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Fluorocycloalkylated Fullerenes in the Systems $C_{60/70}$–$C_2F_4I_2$

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An addition reaction of biradicals thermally generated from $C_2F_4I_2$ was applied to functionalize fullerenes. This resulted in the formation of a number of $C_{60}(C_2F_4)_n$ and $C_{70}(C_2F_4)_m$ compounds. HPLC separation allowed the determination of the molecular structures of $C_{60}(C_4F_8)_2$ (two isomers), $C_{60}(C_4F_8)_6$, and $C_{70}(C_2F_4)_2$ and revealed that these compounds are formed by different modes of [4+2], [4+3], and [2+2] addition, respectively. A new synthetic approach for the preparation of a series of fluorocycloalkylated derivatives of fullerenes should be further exploited.

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Introduction

Radical addition to fullerenes is known to produce a variety of compounds such as halides, perfluoroalkyl, amino-, alkylsilyl-, and metalated derivatives.[1] In these reactions, radicals can be generated thermally or by photolysis. In particular, the preparation of fluoroalkyl derivatives of fullerenes proceeds by their treatment with fluoroalkyl iodides (R_fI), metal trifluoroacetates, or fluoroacylperoxides, which easily generate R_f radicals at heating.[2] In the last few years, a wealth of trifluoromethyl derivatives of C_{60} and C_{70} containing 2–18 R_f groups on the fullerene cage have been obtained, isolated, and unambiguously characterized by X-ray crystallography.[3,4] The syntheses and structures of pentafluoroethylated fullerenes were also described for both C_{60} and C_{70}.[5] Perfluoroalkylated fullerenes possess high chemical and thermal stability and, as a result of their electron acceptor properties, may serve as prospective components for new nanomaterials.[6]

Here we report a new radical reaction of fullerenes with 1,2-diiodotetrafluoroethane, $C_2F_4I_2$, which proved to be an effective method for the preparation of new cycloadducts of fullerenes. Both C_{60} and C_{70} react easily with $C_2F_4I_2$ at heating, which results in a series of products containing up to 18 C_2F_4 groups per fullerene cage. Crystal structure determination for several compounds obtained revealed a variety of addition modes to the fullerene cage.

Results and Discussion

The experiments were carried out in sealed glass ampoules to maintain a high concentration (pressure) of $C_2F_4I_2$. C_{60} or C_{70} (36 or 42 mg, 0.05 mmol) and liquid $C_2F_4I_2$ (≈0.4 mL, ca. 3 mmol) were placed into a two-section glass ampoule and cooled with liquid nitrogen. The ampoule was evacuated and sealed off. It was then heated at 400–450 °C for 4–24 h. After opening the ampoule, the excess amounts of $C_2F_4I_2$ and I_2 were removed by heating at ≈100 °C in open air for some hours. The reaction products were analyzed by MALDI TOF MS with the use of DTCB {*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile} as a matrix. It was found that the products of the reaction with C_{60} contained a mixture of compounds of stoichiometric composition, $C_{60}(C_2F_4)_n$, where n ranged from 1 to 18. On longer reaction times, C_{60} was nearly quantitatively consumed and the fullerene-based yield was 90–95%. Typically, the compounds containing an even number of C_2F_4 groups dominated in the mixture (Figure 1a). Similar results were obtained with C_{70}: the

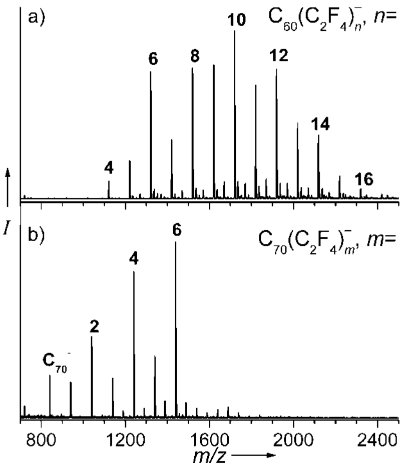

Figure 1. MALDI MS spectra of the products obtained by ampoule reactions of $C_2F_4I_2$ with C_{60} (a) and C_{70} (b).

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number of C_2F_4 groups in the formula $C_{70}(C_2F_4)_m$ varied from 1 to 14, and dominating compositions were found with even values of *m*. However, in some experiments, compounds $C_{70}(C_2F_4)_m$ with odd *m* values were also present (Figure 1b).

The reaction products were then subjected to HPLC separation on a Cosmosil Buckyprep column (10 mm ID × 25 cm) by using toluene or toluene/hexane (3:2) as the eluent (4.6 mL min^{-1}). This resulted in isolation of several fractions containing $C_{60}(C_2F_4)_n$ with $n = 2$, 4 (four isomers), 6 (three isomers), 8, 12, 14 (three isomers), and 16 according to MALDI MS analyses. HPLC separation of the reaction products with C_{70} allowed the isolation of several fractions containing $C_{70}(C_2F_4)_m$ with $m = 2$, 3 (three isomers), and 4. The isolated fractions were concentrated by slow removal of the solvents to give crystalline materials in a few cases. In some other cases, recrystallization was attempted with the use of other solvents such as 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, or mesitylene, and so on. Single crystals could be obtained for a few compounds only. Because of the very small size of the crystals, their analysis by X-ray diffraction was possible only by using synchrotron radiation.[7]

X-ray crystallographic investigation of the four individual compounds, $C_{60}(C_4F_8)_2$ (two isomers), $C_{60}(C_4F_8)_6$, and $C_{70}(C_2F_4)_2$, revealed that the addition can occur in different ways. Addition reactions of C_2F_4 generated from $C_2F_4I_2$ are known for a number of unsaturated compounds such as (cyclo)alkenes, alkynes, and so on.[8] In the case of fullerenes, biradical addition of both monomeric C_2F_4 and dimeric C_4F_8 groups takes places. It is well known that $C_2F_4I_2$ can generate C_2F_4 biradicals thermally and by light or laser activation.[9] $C_2F_4I_2$ undergoes telomerization above 180 °C, which results in the formation of dimeric, oligomeric, and even polymeric $I(C_2F_4)_nI$ molecules.[9] After prolonged heating at 250–300 °C, teflon-like products can be obtained. Obviously, the heating of the reaction mixture fullerene/$C_2F_4I_2$ is accompanied by dimerization/oligomerization of diiodotetrafluoroethane. Therefore, biradical addition to fullerenes can involve not only C_2F_4, but also dimeric C_4F_8 units. This can account for the predominant formation of $C_{60/70}(C_2F_4)_n$ with even values of *n* that, in fact, reflect the presence of presumable $C_{60/70}(C_4F_8)_{n/2}$ products in the reaction mixtures. In some of our syntheses carried out with longer reaction times, the formation of white films on the reaction ampoule walls was observed. Thus, one may suggest that a high degree of telomerization partially occurs under the reaction conditions.

Two investigated bisadducts of the formula $C_{60}(C_4F_8)_2$ were formed as a result of [4 + 2] cycloaddition of perfluorinated butene, C_4F_8, to the 6:6 bonds of the C_{60} cage (Figure 2). The two isomers, $C_{60}(C_4F_8)_2$-I and -II, differ in their addition patterns shown on Schlegel diagrams. The addition patterns of isomers I and II have, respectively, idealized D_{2d} and C_2 symmetry, but the molecular symmetry can be lower depending on the conformation of the fluorinated fragments of the six-membered rings (which, however, are disordered in both crystal structures). Two other isomers of the same composition were isolated by HPLC, but their structures are unknown.

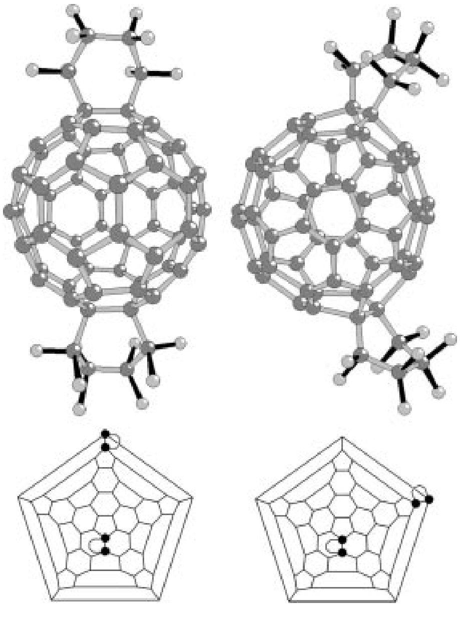

Figure 2. Two isomers of $C_{60}(C_4F_8)_2$ together with their Schlegel diagrams.

X-ray crystallography also established the structure of the only isolated isomer of $C_{60}(C_4F_8)_6$. Its molecular structure of C_2 symmetry contains six attached C_4F_8 groups (Figure 3). Four C_4F_8 groups each form six-member rings by the same [4 + 2] cycloaddition as it was observed in the structure of the $C_{60}(C_4F_8)_2$ isomers discussed above. Two other C_4F_8 groups are attached in a [4 + 3] manner. This kind of addition is not known in fullerene chemistry. Probably, the [4 + 3] addition results from rearrangement to a more energetically favorable conformation of the fluorinated cycles and the formation of an isolated double bond on the fullerene cage. Whereas four six-membered rings have a boat conformation, the seven-membered rings are close to a chair-like form.

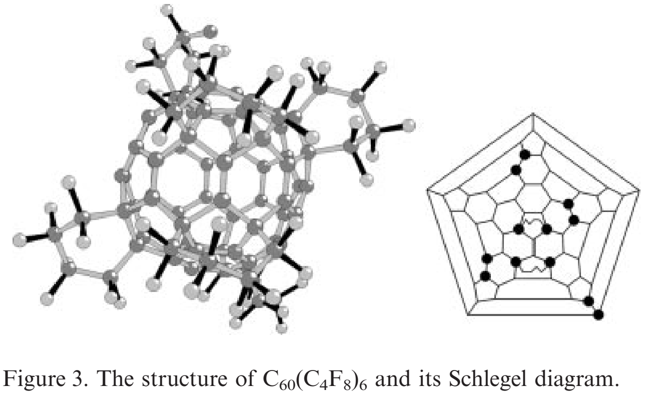

Figure 3. The structure of $C_{60}(C_4F_8)_6$ and its Schlegel diagram.

The molecular structure of the $C_{70}(C_2F_4)_2$ adduct demonstrates a [2 + 2]-type of cycloaddition, which is well-known in fullerene chemistry. This compound and probably other $C_{60/70}(C_2F_4)_n$ derivatives with odd values of *n* are formed by the addition of monomeric C_2F_4 units that are present in the reaction mixture before dimerization/telomerization of $C_2F_4I_2$ occurred to a large extent. Our experiments confirmed that such compounds can be isolated from the reaction products obtained at lower temperatures and/or shorter reaction times. The structure of the $C_{70}(C_2F_4)_2$ molecule possessing (noncrystallographic) C_{2v} symmetry is shown in Figure 4.

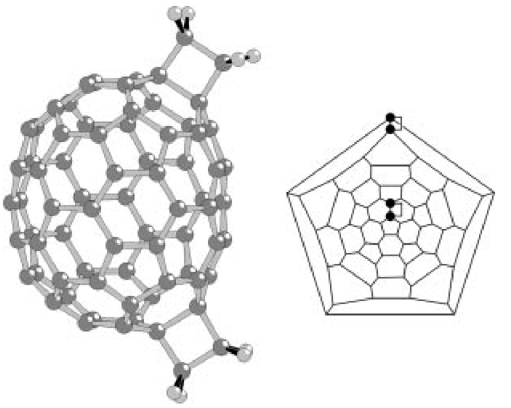

Figure 4. The structure of $C_{70}(C_2F_4)_2$ and its Schlegel diagram.

The addition to the fullerene cage proceeds at the most reactive sites, which are the 6:6 double bonds radiating from the pole pentagons of the C_{70} molecule. For comparison, dimerization of C_{70} to C_{140} with the formation of a cyclobutane ring,[10] as well as [2+2] additions of benzynes,[11]also occur at these sites. Both cyclobutane rings (in each of two crystallographically independent molecules) have a slightly twisted conformation with an average cage C–C distance of 1.616 Å and C–C(F) and C(F)–C(F) distances of 1.555(5) and 1.537(5) Å, respectively.

Conclusions

The addition reaction of C_2F_4 thermally generated from $C_2F_4I_2$ was applied to functionalize fullerenes for the first time. Biradical addition of C_2F_4 and C_4F_8 occurred (the latter was produced in the course of telomerization of $C_2F_4I_2$), which resulted in the formation of a number of $C_{60}(C_2F_4)_n$ and $C_{70}(C_2F_4)_m$ compounds. Molecular structures of $C_{60}(C_4F_8)_2$ (two isomers), $C_{60}(C_4F_8)_6$, and $C_{70}(C_2F_4)_2$ show different modes of [4+2], [4+3], and [2+2] cycloaddition, respectively. Therefore, a new method for the preparation of a series of fluorocycloadducts of fullerenes has been developed.

Supporting Information (see footnote on the first page of this article): Experimental details, chromatograms, mass spectra.

Acknowledgments

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[7] Data collection for crystals was performed with a MAR225 image plate at 100 K by using synchrotron radiation at the BESSY storage ring (λ = 0.9050 Å, BL 14.1, PSF of the Free University of Berlin, Germany). Structure solution with SHELXS97 and structure refinements with SHELXL97. $C_{60}(C_4F_8)_2$-I: monoclinic, $P2_1/c$, a = 10.065(1) Å, b = 12.475(1) Å, c = 15.443(1) Å, β = 105.01(1)°, V = 1872.9(3) Å^3, Z = 2, wR_2 = 0.380 (for 3877 reflections and 437 parameters), R_1 = 0.175 [for 3487 reflections with $I > 2\sigma(I)$]. C_4F_8 group is strongly disordered. $C_{60}(C_4F_8)_2$-II: monoclinic, $C2/c$, a = 12.497(1) Å, b = 29.602(4) Å, c = 10.0441(4) Å, β = 90.24(1)°, V = 3715.6(6) Å^3, Z = 4, wR_2 = 0.432 (for 3963 reflections and 397 parameters), R_1 = 0.210 [for 2892 reflections with $I > 2\sigma(I)$]. C_4F_8 group is disordered. $C_{60}(C_4F_8)_6 \cdot 0.75C_6H_{14}$: triclinic, $P\bar{1}$, a = 11.666(1) Å, b = 13.223(1) Å, c = 23.038(1) Å, α = 75.30(1)°, β = 75.52(1)°, γ = 84.03(1)°, V = 3325.1(4) Å^3, Z = 2, wR_2 = 0.419 (for 6223 reflections and 1217 parameters), R_1 = 0.186 [for 4794 reflections with $I > 2\sigma(I)$]. $C_{70}(C_2F_4)_2 \cdot 1.5C_6H_4Cl_2$: monoclinic, $P2_1/c$, a = 13.4993(1) Å, b = 15.9139(1) Å, c = 42.8973(3) Å, β = 98.0442(3)°, V = 9124.8(1) Å^3, Z = 8, wR_2 = 0.200 (for 15543 reflections and 1901 parameters), R_1 = 0.079 [for 13591 reflections with $I > 2\sigma(I)$]. 1,2-dichlorobenzene molecules are strongly disordered. CCDC-650262 to -650265 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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