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Radical reaction of $C_{70}Cl_{10}$ with $P(OEt)_3$: isolation and characterization of $C_{70}[P(O)(OEt)_2]_nH_n$ (n = 1, 2)

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The Arbuzov-type reaction of chlorofullerene $C_{70}Cl_{10}$ with $P(OEt)_3$ leads to the formation of $C_{70}[P(O)(OEt)_2]H$ and $C_{70}[P(O)(OEt)_2]_2H_2$, whose molecular structures were determined using ESI mass spectrometry in combination with 1D and 2D NMR spectroscopy.

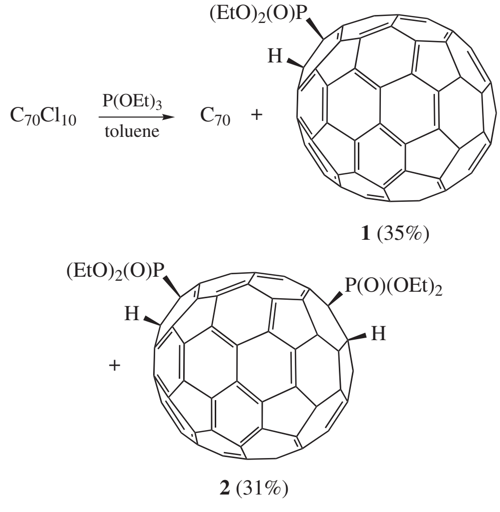
Functionalized fullerene derivatives are promising materials for organic electronics[1–3] and biomedicine[4,5] applications. Cycloaddition reactions are commonly used for the derivatization of the carbon cages of C_{60} and C_{70} fullerenes.[6–11] However, cycloaddition reactions suffer from poor regio- and stereoselectivity.[12,13] The addition of two or more organic addends to the fullerene cage produces hardly separable mixtures of many isomers.[14,15]

Chlorinated fullerenes are accessible precursors for the highly selective synthesis of multifunctional fullerene derivatives. The chlorination of C_{60} or C_{70} using a solution of ICl affords individual isomers of $C_{60}Cl_6$ and $C_{70}Cl_{10}$, respectively.[16–19] High-temperature chlorination of C_{60} results in the quantitative formation of $C_{60}Cl_{24}$, $C_{60}Cl_{28}$ or $C_{60}Cl_{30}$ depending on the reaction conditions.[20–22] Fullerene C_{70} gives $C_{70}Cl_{28}$ under similar conditions.[23]

The chlorofullerenes $C_{60}Cl_6$ and $C_{70}Cl_{10}$ react with C- and O-nucleophiles such as aromatic hydrocarbons in the presence of Lewis acids, MeLi, $H_2C{=}CHCH_2SiMe_3$ and alcohols.[24–29]

We reported the synthesis of water-soluble [70]fullerene derivatives *via* the Friedel–Crafts arylation of $C_{70}Cl_8$ and $C_{70}Cl_{10}$.[30] The first air-stable salts of the fullerene anion $[C_{60}(CN)_5]^-$ were synthesized in the reaction of $C_{60}Cl_6$ with organic cyanides.[31] A family of aminofullerenes was obtained using the reactions of $C_{60}Cl_6$ with amines.[32,33] A novel group of sulfur-containing fullerene derivatives was designed using highly efficient reactions of $C_{60}Cl_6$ with thiols.[34]

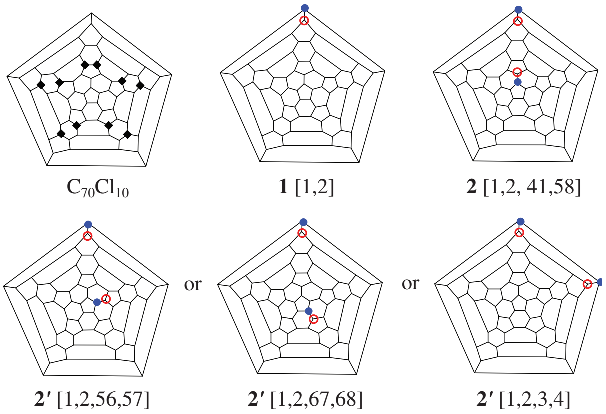
More recently, we reported the Arbuzov reaction of chlorofullerene $C_{60}Cl_6$ with $P(OR)_3$ leading to the highly selective formation of $C_{60}[P(O)(OR)_2]_5H$.[35] Here, we explored the applicability of this reaction to other fullerene halides, in particular, $C_{70}Cl_{10}$. Pristine chlorofullerene $C_{70}Cl_{10}$ (120 mg, 0.1 mmol) prepared in accordance with a published procedure[18] was dissolved in 100 ml of freshly distilled toluene with stirring at room temperature to afford a lemon-yellow solution. A solution of $P(OEt)_3$ (1660 mg, 10 mmol) in 10 ml of toluene was added dropwise to the chlorofullerene solution with stirring. The reaction mixture changed its color to dark red and then to reddish brown. It was stirred for additional 4 h and then poured on the top of a silica gel column (Acros organics, 40–60 μm). Elution with toluene provided non-functionalized C_{70} which was formed from chlorofullerene $C_{70}Cl_{10}$ *via* elimination of addends from the fullerene cage under the action of phosphite. The following elution with toluene–methanol mixtures produced $C_{70}[P(O)(OEt)_2]H$ **1** and $C_{70}[P(O)(OEt)_2]_2H_2$ **2** in 35 and 31% yields, respectively (Scheme 1).



Scheme 1

The molecular compositions of compounds **1** and **2** were confirmed using ESI mass spectrometry, which revealed only the peaks corresponding to the title products with *m*/*z* 977 due to $[\mathbf{1}-H]^-$ and *m*/*z* 1115 due to $[\mathbf{2}-H]^-$ (Figures S1 and S10, Online Supplementary Materials).

The ^1H NMR spectrum of **1** (Figure S2) revealed the signals corresponding to the ethoxy group protons (~1.65 and ~4.65 ppm) along with the characteristic signal of the proton attached to the fullerene cage (~5.2 ppm). The high field part of the ^{13}C NMR spectrum (Figure S4) demonstrated three signals corresponding to the sp^3 carbon atoms: two signals at 16.9 and 65.1 ppm for the



$C_{70}Cl_{10}$ **1** [1,2] **2** [1,2, 41,58]

2′ [1,2,56,57] or **2′** [1,2,67,68] or **2′** [1,2,3,4]

Figure 1 Schlegel diagrams of $C_{70}Cl_{10}$, products **1**, **2** and possible molecular structures of minor component **2′**. Filled circles denote H, opened circles denote $P(O)(OEt)_2$, and filled diamonds denote Cl.

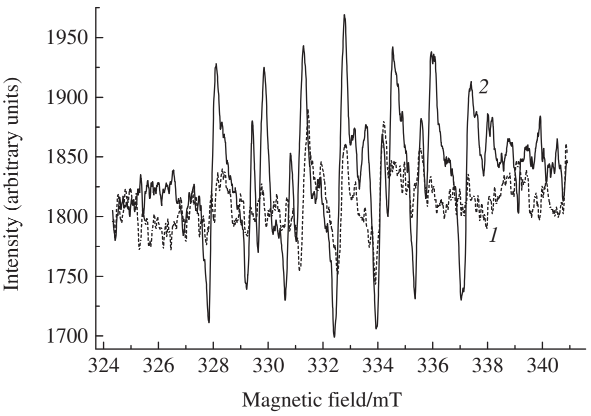


Figure 2 ESR spectra of (*1*) $P(OEt)_3$–DMPO (weak signal due to some impurity is visible) and (*2*) the reaction mixture $P(OEt)_3$ + DMPO + $C_{70}Cl_{10}$ in toluene.

ethoxy unit and one signal at 48.7 ppm for the carbon atom of the fullerene cage bearing hydrogen. This assignment was proved by H–C HMQC spectrum (Figure S8). A signal for the cage carbon atom bearing the phosphonate group was not observed presumably due to strong C–P splitting. The low field ^{13}C NMR spectrum (Figure S5) showed 38 peaks due to the cage *sp*^{2} carbons, which evidenced C_s molecular symmetry of compound **1**. A somewhat larger number of peaks (38 instead of 35 expected) is related to the splitting of some signals on the phosphorus attached to the carbon cage. Two-dimensional H–P HMBC (Figure S6) and H–H ROESY (Figure S7) indicated that the phosphonate group and hydrogen atom are attached to the neighboring positions of the fullerene cage. It is well known that the absorption spectra of C_{70} derivatives are very characteristic, and they can be used to reveal an exact addition pattern for many fullerene derivatives.[13] The absorption spectrum of **1** (Figure S9) unambiguously proved that the addition of phosphonate group and hydrogen occurs across the 1–2 double bond according to the Taylor's numbering scheme as shown in Figure 1.

Thus, we found that compound **1** has the molecular structure of 1,2-addition product, as depicted in Figure 1 and Scheme 1. Note that similar C_{60} derivatives were obtained previously in the nucleophilic addition reaction of parent [60]fullerene with $HP(O)(OEt)_2$.[36]

The ^1H NMR spectrum of **2** (Figure S11) revealed that the sample consists of two components (**2** and **2′**) formed in a 3 : 1 ratio. We will focus on the discussion of the spectral properties of major component **2** since the weaker features corresponding to minor component **2′** could not be confidently detected and resolved in all cases. Thus, the ^1H NMR spectrum showed that both hydrogen atoms and phosphonate groups are symmetrically equivalent in **2**. This conclusion is also supported by the ^{31}P NMR spectrum (Figure S12). The high field ^{13}C NMR spectrum contained signals due to ethoxy group carbons at 16.9 and 65.0 ppm. A sharp signal at 49.3 ppm corresponded to the cage carbon linked with hydrogen. Two broader signals at 56.5 and 57.5 ppm could be attributed to the cage carbon bearing the phosphonate group. Note that minor component **2′** exhibited weak signals at 22.7 (Me) and 48.4 ppm (cage CH). This assignment was proved by the 2D H–C HMQC spectrum (Figure S17). In the low field ^{13}C NMR spectrum 55 signals of different intensities due to the *sp*^{2} carbons of **2** and **2′** were observed. This number can be obtained for a mixture of C_{2v} symmetrical isomer **2** with C_2 (or C_s) symmetrical isomer **2′**. In this case, the expected number of signals should be in a range of 52–53 (19 + 33 or 19 + 34), though C–P splitting and incident overlapping of some signals might alter this number. Both H–P HMBC (Figure S15) and H–H ROESY (Figure S16) spectra confirmed that hydrogen atoms and phosphonate groups are attached in the adjacent positions of a carbon cage in **2** and **2′**. Only one reasonable C_{2v}-symmetrical structure of major component **2** is shown in Figure 1 and Scheme 1, which satisfies all obtained spectral data. Moreover, it is strongly supported by the absorption spectrum (Figure S18), which resembles closely the absorption spectra of C_{2v}-symmetrical C_{70} adducts with a 1,2,41,58-addition pattern reported previously.[37] The molecular structure of minor component **2′** can be ascribed to the C_2-symmetrical 1,2,56,57- or 1,2,67,68-isomers with slightly different arrangements of two pairs of addends at opposite poles of the C_{70} cage (Figure 1). Alternatively, it could be represented by a C_s-symmetrical 1,2,3,4-isomer with all organic addends attached to the same pole of the C_{70} cage. The last option seems the most plausible since the signal of the protons attached to the carbon cage in **2′** is downfield shifted by ~0.15 ppm compared to the signal of the same type of protons in **2**. The observed downfield shift can be related to the presence of two electron-withdrawing phosphonate groups surrounding each proton in 1,2,3,4-**2′** compared to the only one phosphonate group in the major 1,2,41,58-isomer **2**.

Thus, using a combination of ESI mass spectrometry and different NMR-spectroscopic techniques, we deduced the molecular structures of compounds **1** and **2** and proposed possible structures for minor component **2′**. Figure 1 shows that the molecular structures of **1** and **2** have nothing similar with the molecular structure of the parent chlorofullerene $C_{70}Cl_{10}$. In contrast to the Arbuzov-type reaction of $C_{60}Cl_6$, which ends up with the simple replacement of chlorine atoms with five phosphonate groups and hydrogen, a similar reaction of $C_{70}Cl_{10}$ obviously proceeds *via* a more complicated route. First, a number of chlorine atoms are eliminated from the fullerene cage under treatment with $P(OEt)_3$ which is a strong reducing agent. At the same time, the formal chlorine substitution occurring at some reaction stages leads to the addition of phosphonate groups and hydrogen atoms to the poles of the C_{70} cage, while all chlorine atoms were attached to the equator in $C_{70}Cl_{10}$. In view of the fact that the test reaction included multiple chlorine eliminations, substitutions and rearrangements, the formation of just four isolable products (C_{70}, **1**, **2** and **2′**) denotes unusually high selectivity of these processes. Moreover, the formation of only two $C_{70}[P(O)(OEt)_2]_2H_2$ isomers (**2** and **2′**) also evidences extraordinary high selectivity of the reaction.

The exact mechanism of the reaction of $C_{70}Cl_{10}$ with $P(OEt)_3$ is unclear. However, it was possible to figure out what type of the reaction occurs between the chlorofullerene and phosphite using ESR spectroscopy with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a radical trap. The ESR spectrum of a $P(OEt)_3$–DMPO mixture (Figure 2) showed a weak signal of a radical impurity, which was also detected in the solution of DMPO.

However, the addition of $C_{70}Cl_{10}$ to the $P(OEt)_3$–DMPO mixture resulted in the appearance of a strong multi-line signal, that can be attributed to the formation of several different radical species, which are supposed to be reaction intermediates trapped with DMPO.

In conclusion, we studied the reaction of $C_{70}Cl_{10}$ with $P(OEt)_3$ and revealed the formation of $C_{70}[P(O)(OEt)_2]H$ (**1**) and $C_{70}[P(O)(OEt)_2]_2H_2$ (**2** and **2′**) along with unfunctionalized C_{70}. Molecular structures of all isolated products were deduced from the obtained spectroscopic data. Using ESR spectroscopy and DMPO as a radical trap, we revealed the formation of radical species in the $C_{70}Cl_{10}$ + $P(OEt)_3$ reaction mixture. This observation allowed us to assume that the investigated reaction between chlorofullerene $C_{70}Cl_{10}$ and $P(OEt)_3$ proceeds *via* a complicated radical mechanism.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.06.007.

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