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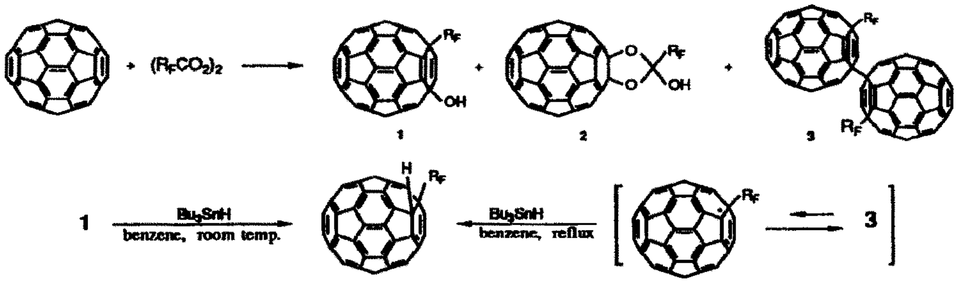
Reactions of Fullerols and Fullerene Dimer Containing Perfluoroalkyl Groups with Tributyltin Hydride

Masato Yoshida,* Ayako Morishima, Yoshihiro Morinaga, and Masahiko Iyoda*

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Hachioji, Tokyo 192-03, Japan

Abstract: Unusual reduction of $C_{60}(R_F)(OH)$ to $C_{60}(R_F)(H)$ with Bu_3SnH proceeded efficiently at room temperature. $C_{60}(R_F)(H)$ was also obtained from fullerene dimer (R_FC_{60}-$C_{60}R_F$) with Bu_3SnH in benzene under reflux.

The functionalization of C_{60} with various organic functional groups is one of the important subject in fullerene chemistry. We have investigated the reaction of C_{60} with diacyl peroxide containing fluoroalkyl groups to give three types of products **1**, **2**, and **3**.[1] In the course of the study, we found that both **1** and **3** gave same product **4** by treating with Bu_3SnH. We would like to report the results in this communication.



a: $R_F = C_3F_7$ b: $R_F = CF_3$ c: $R_F = CF_2Cl$

Scheme 1

Though the reduction of RCF_2Cl to RCF_2H with Bu_3SnH in the presence of AIBN in benzene reflux is well known,[2] the reaction of **1c** with Bu_3SnH, interestingly, did not give $C_{60}(CF_2H)(OH)$ but **4c** $(CF_2Cl)(H)$ in 71% yield. This prompted us to investigate the reaction of **1** with Bu_3SnH under various conditions; the reduction proceeded even at room temperature without AIBN. When **1a** was allowed to react with Bu_3SnH (1.5 equiv. to **1a**) in benzene at room temperature for 15 h, **4a** was obtained as a sole product (isolated yield: 41%).[3,4] Compound **4a** had a singlet at δ_H 7.12 in ^1H-NMR, and the C-H carbon was observed at δ_C 54.92 (doublet by off-resonance decoupling). ^{13}C-NMR spectrum of **4a** showed 32 signals for C_{60} skelton and that of **1a** showed 47 peaks; this suggests that **4a** has one symmetry plane including H and C_3F_7 on the C_{60} skelton

(1, 2-adduct at 6, 6-junction depicted in Scheme 1), though **1a** has unsymmetrical structure (all 60 carbons in C_{60} skelton in **1a** are theoretically unequivalent, but 47 signals were observed for the overlapping of the signals). In ^{19}F-NMR, two fluorine of the CF_2 group attached to C_{60} moiety are unequivalent in **1a** (δ_F = -35.54 and -32.98) but equivalent in **4a** (δ_F = -32.73) reflecting the unsymmetrical structure of **1a** and C_s symmetry in **4a**, respectively. The results presented here show the unusual reactivity of fullerols. Though the reduction of hydroxy group to hydrogen with organotin hydrides is known under strong acidic conditions,[5] the reduction of **1** to **4** proceeds smoothly under very mild reaction conditions. The occurence of the reduction at room temperature without acid suggests the possibility that Bu_3SnH itself could act as the electron-transfer reagent in the initiation step as was proposed by Tanner et al,[6] due to the strong electron affinity of fullerols. Tris(trimethylsilyl)silane reduces many halides to hydrocarbons under radical conditions. However, the reaction of **1a** with $(Me_3Si)_3SiH$ did not occur, and only the starting material was recovered. Interestingly, a similar reduction of **1a** to **4a** was performed with SmI_2 - 2-PrOH which is well known to be one-electron reduction system.

In our previous paper,[1] **3** was reported as unidentified C_{60} derivatives. Now, we assigned **3** as the C_{60} dimer containing fluoroalkyl group;[7] one plausible regioisomer for **3** is depicted in Scheme 1. The product **3** was a mixture of the isomers, and it was difficult to separate each other completely. We obtained some spectral data for the isomers of **3a**,[8] and the data are consistent with the dimer structure for **3**. The fullerene dimer is known to exist in equilibrium with C_{60} radicals[7] which abstract the hydrogen of Bu_3SnH.[9] Thus, we investigated the reaction of **3a** with Bu_3SnH in benzene under reflux and obtained **4a** in 73% yield. In this reaction, even when the starting **3a** was a mixture of the isomers, the single regioisomer of $C_{60}(C_3F_7)(H)$ was produced. The formation of **4a** in this reaction supports the dimer structure of **3**.

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References and Notes

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4. Data of **4a**: ^{13}C-NMR (CS_2 : Acetone-d_6 = 7:1, $Cr(acac)_3$ was added as a reluxation reagent): δ 54.92, 68.16 (t, J_{CCF}=22.8Hz), 135.65, 138.04, 139.83, 141.03, 141.17, 141.87, 142.03, 142.44, 142.44, 142.49, 142.98, 143.08, 143.46, 144.48, 144.98, 145.01, 145.62, 145.67, 145.85, 145.93, 146.40, 146.50, 146.59, 146.68, 146.88, 146.93, 146.93, 147.52, 147.90, 151.43; ^{1}H-NMR (CS_2 : Acetone-d_6 = 7:1) δ 7.12; ^{19}F-NMR (CS_2 : Acetone-d_6 = 7:1, from ex. CF_3COOH) δ -44.83 (2F), -32.73 (2F), -6.22 (3F); FAB-MS (Pos., *m*-nitrobenzyl alcohol) m/z 891(M+1), 720.
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8. Selected spectral data for one of the isomer of **3a**: ^{13}C-NMR(CS_2 : Benzene-d_6 = 5 : 1, $Cr(acac)_3$ was added): δ 59.32 (t, J_{CCF}=28.4Hz), 60.04 (sp^3 carbon in C_{60} skelton attached to another C_{60}); ^{19}F-NMR(CS_2 : Benzene-d_6 5 : 1, from ex. CF_3COOH) δ -45.89 (2F), -33.80 and -31.57 (ABq, J=274 Hz), -4.73 (3F); FAB-MS (Pos., *m*-nitrobenzyl alchohol) m/z 890($C_{63}F_7$ +1), 720.
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