Convenient Synthesis of 1-Fluoroalkyl-2-hydro[60]fullerene Using Fluoroalkyl Halide with Tributyltin Hydride under Radical Conditions

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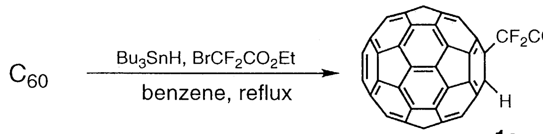
A convenient method for the preparation of fluoroalkyl-modified C_{60} using fluoroalkyl halides with Bu_3SnH under radical conditions has been developed; 1-fluoroalkyl-2-hydro-[60]fullerenes at 6,6-junction ($C_{60}(R_F)H$: $R_F = CF_2CO_2Et$, n-C_6F_{13}, CF_2Br, n-$C_{12}F_{25}$, and $(CF_2)_6I$) were synthesized effectively.

Recently, the chemical modifications of [60]fullerene (C_{60}) with organic functional groups have attracted much attention because of the interesting properties and the potential utility of these molecules.[1] The introduction of fluoroalkyl groups into organic molecules is known to bring about dramatic enhancement or improvement of the properties of the parent molecules.[2] Thus, we have been interested in the modifications of C_{60} with fluoroalkyl groups. Although the addition of an alkyl group to C_{60} using lithium or Grignard reagents has been reported,[3,4] the applicability of these methods to fluoroalkyl analogues is very limited due to the thermal instability of the corresponding lithium and Grignard reagents, which undergo α- or β-elimination of the fluoride ion. On the other hand, fluoroalkyl radical species are thermally stable, generated relatively easy, and used for the synthesis of various organofluorine compounds.[5] Accordingly, it is very useful to investigate the fluoroalkylation of C_{60} with a fluoroalkyl radical. In our previous paper, we reported the formation of fluoroalkylated C_{60} by the reaction with the diacyl peroxide containing fluoroalkyl groups ($(R_FCO_2)_2$);[6] the reaction was initiated by single-electron transfer from C_{60} to the peroxide to give fluoroalkyl radical. Although the reaction proceeded well under mild conditions, the method is only applicable to the introduction of the limited fluoroalkyl groups, because only a few types of diacyl peroxides are available in literatures: (n-$C_nF_{2n+1}CO_2)_2$ (n = 1-7), $(CF_2ClCO_2)_2$ and so on.[7] Herein, we now wish to report a novel synthesis of C_{60} derivatives possessing various types of fluoroalkyl groups such as CF_2CO_2Et, n-C_6F_{13}, CF_2Br, n-$C_{12}F_{25}$, and $(CF_2)_6I$ using the corresponding fluoroalkyl halides with Bu_3SnH under radical conditions. The method is expected to be versatile and practical, because various types of fluoroalkyl halides are commercially available and easy to handle.

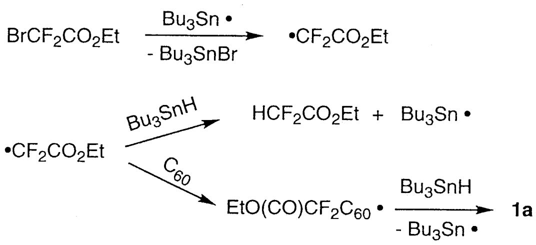
A benzene solution of $BrCF_2CO_2Et$ (495 mg, 2.4 mmol), C_{60} (144 mg, 0.20 mmol), and Bu_3SnH (292 mg, 1.0 mmol) was refluxed under nitrogen for 30 h. The products were separated by gel-permeation chromatography (JAI model LC-908 liquid chromatograph equipped with JAIGEL-1H-40 and 2H-40 columns) using toluene as eluent. As a product, 30 mg of **1a** (eq. 1) was obtained, and 75 mg of C_{60} was recovered: the yield of **1a** based on consumed C_{60} is 37%. The structure of the product **1a** was determined by ^{13}C-NMR, ^{1}H-NMR, ^{19}F-NMR, and FAB-MS.[8] The ^{1}H-NMR spectrum of **1a** shows a singlet at δ_H 6.96, which is characteristic of the hydrogen directly attached to the C_{60} skeleton.[9] Two sp^3 carbons assignable to the C-H and the C-R_F carbon of the C_{60} skeleton are observed at δ_C 55.01 and 69.01 (triplet for C-F coupling), respectively. Further, the ^{13}C-NMR spectrum shows 29 sp^2 carbon signals for the C_{60} skeleton (including a pair of coincident peaks); this indicates the *Cs* symmetry in **1a**. The symmetry is also supported by the ^{19}F-NMR spectrum, in which signal for CF_2 was observed as a singlet at δ_F -30.1. Thus, we propose the 1,2-adduct of fluoroalkyl and hydrogen at 6,6-junction shown in eq. 1.



(1)

1a

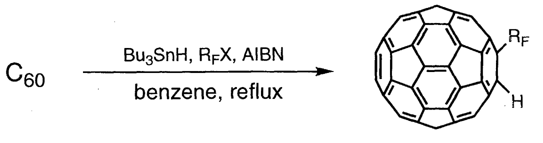
A radical chain reaction should be involved for the formation of **1a** (Scheme 1). There are mainly two reaction paths for the CF_2CO_2Et radical: hydrogen abstraction from Bu_3SnH to give HCF_2CO_2Et and radical addition to C_{60}. The desired reaction proceeds with the attack of the CF_2CO_2Et radical to C_{60} to give fullerene radical.[10] Since C_{60} is known to be a very good radical-trapping reagent,[11] the attack of the CF_2CO_2Et radical to C_{60} occurs effectively. The hydrogen abstraction from Bu_3SnH by the R_FC_{60} radical generates **1a** and new Bu_3Sn radical, which enters a new cycle. The addition of the R_F radical to C_{60} has been well investigated mainly by means of ESR spectroscopy.[12] However, little is known about its application to synthetic chemistry.[6,13,14] In this work, the effective production of **1a** was achieved by the addition of Bu_3SnH to the reaction system as a hydrogen source.



Scheme 1.

On the other hand, no C_{60} derivatives containing n-C_6F_{13} were obtained on the reaction with n-$C_6F_{13}I$ in the presence of Bu_3SnH under similar conditions. The addition of a catalytic amount of AIBN (0.1 eq. to C_{60}) realized the formation of the adduct **1b**.[15,16] Probably, the radical chain reaction was not initiated effectively without AIBN. Similarly, on the reaction with CF_2Br_2, n-$C_{12}F_{25}I$, and $I(CF_2)_6I$, **1c** - **1e** were obtained. Typical examples for the reaction are summarized in Table 1. The spectral data for **1c** - **1e** are consistent with the proposed structure.

Table 1. Introduction of various fluoroalkyl groups into C_{60}



b: n-C_6F_{13} **c**: CF_2Br **d**: n-$C_{12}F_{25}$ **e**: $(CF_2)_6I$

R_FX/ eq[a]	Bu_3SnH / eq[a]	Yield / %[b]	(recovered C_{60} / %)
n-$C_6F_{13}I$ (12)	5	31	(64)
CF_2Br_2 (20)	14	26	(57)
n-$C_{12}F_{25}I$ (12)	14	26	(67)
$I(CF_2)_6I$ (6)	15	41[c]	(61)

[a] Based on C_{60}.
[b] Isolated yields based on consumed C_{60}.
[c] A small amount of $C_{60}[(CF_2)_6H](H)$ was included.

The fluoroalkyl groups such as CF_2Br, $(CF_2)_6I$, and CF_2CO_2Et to be introduced by this method are expected to be used for further elaboration. In addition, the hydrogen attached to the C_{60} carbon is known to be very acidic, and consequently the hydrogen of **1** might be convertible to other functional groups under weak basic conditions via the R_FC_{60} anion.[17] Thus, **1** has high potential as a precursor for the synthesis of various types of fluoroalkyl-modified C_{60}.

References and Notes

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8 Selected spectral data for **1a**: ^{1}H-NMR (400 MHz, C_6D_6:CS_2=1:1) δ = 6.96(1H, s), 4.21(2H, q, J=7.1Hz), 1.11(3H, t, J=7.1Hz); ^{13}C-NMR (100 MHz, C_6D_6:CS_2=1:1) δ = 151.67(2C), 147.57(1C), 147.26(1C), 147.18(2C), 146.73(2C), 146.62(4C), 146.42(2C), 146.31(2C), 146.22(2C), 146.07(2C), 145.70(2C), 145.56(2C), 145.43(2C), 145.36(2C), 144.73(2C), 144.33(2C), 143.20(2C), 142.78(2C), 142.69(2C), 142.27(2C), 142.21(2C), 142.16(2C), 141.78(2C), 141.64(2C), 141.09(2C), 140.66(2C), 139.69(2C), 137.84(2C), 135.83(2C), 116.06(CF_2, t, J=261Hz), 69.01(1C, t), 63.77(CH_2), 55.01(1C), 14.17(CH_3); ^{19}F-NMR (376 MHz, ppm from ex. CF_3CO_2H, C_6D_6:CS_2=1:1) δ = -30.1; FAB-MS (*m*-nitrobenzyl alcohol) m/z = 844 (M^+), 720.

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15 Selected spectral data for **1b**: ^{1}H-NMR (400 MHz, C_6D_6:CS_2=1:1) δ = 6.61(1H, s); ^{13}C-NMR (100 MHz, C_6D_6:CS_2=1:1) δ = 151.00(2C), 147.84(1C), 147.48(1C), 146.84(4C), 146.71(2C), 146.64(2C), 146.51(2C), 146.43(2C), 146.29(2C), 145.81(4C), 145.56(4C), 144.94(4C), 144.40(2C), 143.38(2C), 143.03(2C), 142.89(2C), 142.39(6C), 141.94(2C), 141.83(2C), 141.11(2C), 140.82(2C), 139.83(2C), 137.95(2C), 135.57(2C), 68.72(1C, t), 54.85(1C); ^{19}F-NMR (376 MHz, ppm from ex. CF_3CO_2H, C_6D_6:CS_2=1:1) δ = -5.7, -32.5, -41.0, -46.2, -47.2, -50.7; FAB-MS (*m*-nitrobenzyl alcohol) m/z = 1040 (M^+), 720.

16 A small amount of $C_{60}(CMe_2CN)(H)$ was also produced by the reaction of C_{60} with CMe_2CN radical generated from AIBN.

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