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Tetrahedron Letters 47 (2006) 2969–2972

Tetrahedron Letters

Reaction of [60]fullerene with $CF_3COOHal$ affords an unusual 1,3-dioxolano-[60]fullerene

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Received 7 November 2005; revised 30 January 2006; accepted 16 February 2006

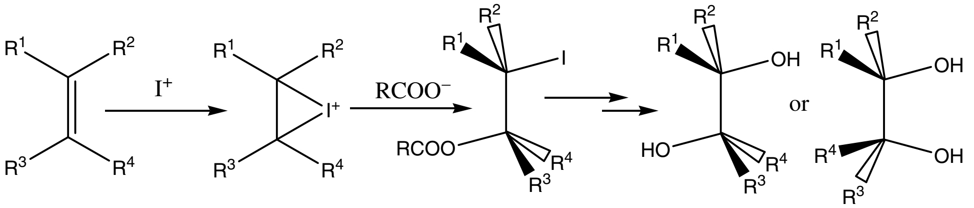
Abstract—Reaction of C_{60} with acyl hypohalogenites CF_3COOBr or CF_3COOI in the presence of water affords an orthoester-type 1,3-dioxolanofullerene in 40–50% yield. This method cannot be applied for the synthesis of 1,3-dioxolanofullerenes bearing aryl- or alkyl-groups since they undergo non-selective halogenation under the reaction conditions.

The chemistry of fullerenes has been investigated thoroughly during the last decade, nevertheless it continues to excite with further novel and unusual reactions and compounds being discovered.[1] The goal of the present work was to investigate the reactivity of [60]fullerene towards acyl hypohalogenites, reagents commonly used in organic chemistry for the hydroxylation of alkenes (the Prévost–Woodward method).[2,3] Initially, alkenes react with I^+ formed from RCOOI to yield the intermediate iodonium ion, which is then attacked from behind by the nucleophilic $RCOO^-$ to form the corresponding β-iodoester (Scheme 1). The latter can be transformed to *erythro* and *threo* diols using different procedures.

Fullerene C_{60} is a very poor nucleophile, which does not react with electrophiles such as I^+. Moreover, even if a hypothetic iodonium ion $C_{60}I^+$ is formed, there is no nucleophile inside the cage to react with this intermediate. Thus one can expect [60]fullerene to be either inert to acyl hypoiodites or to yield some unusual products formed via a mechanism different from those occurring with alkenes.

In this work we show that C_{60} reacts instantly with trifluroracetyl hypoiodite, formed in situ from CF_3COOAg and I_2, to yield orthoester-type 1,3-dioxolanofullerene **1** (Scheme 2).

Silver trifluoroacetate (125 mg, 0.57 mmol) was added to a solution of C_{60} (200 mg, 0.28 mmol) in 40 ml of 1,2-dichlorobenzene (1,2-DCB) and the resulting mixture was stirred for 15 min. Dropwise addition of iodine (150 mg, 0.59 mmol) in 25 ml of 1,2-dichlorobenzene was followed by the introduction of 0.5 ml of water in 10 ml of 1,4-dioxane and then the reaction mixture was stirred for 1 h. The precipitated AgI was removed by filtration and the filtrate was concentrated in



Scheme 1.

Keywords: Fullerenes; C_{60}; Radical addition.

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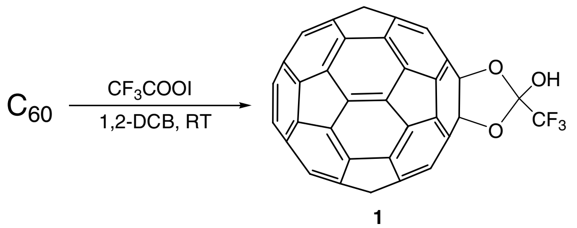
doi:10.1016/j.tetlet.2006.02.106



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Scheme 2.

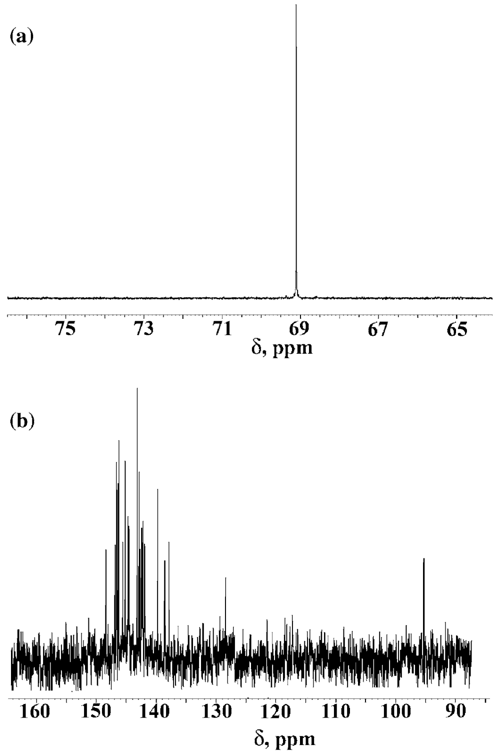


Figure 1. ^{19}F (a) and ^{13}C NMR (b) spectra of **1**.

vacuum. The residue was dissolved in CCl_4 and purified by column chromatography (silica gel 40–60 μm, 60 Å, Acros). Elution with CCl_4–toluene 1:1—pure toluene resulted in a single fraction that was concentrated to give **1** as a brownish solid (yield 40–50%).

The composition of **1** was determined from chemical analysis data and confirmed by mass spectrometry. The positive ion MALDI-TOF mass spectrum exhibited an intense signal for the molecular ion at $m/z = 850$ amu along with fragment ions at $m/z = 752$ ($C_{60}O_2$) and 736 ($C_{60}O$) amu.

The ^{19}F NMR spectrum of **1** showed a signal due to the CF_3 group at $\delta = 69.17$ ppm (Fig. 1).[†] The ^{13}C NMR spectrum exhibited a single line at 95.08 ppm, which corresponds to two equal fullerene cage sp^3 carbons, and 32 lines in the sp^2 region (for the rest of the cage carbons). Signals for the CF_3 group and dioxolane ring bridgehead carbon were not distinct, perhaps due to C–F splitting. Such spectroscopic data are only compatible with the C_s symmetrical structure of **1** as shown in Scheme 2. This structure was also supported by the FTIR spectrum, which demonstrated all the expected vibrations for structure **1** and no bands corresponding to ester carbonyl groups (these should be evident in the hypothetic $C_{60}(OOCCF_3)OH$ compound). The UV–vis (cyclohexane) spectrum of **1** showed a band at 430 nm, which is characteristic for fullerene derivatives formed as a result of 1,2-addition across a 6,6-double bond.

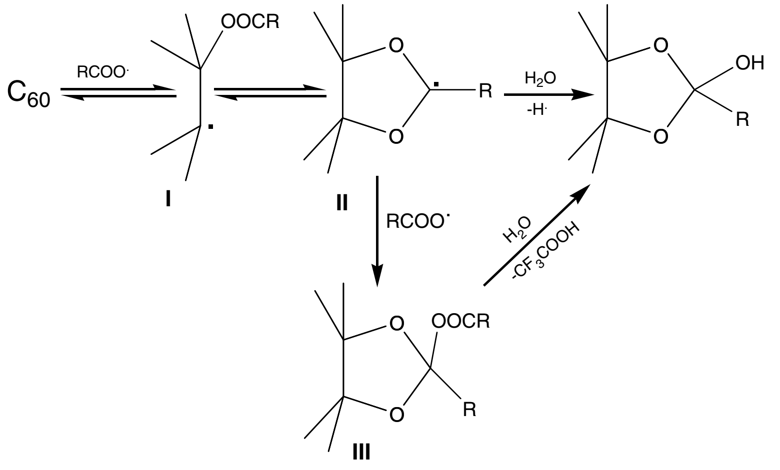
Dioxolanofullerene **1** was previously obtained as one of the products formed in the reaction of C_{60} with the diacylperoxide $CF_3C(O)OO(O)CF_3$.[4] Similar spectroscopic data were reported along with a suggested complex mechanism for formation of the 1,3-dioxolane ring on the fullerene cage.[4] We suggest that both $CF_3C(O)OO(O)CF_3$ and CF_3COOI serve as sources of $CF_3COO^{\bullet}$ radicals. Fullerene quenches these radicals to afford intermediate **I**, which can undergo further rearrangement to give radical **II**. Next, **II** can be converted to **1** directly by reaction with water or via intermediate ester **III** (Scheme 3). Possibly, ester **III** is very sensitive towards hydrolysis, which prevented its isolation. The following observations also support this mechanism:

(i) The reaction does not proceed in toluene or xylenes even if a 40-fold excess of the reagent (CF_3COOAg–I_2) is introduced. The reacting species are quenched by the solvent to yield side-chain halogenation products. The slower rate of chlorination of [60]fullerene in toluene by ICl was previously considered as proof of the radical reaction mechanism.[5]

(ii) The radical mechanism is also supported by isolation of fullerenol $C_{60}(OH)CF_3$ (**2**), which was formed as a by-product in ca. 2–3% yield. The composition of **2** was evident from its MALDI TOF mass spectrum, which exhibited intense signals at $m/z = 805$ (**2**-H), 737 (**2**-CF_3), 736 (**2**-CF_3–H), 720 (C_{60}) and a low intensity peak at 789 (**2**-OH) amu. The ^{19}F NMR spectrum of **2** consisted of a single line at $\delta = 78.80$ ppm. The poor solubility of **2** in organic solvents did not allow us to obtain its ^{13}C NMR spectrum and conclude on the arrangement of the CF_3 and OH groups on the fullerene cage. The $CF_3C_{60}OH$ compound was previously isolated in the reaction of C_{60} with $CF_3C(O)OO(O)CF_3$; a 1,4-addition pathway was proposed in this case.[4] However, the unsymmetrical structure 5,6-$C_{60}OH(CF_3)$ also fits all the reported spectroscopic data and the recently reported radical trifluoromethylation of C_{60} and C_{70} across the 6–5 bonds[6] supports this possible pathway.

(iii) It was observed that addition of water to the reaction mixture resulted in improved yields of **1** (40–50%), which agrees with the suggested mechanism.

[†] ^{19}F NMR (376.3 MHz, $CDCl_3$, CF_3COOH external standard; $\delta = 0$ – $CFCl_3$), $\delta = 69.17$ ppm; ^{13}C NMR (100 MHz, CS_2–C_6D_{12} 10:1), $\delta = 148.23$, 147.85, 146.40, 146.35, 146.32, 145.40, 145.02, 144.97, 144.50, 144.47, 144.37, 144.28, 142.95, 142.66, 142.58, 142.23, 142.17, 142.06, 141.98, 141.75, 141.68, 139.56, 138.38, 137.68, 128.18, 95.08 ppm; FTIR (KBr disc): $v = 527$, 553, 561, 578, 591, 737, 783, 870, 889, 936, 959, 992, 1055, 1069, 1083, 1113, 1142, 1149, 1165, 1188, 1252, 1286, 1383, 1437, 3440 (b) cm^{-1}.



Scheme 3.

(iv) Conducting the reaction with vigorous exclusion of moisture (dried C_{60}, CF_3COOAg and solvents) yielded a complex mixture of products that could not be separated by column chromatography.

(v) The MALDI TOF mass spectrum of the crude reaction product (obtained in the presence of small amounts of water in the solvents) exhibited peaks corresponding to molecular ion $\mathbf{1}^+$, bis-adducts $C_{60}(O_2CCF_3(OH))_2$ $\mathbf{3}^+$ ($m/z = 980$ amu) along with intense signals at 1682 and 1812 amu (Fig. 2). We believe that these peaks correspond to the fullerene dimer **4** (1682 amu) (Scheme 4) and cross-dimers **5** presumably formed from radical **II** (Scheme 3) and bis-adducts **3** ($[C_{60}(O_2CCF_3(OH))(O_2CCF_3)]O[C_{60}(O_2CCF_3)]$, 1812 amu).

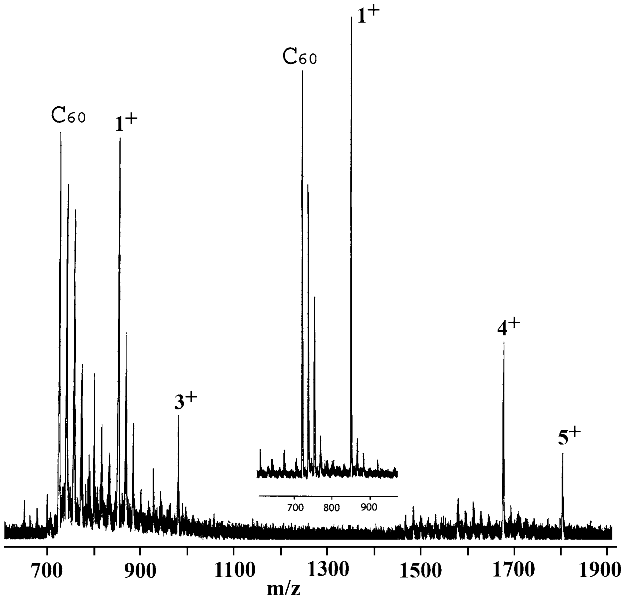
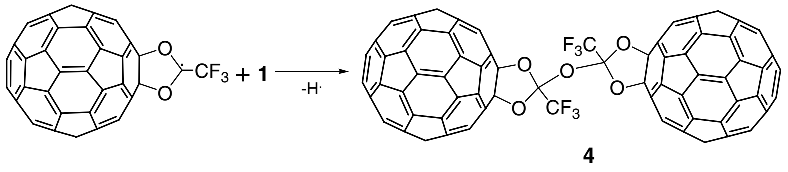


Figure 2. MALDI TOF mass spectrum of the crude product mixture (inset shows the MALDI TOF mass spectrum of **1**).

The treatment of C_{60} with CF_3COOBr (formed in situ from CF_3COOAg and Br_2) in the presence of water gave **1** in 30–40% yield; the same results were achieved using 1:2 molar combinations of $Hg(CF_3COO)_2$ and I_2 or Br_2 as reagents. Corresponding systems based on lead(II) and copper(II) trifluoroacetates give unsatisfactory yields of products (0–5%). Reactions of C_{60} with $CH_3COOHal$ and PhCOOHal (formed in situ from silver salts) yielded complex mixtures of products represented by the expected 1,3-dioxolanes and various halogenated derivatives (formed via substitution of hydrogen atoms in the methyl and phenyl groups as revealed from MALDI TOF mass spectra). Our attempts to separate these mixtures by column chromatography were unsuccessful.

These results demonstrate that the synthetic potential of the reaction of [60]fullerene with acyl hypohalogenites seems to be limited to a specific range of substrates that are stable towards radical halogenation. In particular, it provides a facile synthetic route to substituted 1,3-dioxolanofullerene **1**; the possibility of further modification of the –OH group allows for its utilization as a building block in fullerene chemistry.



Scheme 4.

Acknowledgements

This work was supported by RFBR (Grant No. 04-03-32870a), INTAS (Grant No. 04-83-3733) and Russian Science Support Foundation. P.A.T. gratefully acknowledges Mr. A. Sukhorukov for participation in this work at the initial stage and Professor V. A. Smith and A. I. Zinin (N. D. Zelinskii Institute of Organic Chemistry) for helpful discussions concerning the Prévost–Woodward hydroxylation of alkenes.

Supplementary data

Supplementary data (IR and ^{13}C NMR (50 MHz) spectra of **1**, and the ^{19}F NMR spectrum and MALDI TOF mass spectrum of **2**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.106.

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