as a reducing agent. All synthesized fulleroids are more stable than the initial peroxides and retain their structure in air for many weeks.

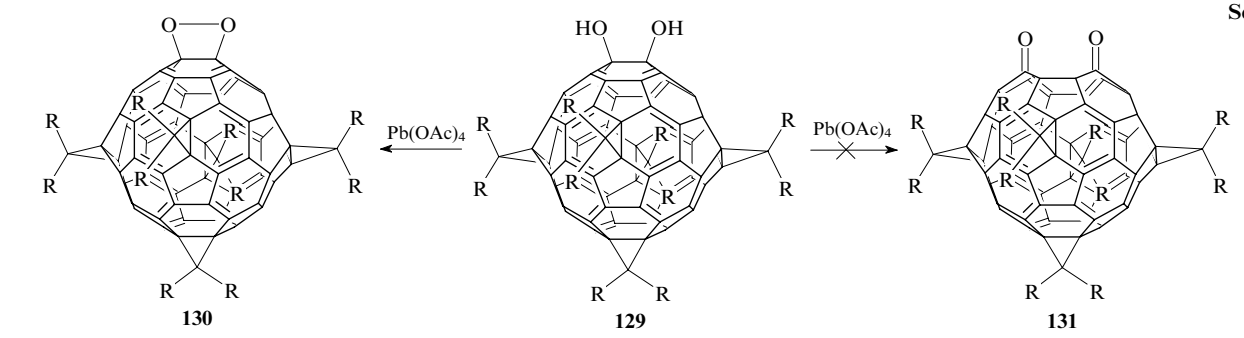
IV. Formation and decomposition of fullerene dioxetanes

Information on fullerene dioxetanes is also available in the literature. They can be obtained by oxidation of fullerene and its derivatives both in purely chemical reactions and in photochemical processes involving singlet oxygen, as well as without it. We have focused on the dioxetanes in which the oxygen atoms of the peroxide group are covalently bonded to carbon atoms of the fullerene cage. It should be noted that, in the chemistry of fullerenes, synthesis of dioxetanes is not a target task, and relevant studies deal with the fabrication of open-cage fullerene derivatives.

Among the known methods of fullerene cage opening, the photochemical method seems to be most popular. Its key stage is the [2+2]-cycloaddition of singlet oxygen ($^1O_2^*$) to the C=C bond to form a dioxetane intermediate. In the ring opening reaction, the latter is rearranged into a diketone or ketolactam fullerene adduct. This process has been well studied and is used for synthesis of a number of open-cage fullerene derivatives.[73,86–88] Only in two works,[7,89] fullerene dioxetanes have been isolated and characterized. In the other studies, they have been proposed (quite rightly) as intermediates, relying on the identification of dioxetane precursors and stable end products, mainly, diketone and ketolactam derivatives.[73,86–88,90]

The first fullerene dioxetane was synthesized in nearly quantitative yield by a chemical method, without irradiation.[89] The oxidation of vicinal fullerenediol adduct $C_{65}(CO_2Et)_{10}(OH)_2$ (**129**) by lead acetate (combined in a molar ratio of 19 : 96) in CH_2Cl_2 for 20 h at room temperature gave a yellow solution of dioxetane **130**, which was purified by column chromatography (Scheme 63). The result was unexpected for the authors of this study since they intended to synthesize open diketone **131**. It has been suggested by other researchers[7] that closed dioxetane struc-

Scheme 63

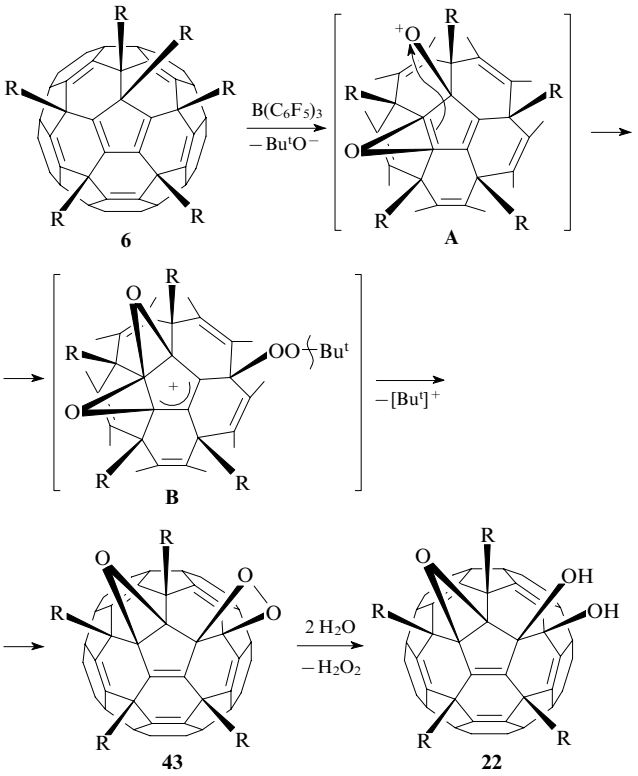


ture **130** is preferred for the high-symmetry adduct over the formation of fullerene diketone from dioxetane.

Fullerene dioxetane **130** has been characterized by mass spectrometry, UV/Vis spectroscopy, IR spectrophotometry and ^{1}H and 13C NMR.[89] Although these data have not been discussed by the authors, we can underline the following characteristics indicating the formation of dioxetane. According to mass spectrometry data, the mass of dioxetane **130** is 2–3 a.m.u smaller than that of its precursor — diol **129**; comparison of the ^{1}H NMR spectra of these compounds shows that the spectrum of **130** lacks the signal at 5.13 ppm (OH) observed in the spectrum of diol **129**. In the ^{13}C NMR spectrum of compound **130**, the signal at 104.05 ppm of the tertiary carbon atoms to which the dioxetane ring is annulated is close to a similar signal at 103.6 ppm in the spectrum of 1,2-cyclobutadiene-1,2-dioxetane;[91] likewise, the absorption band in the IR spectrum at 858 cm^{-1} is close to the band at 885 cm^{-1} (δ_{O-O}) of adamantylideneadamantane-1,2-dioxetane.[92]

Another compound — 4,11,15,30-tetrakis(*tert*-butylperoxy)-1,2-peroxy-3,14-epoxy-1,2,3,4,11,14,15,30-octahydro[60]-fullerene (**43**), which contains the dioxetane ring annulated to the [6,6]-bond, has also been obtained by the reaction of peroxide $C_{60}(OOBu^t)_6$ (**6**) with $B(C_6F_5)_3$ (Scheme 64).[7]

Scheme 64



R = OOBu^t

In a dry atmosphere, unstable dioxetane **43** slowly decomposes to form a complex product mixture. In addition, the dioxetane ring is readily hydrolyzed, and the strongest peak in its mass spectrum (ESI) corresponds to a hydrolysis product — the $C_{60}(O)(OH)_2(OOBu^t)_4$ compound (**22**). According to the suggested mechanism of formation of dioxetane, at the first stage, a Lewis acid [$B(C_6F_5)_3$] induces heterolysis of the OOBu^t addend at the central CPD moiety of peroxide **6**, which results in elimination of the OBu^t group and formation of cation **A** (see Scheme 64). Addition of the positively charged oxygen atom of this cation to the neighbouring C=C bond of the central pentagon gives allyl cation **B**, and after elimination of the $[Bu^t]^+$ cation from the peroxide group, it converts into dioxetane **43**, which is hydrolyzed to compound **22**.

A rather simple procedure has been used for preparation of milligram amounts of dioxetane **43**. To a solution of peroxide **6** in CH_2Cl_2, $BF_3 \cdot Et_2O$ was added, the mixture was stirred for 2.5 h at 30 °C and washed with water, and the residue was dissolved in a benzene–ether mixture. Chromatographic purification gave product **43** in 8% yield. Because of the instability of dioxetane **43**, the spectra were recorded immediately after the synthesis. Compound **43** has been characterized by ESI-MS spectra, as well as by ^{1}H and ^{13}C NMR.

In the other cases considered below, dioxetanes form in photochemical reactions. For example, the formation of fullerene 1,2-dioxetane is a key stage preceding the fullerene cage opening under Ar^+ laser irradiation (λ = 488 nm, laser power density E_e = 800 mW cm^{-2}) of a thin (0.5 m) fullerite film (obtained by deposition of the C_{60} sublimate onto a KBr crystal) in an oxygen atmosphere.[93] The differential IR spectra of the sample show two new bands: one band at 1000–1100 cm^{-1} (ν_{COC}) and the narrower band at 1755 cm^{-1} ($\nu_{C=O}$). The spectrum does not show the bands of CO_2 group vibrations, which is evidence of a relatively small change in the C_{60} structure caused only by cage opening and formation of the diketone O=C_{60}=O. Quantum chemical simulation has demonstrated good agreement between the experimental and calculated IR spectra of the diketone. The EI mass spectrum of the irradiation product shows two well-defined peaks corresponding to $C_{60}O_2$ (m/z 752) and C_{60} (m/z 720) ions; upon longer-term irradiation, the spectra show a new peak of the tetraketone $C_{60}O4$ (m/z 784).

A 'dioxetane' mechanism of oxidation of C_{60} has been suggested (Scheme 65).[93] Upon absortion of light quanta by the initial molecule, a singlet excited state of fullerene ($^1C_{60}^*$) is generated, which undergoes intersystem crossing to a triplet excited fullerene $^3C_{60}^*$ [reaction (1) in Scheme 65].

Scheme 65

$$C_{60} + h\nu \longrightarrow {}^1C_{60}^* \longrightarrow {}^3C_{60}^* \quad (1)$$

$$^3C_{60}^* + O_2 \longrightarrow {}^1O_2^* \quad (2)$$

$$C_{60} + {}^1O_2^* \longrightarrow C_{60}O_2 \longrightarrow O{=}[C_{60}]{=}O \quad (3)$$

$$^3C_{60}^* + {}^1O_2^* \longrightarrow C_{60}O_2 \longrightarrow O{=}[C_{60}]{=}O \quad (4)$$

The latter transfers its energy to the O_2 molecule, thus converting it to the singlet excited state $^1O_2^*$ [reaction (2)]. Then, 1,2-addition of $^1O_2^*$ to the [6,6]-bond C=C leads to fullerene dioxetane $C_{60}O_2$. Thermal decomposition of the dioxetane with simultaneous cleavage of the O–O bond and two C–O bonds gives the end product — diketone O=C_{60}=O [reaction (3)]. It is worth noting that formation of diketone upon the photochemical decomposition of dioxetane cannot be ruled out.

In contrast to this mechanism, other researchers have found that singlet oxygen is unable to oxidize fullerene being in the ground state [see reaction (3)]. Oxidation occurs

only in the reaction of singlet oxygen with triplet excited fullerene molecule [reaction (4)].[94] This has been demonstrated when studying the photooxidation of C_{60} crystal solvates, which are solid films fabricated by evaporation of the solvent from C_{60} solutions. In such films, the C_{60} molecules are coordinated to solvent molecules.

On the basis of direct experiments on modelling this reaction, another mechanism of photooxidation of C_{60} has been established. Indeed, when a flow of gaseous $^1O_2^*$ contacts a film of fullerene crystal solvate, obtained by evaporation of toluene or hexane from a C_{60} solution spread over a KBr disk, fullerene is not oxidized. Accordingly, the HPLC pattern of a solution of the crystal solvate thus treated shows the absence of new peaks. At the same time, after a C_{60} solution saturated with 'ordinary' O_2 has been irradiated with a pulsed excimer XeCl laser ($E_e = 4.1 \times 10^3$ W cm^{-2}), the chromatogram shows a twofold increase in the intensity of the peak of epoxide $C_{60}O$ (a small amount of $C_{60}O$ is also present in the initial solution).

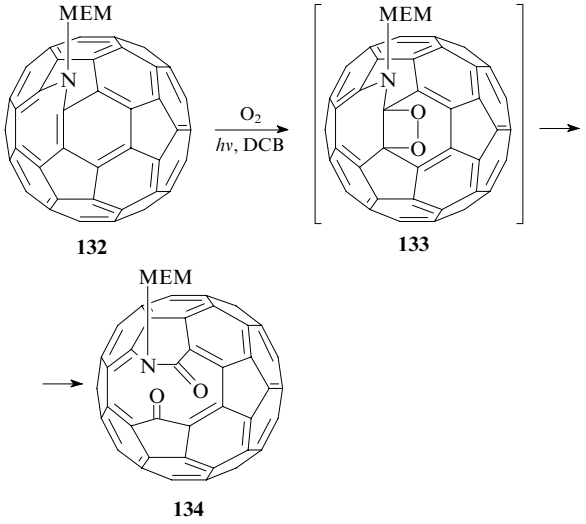
On the basis of these data, the proposed mechanism of fullerite photooxidation [93] has been refined by Juha *et al.*,[94] who have suggested, instead of reaction (3), an alternative reaction of $^1O_2^*$ with the triplet excited molecule $^3C_{60}^*$ — equation (4). These results are in contradiction with computation data,[95] according to which dioxetane $C_{60}O_2$ can form even in the reaction of unexcited C_{60} and O_2 molecules upon thermal oxidation of fullerite with oxygen. In this theoretical work,[95] it has been calculated that the O–O bond in the structure of dioxetane $C_{60}O_2$ (1.502 Å) is noticeably longer than in the triplet oxygen molecule (1.223 Å), and the C–O and C–C bond lengths are 1.460 and 1.572 Å, respectively. It has been assumed that concurrent thermolysis of these bonds generates nearly parallel C=O groups with a heat of 33.6 kcal mol^{-1}.

In the case of this ambivalent interpretation of the possibility of formation of fullerene dioxetane, with or without participation of two excited molecules (fullerene and oxygen), preference should be given to the results of direct experiments.[94] In addition, in earlier works, Arbogast and coworkers have also shown that neither C_{60},[96] nor C_{70} (Ref. 97) can be oxidized by $^1O_2^*$. This follows from the absence of changes in the UV/Vis spectra and from HPLC data after photoirradiation of oxygen-containing fullerene solutions in C_6D_6 by several hundreds of laser pulses at the wavelength of the $^3O_2$ excitation band or by a wider spectrum of radiation of a high-power lamp for many hours. The chemical inertness of unexcited fullerenes toward $^1O_2^*$ characterizes fullerenes as stable and highly efficient sensitizers suitable for photochemical generation of singlet oxygen.

Photoirradiation of a solution of *N*-methoxyethoxymethyl-substituted [5,6]-azafulleroid **132** in *o*-dichlorobenzene (DCB) presumably induces the formation and decomposition of 1,2-dioxetane intermediate **133** (Scheme 66).[73]

As a result, the C_{60} cage is opened (showing a 11-membered-ring orifice) to form ketolactam **134**. Note that, historically, this is the first synthesized open-cage fullerene derivative. Later, this scheme was confirmed by Reuther and Hirsch,[86] who subjected [5,6]-azahomofullerene **132** to self-sensitized photooxidation resulting in selective formation of ketolactam **134**, 1,2-dioxetane **133** being believed to be its precursor.

Scheme 66

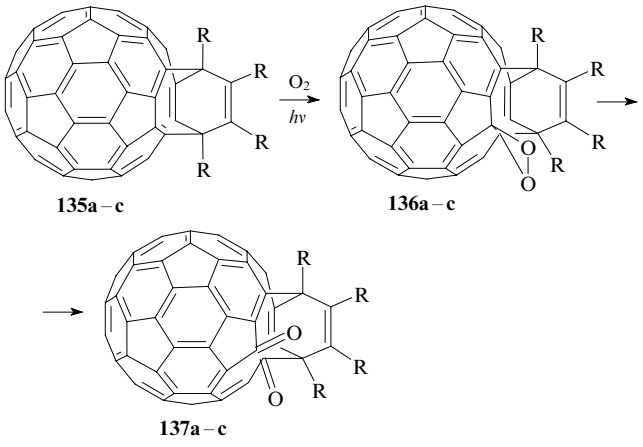


132 **133** **134**

MEM is methoxyethoxymethyl

To expand the orifices on the fullerene cage, an approach has been suggested involving photochemical bond cleavage in tetrasubstituted bisfulleroids **135a–c** through the formation of dioxetane adducts **136a–c** (Scheme 67).[87] This has made it possible to obtain, in a solution in toluene or CH_2Cl_2, diketone derivatives **137a–c** (95%, 87% and 58% yields) with a 12-membered-ring orifice. The oxidant that is added to a C=C bond of adduct **135** is singlet oxygen generated through energy transfer from the excited state of the initial fullerene to the oxygen molecule in the common triplet state.

Scheme 67



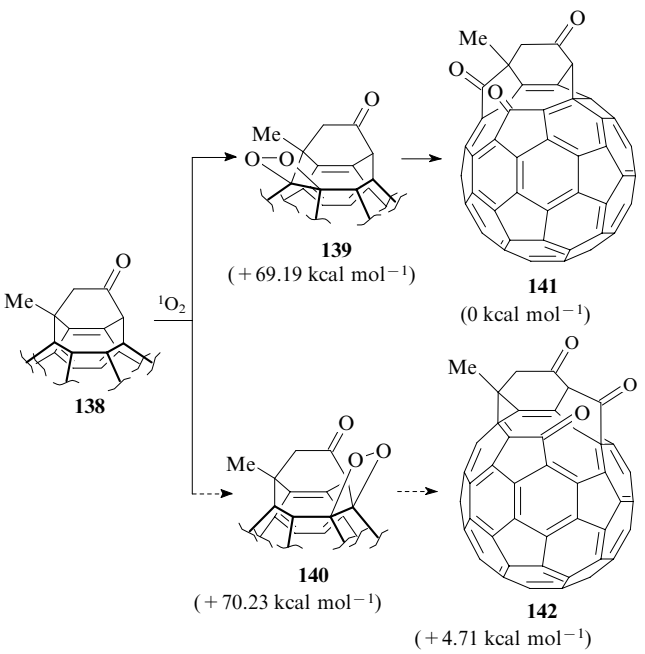
135a–c **136a–c** **137a–c**

R = CO_2Me (**a**), $CO_2CH_2CF_3$ (**b**), CO_2Bu^t (**c**)

Quantum chemical calculations (AM1) of compound **135a** have shown that the C=C subjected to oxidative cleavage has the highest electron density of the highest occupied molecular orbital (HOMO) and, therefore, is most reactive toward electrophilic singlet oxygen.

A dioxetane fullerene adduct is also assumed to form upon photochemical oxidation of open-cage keto-containing fullerene derivative **138** with a 8-membered-ring orifice (Scheme 68).[88]

Scheme 68

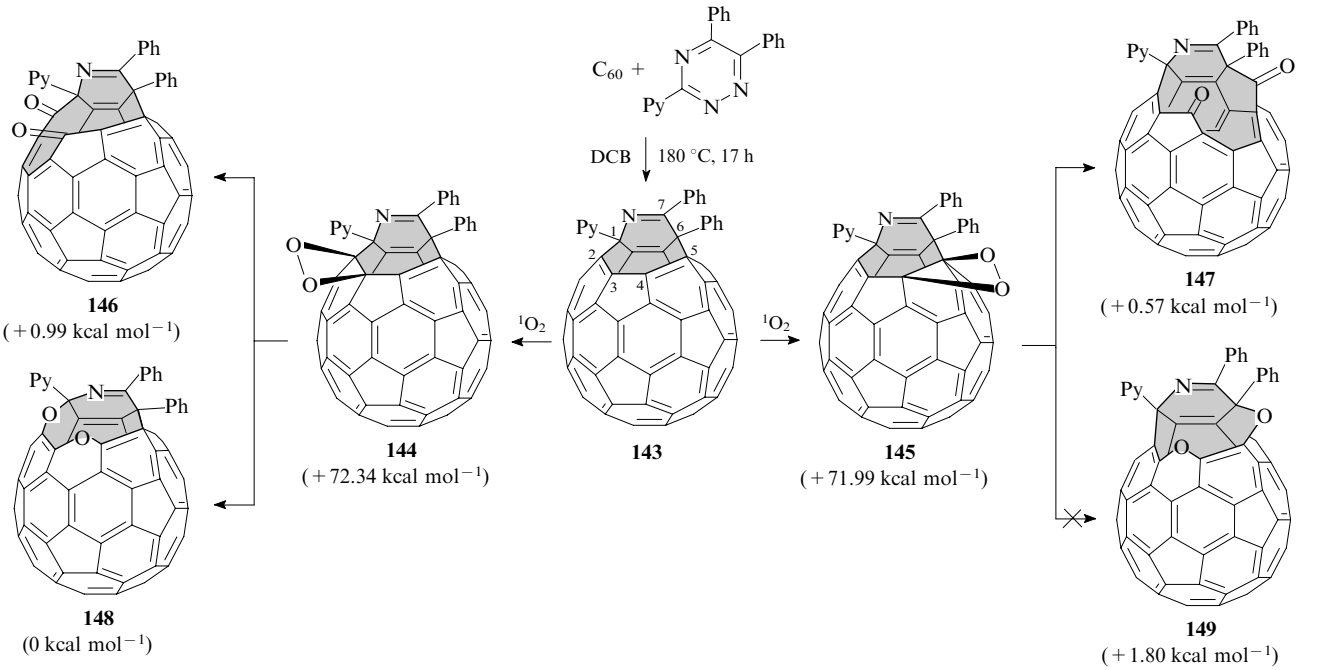


After 1-h irradiation with daylight of an air-saturated solution of compound **138** in CS_2, the solution changes colour from violet to brown. The appearance of two new carbonyl groups is attributed by the authors to [2+2]-cycloaddition of $^1O_2^*$ to the double bonds of adduct **138** to form two possible dioxetanes **139** and **140**. Density functional theory (DFT) analysis has shown that the HOMO of adduct **138** is initially localized on two C=C bonds; the absolute values of coefficients for the C(4) and C(5) atoms (−0.32 and −0.27) are slightly higher than those for the C(7) and C(6) atoms (+0.32 and +0.24). Therefore, the attack of $^1O_2^*$ species at the C(4)=C(5) bond is preferred. Comparison of the relative energies (parenthesized values in Scheme 68) of the optimized structures of triketones **141** and **142** demonstrates that, for compound **141**, it is 4.71 kcal mol^{-1} lower. Correspondingly, dioxetane **139** is 1.04 kcal mol^{-1} more stable than isomer **140**. The calculated chemical shifts in the ^{13}C NMR spectrum for triketone **141**, which has a 12-membered-ring orifice, correlate better with the experimental values. After chromatographic purification, triketone **141** was obtained in 60% yield as a brown powder.

In continuation of this study, Murata *et al.*[90] have proposed the formation of dioxetane as an intermediate under photoirradiation of open-cage aza adduct **143**, synthesized by the reaction of C_{60} with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (Scheme 69). Singlet oxygen generated under irradiation adds to the C(2)=C(3) and C(4)=C(5) double bonds to give dioxetanes **144** and **145**, which are opened to form stable diketones **146** and **147**, as well as a minor product — diether **148** (yield, 2%). Quantum chemical calculations (B3LYP/6-311G**) of the optimized structures and energies (parenthesized values in Scheme 69) of products **144**, **145**, **148** and **149** show that the addition of $^1O_2^*$ to the C(2)=C(3) bonds is thermodynamically less favourable. However, it is kinetically preferred over addition to the C(4)=C(5) bond because of the presence of two bulky phenyl groups in the immediate proximity of the latter. Diketone **146** forms through O–O and C(2)–C(3) bond cleavage in dioxetane **144**; and an alternative product — ether **148** — is a product of insertion of oxygen atoms into the C(1)C(2) and C(3)–C(4) bonds with concomitant O–O bond cleavage. Such a reaction route implies the formation of diketone **147** from dioxetane **145**; however, diether **149** (which, according to calculations, is less stable) has not been identified among the reaction products.

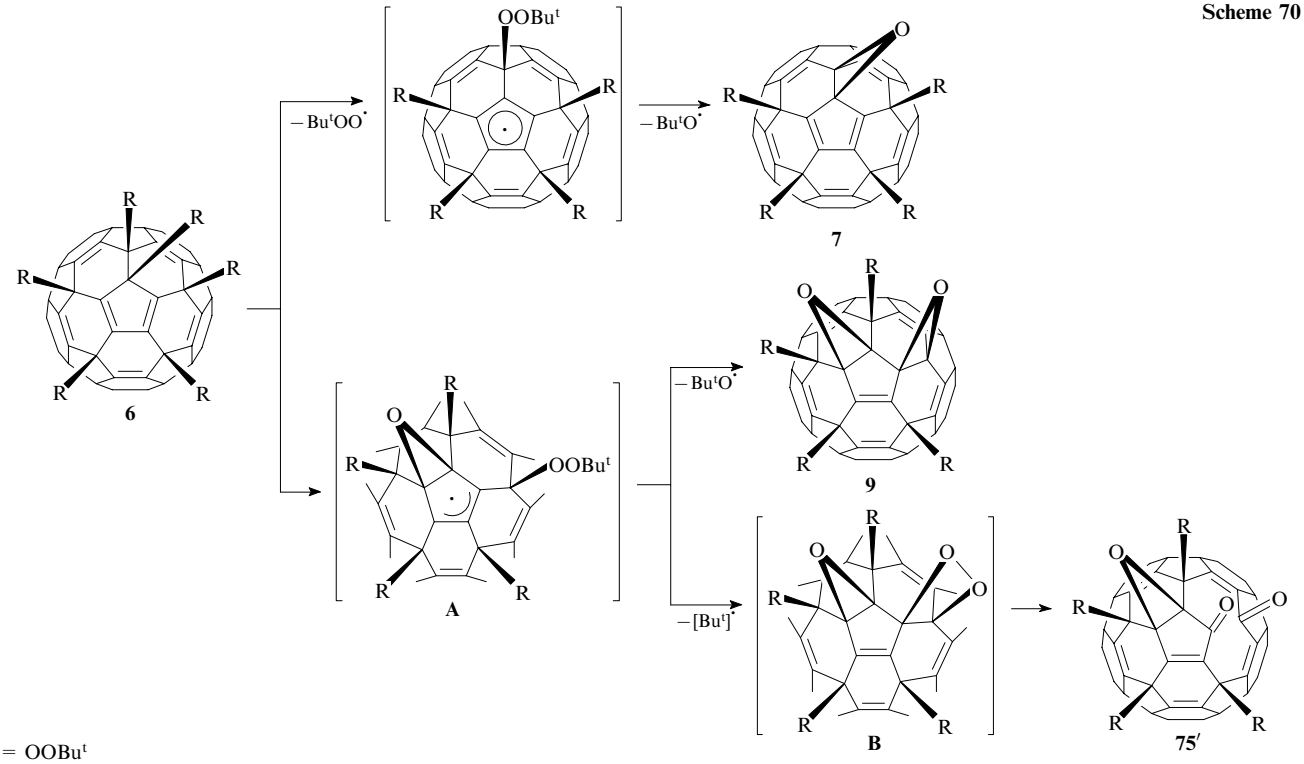
Dioxetane fullerene adducts are also proposed to be intermediates of photochemical reactions in transformations involving peroxides. There are two interpretations of the mechanism of formation of fullerene dioxetanes under photoirradiation of $C_{60}(OOBu^t)_6$ (**6**) (Scheme 70).

Scheme 69



Py is 2-pyridyl

Scheme 70



R = $OOBu^t$

In particular, it has been initially assumed that exposure to daylight leads to homolysis of the O–O bond of the peroxide addend at the CPD moiety to give intermediate **A** containing the epoxide ring annulated to the [5,6]-bond and the allyl radical moiety.[2,5] Then, upon homolysis of the O–Bu^t bond with elimination of the *tert*-butyl radical, the unpaired electrons of the peroxide residue C_{60}–O–O$^{\bullet}$ and allyl radical moiety form a covalent bond to give a dioxetane ring. The latter decomposes to form open-cage diketone derivative **75′**. The presence of molecular iodine in the reaction solution makes the reaction more selective and effective, presumably, because it binds $[Bu^t]^{\bullet}$ radicals. The yield of the product increases when radiation with λ_{max} = 470 nm is used instead of daylight.[12]

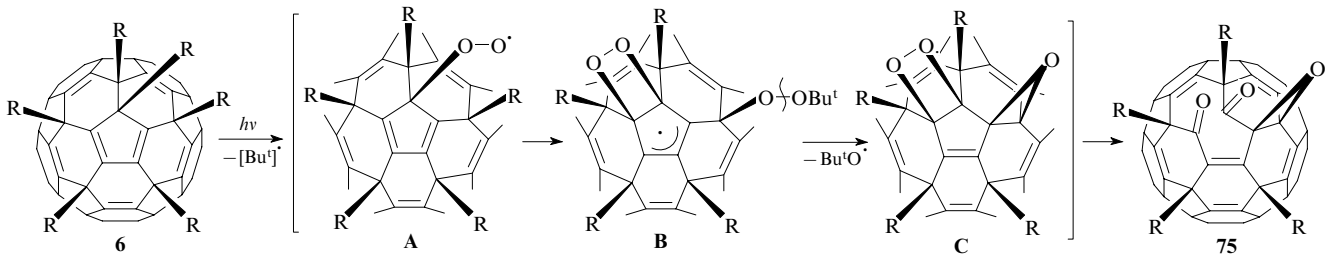
In the last work, the authors revised the suggested mechanism[2,5] and refined the structure of the reaction product. The main difference between the mechanisms is that the dioxetane ring rather than the epoxide ring is suggested to form first as a result of the elimination of the $[Bu^t]^{\bullet}$ radical upon homolytic cleavage of the O–Bu^t bond of the peroxide group bonded to the central pentagon of compound **6**.[12] This leads to fullerene peroxyl radical **A** (Scheme 71). Subsequent cleavage of one C=C bond in the central CPD moiety promotes the intramolecular addition of the peroxyl group of radical **A** to form the 1,2-dioxetane ring and allyl radical moiety in intermediate **B**. The elimination of the $Bu^tO^{\bullet}$ radical from **B** gives intermediate **C**, containing two rings: the dioxetane and epoxide rings. Finally, the opening of the dioxetane ring leads to stable diketone **75**.

An unusual (non-'dioxetane' one) route of photochemical fullerene cage opening has been suggested by Shick *et al.*[98] In the case of complex adduct **150**, which contains two nitrogen atoms covalently bonded to two 1,4-carbon atoms of the six-membered ring, singlet oxygen does not attack the C=C bonds of this ring; rather it is annelated to these atoms to form the endoperoxide moiety (Scheme 72).

Then, endoperoxide **151** undergoes spontaneous rearrangement with [2+2+2] ring opening and formation of two amide moieties of adduct **152**. The heat of this fragmentation calculated by the AM1 method, 130–134 kcal mol^{-1}, indicates that the formation of adducts **152a**,**b** is highly exothermic.

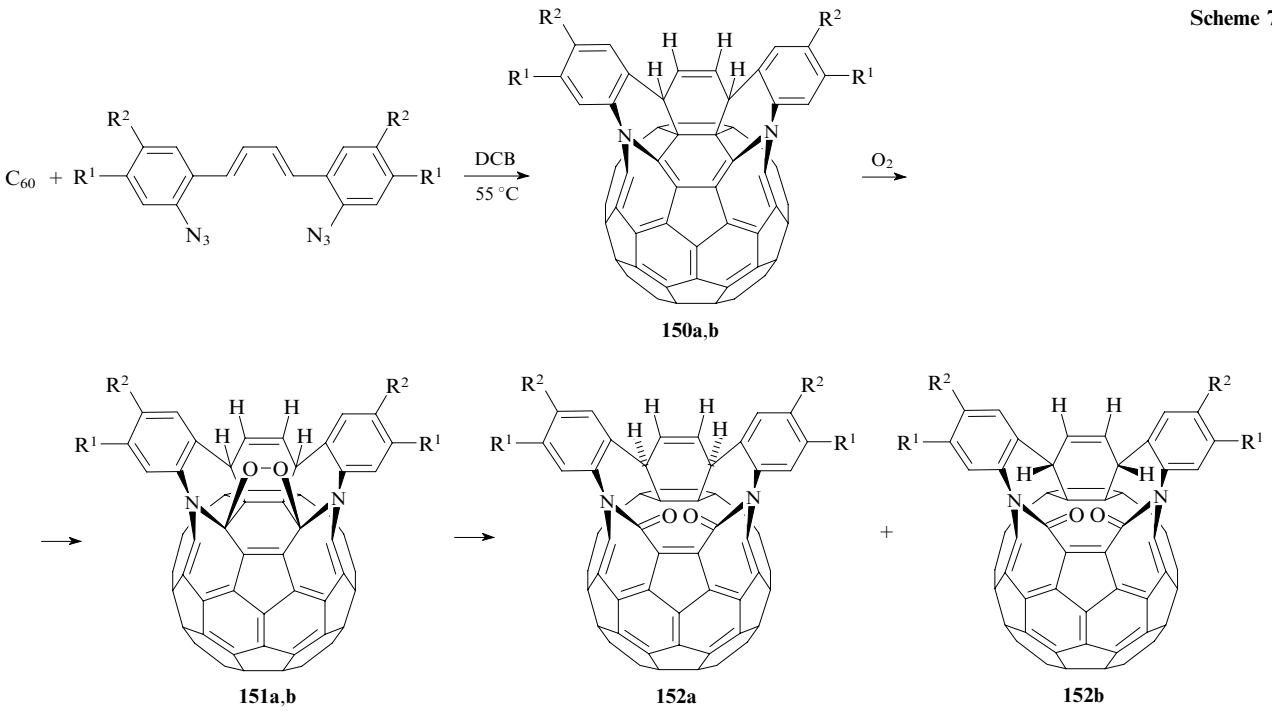
It should be noted that observation of chemiluminescence (CL) would be a good experimental proof of formation of fullerene dioxetanes and keto-containing products of their decomposition. Indeed, CL upon decomposition of organic dioxetanes is well known.[99–101] Unlike short-wave CL of organic dioxetanes (λ_{max} = 420 nm), CL in the case of fullerene dioxetanes should be observed in a near-IR range, similarly to the CL of fullerene polyketones (λ_{max} = 620–660 nm) generated upon ozonolysis of C_{60}.[102]

Scheme 71



R = $OOBu^t$

Scheme 72



150a,b **151a,b** **152a** **152b**

Isomers: *endo* (**a**) and *exo* (**b**); R^1 = H: R^2 = H, Cl; R^1 = Bu^t, R^2 = H

V. Fullerene peroxides — major products of the key reaction of inhibition of hydrocarbon oxidation by fullerenes C_{60} and C_{70}

The ability of fullerenes to effectively add a large number of free radicals to the C=C multiple bonds[82,103–106] has favoured the development of a new line in the field of radical chemistry of fullerenes — study of their inhibiting properties. These issues have been addressed in a considerable number of publications covered in monographs.[107,108] It should be noted that owing to a large number of C=C bonds and the absence of C–H bonds in fullerene molecules, reactions of deactivation of active radical species $X^{\bullet}$ generated upon hydrocarbon oxidation must be radically different in the case of inhibition by fullerenes [reaction (1) in Scheme 73] and by classical inhibitors [reaction (2) in Scheme 73].

Scheme 73

$$X^{\bullet} + C_{60} \longrightarrow XC_{60}^{\bullet} \quad (1)$$

$$X^{\bullet} + InH \longrightarrow X-H + In^{\bullet} \quad (2)$$

$$X^{\bullet} + C_{60}(R-H) \longrightarrow XH + RC_{60}^{\bullet} \quad (3)$$

$X = RO_2^{\bullet}$, $R^{\bullet}$; $In^{\bullet}$ is inactive radical moiety of an inhibitor; $C_{60}(R-H)$ is fullerene derivative with an addend containing a mobile H atom.

In the former case, radical $X^{\bullet}$ is added to the fullerene molecule; in the latter case, the reaction involves abstraction of a hydrogen atom from the inhibitor molecule. However, if an inhibitor is a fullerene adduct containing a mobile hydrogen atom in the addend, inhibition can occur both through the addition of $X^{\bullet}$ species to the fullerene cage [reaction (1) in Scheme 73] and through the abstraction of hydrogen atom [reaction (3) in Scheme 73]. The interpretation of the mechanism of antioxidant action of fullerenes, namely, identification of the reaction responsible for the inhibitory effect of fullerenes, has been controversial for a long time. For example, suppression of the thermooxidative destruction of polymers by fullerene C_{60} has been presumably attributed to the reaction of fullerene C_{60} molecule with peroxyl macroradicals $R^iO_2^{\bullet}$ leading to fullerene epoxide [reaction (1) in Scheme 74].[109–113]

Scheme 74

$$R^iO_2^{\bullet} + C_{60} \longrightarrow R^iO^{\bullet} + C_{60}O \quad (1)$$

$$LO_2^{\bullet} + 2C_{60} \longrightarrow L'-L' + 2C_{60}O \quad (2)$$

$$R^{\bullet} + C_{60}/C_{70} \longrightarrow {}^{\bullet}C_{60}/C_{70}-R \quad (3)$$

R^i is macroradical of a polymer; L, L′ is lipid moieties; $R^{\bullet}$ is hydrocarbon radical

A similar mechanism has also been proposed to explain the inhibition of oxidation of ethyl oleate and cyclohexane in the presence of fullerene C_{60} added [reaction (2) in Scheme 74].[114,115]

The last conclusion has been based on the appearance of a maximum at 433 nm assigned to 1,2-epoxide $C_{60}O$ in the electronic absorption spectrum of the products of oxidation of these substrates. In addition, HPLC analysis of the products has identified, among them, cyclohexane dimers and trimers [see reaction (2) in Scheme 74]. On the other hand, on the basis of the absence of the induction period on the kinetic curves of oxygen absorption, Zeynalov *et al.*[116] have attributed the inhibitory effect of fullerenes C_{60} and C_{70} on the reaction of cumene oxidation to the addition of alkyl radicals $R^{\bullet}$ [reaction (3) in Scheme 74]. At the same time, studying the effect of fullerene C_{60} and halofullerenes $C_{60}Cl_6$, $C_{60}F_{36}$ and $C_{60}F_{48}$ on kinetic characteristics of initiated oxidation of benzyl alcohol has enabled the conclusion that the oxidation chain termination is caused by the reaction of fullerene C_{60} and its halo derivatives with both alkyl ($R^{\bullet}$) and peroxyl ($RO_2^{\bullet}$) radicals.[117,118] The same conclusion has been drawn from the results of studying the antioxidant activity of fullerenes C_{60} and C_{70} in initiated oxidation of methyl linoleate.[119] The mechanism of inhib-

ition by fullerene C_{60} of the oxidation of primary and secondary alcohols, as well as of styrene and ethylbenzene, has been explained in the same way.[117]

In contrast to the above data, the liquid-phase chemiluminescence observed upon oxidation of ethylbenzene in the presence of fullerene has been assigned to the emission of fullerene ketones — the products of thermal decomposition of fullerene peroxides formed upon addition of peroxyl radicals $RO_2^{\bullet}$ to the C_{60} molecule.[120] This conclusion is supported by the presence, in the CL spectrum, of long-wavelength maxima at 645 and 685 nm, their positions being close to the CL maxima of fullerene polyketones generated upon ozonolysis of C_{60} in a solution of CCl_4.[102] Inhibition of cumene oxidation by 3,5-di(*tert*-butyl)-4-hydroxyphenyl derivatives of fullerene C_{60} has been described, and the inhibitory effect has been attributed to the addition of $RO_2^{\bullet}$ (and, presumably, $R^{\bullet}$) radicals.[121] It is worth noting that these contradictions are due to that the composition of the products of reaction of fullerenes with radical intermediates of inhibited liquid-phase oxidation of organic compounds has not been studied.

Indeed, the fact that fullerenes are involved in inhibited oxidation has been established mainly on the basis of the decrease in the oxidation rate of organic compounds.[109–113, 116–119, 121–123] A more vivid proof of the participation of fullerenes in this process has been reported.[124] The authors have demonstrated that, upon initiated cumene oxidation in the presence of C_{60} or C_{70}, significant consumption of fullerene is observed, which follows from the decrease of the HPLC peaks of C_{60} [retention time (t_r) 10.4 min] or C_{70} (t_r = 17.5 min) and from the emergence of new peaks of products with t_r = 4.7–5.7, 11.6 and 13.3 min (for C_{60}) or with t_r = 4.4–5.1, 7.1–7.6, 20.7 and 24.2 min (for C_{70}).

After the 2-h initiated [by azobis(isobutyronitrile)] cumene oxidation at 70 °C in the presence of C_{60}, two major products have been isolated by semipreparative HPLC of the reaction solution: 1,2-epoxydihydro[60]fullerene $C_{60}O$ (**1**) with t_r = 11.6 min and fullerene peroxide — bis(2-phenylpropan-2-ylperoxy)[60]fullerene [$C_{60}(OOCMe_2Ph)_2$, **153**] with t_r = 5.7 min. Epoxide **1** has been characterized byh UV spectroscopy (λ_{max} = 423 nm in toluene) and mass spectrometry (*m*/*z* 736, MALDI TOF, S-matrix). Peroxide **153** has been identified by IR spectroscopy, NMR (^1H, ^{13}C) and mass spectrometry. The positive ion mass spectrum (ESI) of sample **153** shows only one peak with *m*/*z* 1082 ($[M + H + MeCN + H_2O]^+$). At the same time, the MALDI TOF mass spectrum of compound **153** shows only the peaks of epoxides $C_{60}O_{1-12}$. This spectrum coincides with the analogous spectrum of CFP 7.[2] In the ^{13}C NMR spectrum of product **153**, the signals at 83.71 and 84.38 ppm, assigned to the C(sp^3) atoms of the cumyl moiety (CMe_2Ph) and fullerene cage, are close to the signals at 84.46 and 84.96 ppm of the *tert*-butyl and fullerene carbon atoms in the spectrum of the 1,4-isomer of peroxide $C_{60}(O)(OOCMe_2Ph)_4$.[2] Taking into account that the signals of C(sp^3) atoms in the NMR spectra of 1,2-isomers of fullerene peroxides are observed at lower field, the authors[124] have arrived at the conclusion that compound **153** is a 1,4-isomer.

Thus, the demonstration of formation of peroxide **153** in the course of inhibited cumene oxidation in the presence of fullerene C_{60} made it possible to attribute the inhibitory effect of fullerenes on liquid-phase oxidation of organic compounds to the reaction of addition of precisely peroxyl radicals to fullerene molecules.[124]

VI. Conclusions

Nowadays, the chemistry of fullerene peroxide derivatives offers extremely wide possibilities to synthesize very different classes of derivatives of cage molecules, including open-cage (capsule) forms. At the same time, as follows from the above studies, the number of peroxide types differing in the mode of O–O group addition to the carbon atoms of the fullerene cage is rather limited. Indeed, the vast majority of studies have focused only on the alkyl peroxides with the $ROO-C_{60(70)}$ bond, where R = Bu^t, $CHMe_2Ph$. As noted above (see Section II), $C_{60}(O)(OOCMe_2Ph)_4$ has been first obtained[2] by catalytic decomposition of cumene hydroperoxide ($PhCMe_2OOH$) under the action of $Ru(PPh_3)_3Cl_2$ in the presence of C_{60}. Hence, by now, only the peroxides formed by addition of tertiary peroxyl radicals to the fullerene cage have been reliably identified: $Bu^tOO^{\bullet}$ and $PhCMe_2OO^{\bullet}$. This can likely be explained by the lower recombination rate constant of such radicals: $k_6 = 1 \times 10^4$ and 3×10^4 litre mol^{-1} s^{-1}, respectively.[125] Owing to this fact, the reaction system is characterized by a rather high stationary concentration of tertiary radicals as compared with the primary and secondary ones, for which k_6 1×10^7 litre mol^{-1} s^{-1}. As a result, the probability of tertiary radicals $RO_2^{\bullet}$ adding to fullerene is considerably higher and, presumably, this factor is a key one for the successful synthesis of fullerene peroxides.

There is one work[26] where hydroperoxide with the $HOO-C_{60}$ bond has been synthesized; two works[7,89] have focused on synthesis and isolation of fullerene dioxetanes, which are also proposed to be intermediates of chemical and photochemical oxidation of C_{60} and its derivatives. In addition, fullerene derivatives containing the peroxide O–O group are considered to be potential products of oxidation of fullerene anions by oxygen[126] and of fullerenes by ozone.[127,128] In the first case, this the reaction of the C_{60}^{n-} anion with molecular oxygen leading to formation of rather stable $C_{60}O_2^-$ anions — the products of [6,6]- and [5,6]-addition of dioxygen.[126] In the second case, this is preparation of labile intermediates of ozonolysis of fullerenes C_{60} (see Refs 127 and 128) and C_{70}:[128] oxafullerenecarbonyl oxides $C_{59}C^+-OO^-$ and $C_{69}C^+O-O^-$. Recombination and isomerization of these anions are the light stages of chemiluminescence that appears upon ozonolysis of fullerenes; it has been described in detail in our review.[46]

Thus, as distinct from the variety of organic peroxides, peroxy acids $C_{60}(O)OOH$, acyl peroxides $C_{60}(O)OOC(O)R$, dioxiranes and many other classes are still unknown for fullerene peroxide derivatives.[129,130] However, we believe that the excellent potential of fullerene alkyl peroxides as precursors for various transformations, considered in this review, in combination with the mentioned 'blank spots', will serve as a stimulating factor for the development and further study of this interesting field of chemistry.

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[a] — *Dokl. Phys. Chem. (Engl. Transl.)*
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