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C_{60}^{2-} Chemistry: C_{60} Adducts Bearing Two Ester, Carbonyl, or Alcohol Groups

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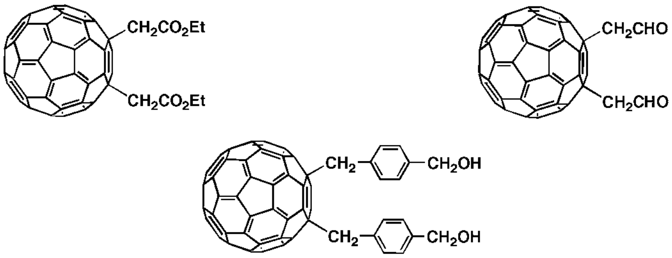
ABSTRACT



Reactions of activated halo compounds XCH_2-A (X = Br, I; A = ester, ketone) with C_{60}^{2-} anion give rise to $C_{60}(CH_2\text{-}A)_2$ adducts (major products) along with unexpected methanofullerenes C_{60}>CH-A and monosubstituted dihydrofullerenes $C_{60}(H)(CH_2\text{-}A)$ (minor products). Methanofullerenes are shown to come from side reactions with X_2CH-A traces.

Due to their outstanding physical and chemical properties, C_{60} fullerene derivatives have proven to be attractive compounds in various fields such as photovoltaïcs,[1] nonlinear optics,[2] artificial photosynthesis,[3] organic materials,[4] and biology and medicine.[5] Thus, a large development of the covalent functionalization of C_{60} was observed in recent years. The chemical reactivity of C_{60} is typical of an electron-deficient olefin,[6] and most organo-derivatives of C_{60} are obtained through two main methods: [4 + 2] Diels Alder[7] and [3 + 2][8] cycloaddition methodology and nucleophilic additions as exemplified by the Bingel cyclopropanation reaction.[9]

Alternatively, the functionalization of the C sphere can also be achieved by the reaction of C_{60}^{2-} anion with electrophilic reagents. Recently, we have shown that this anion can be easily and selectively obtained via a chemical reduction of C_{60} using an excess of sodium methanethiolate in acetonitrile.[10] Then, after addition of monoiodoalkane R−I (R = Me, Et, *n*-Bu) or diiodoalkane $I-(CH_2)_n-I$ ($n = 3, 4$) into this medium, we obtain the corresponding adducts $C_{60}R_2$ or fused cycloadducts $C_{60}(CH_2)_n$ in good yields. The formation of 1,2- and 1,4-dialkyl adducts $C_{60}R_2$ is highly regioselective, the relative molar ratio 1,2/1,4 being ca. 9/1 when R = Me and ca. 1/9 with other alkyl groups. We have also extended our process to reactions with halo-derivatives bearing a second functional group (halo, ester, ketone).[11] These reactions give rise to new organo C_{60} derivatives such as the fused cyclopentanone $C_{60}(CH_2)_2CO$, which can be used

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as a starting building block in the synthesis of new donor−acceptor covalent assemblies.

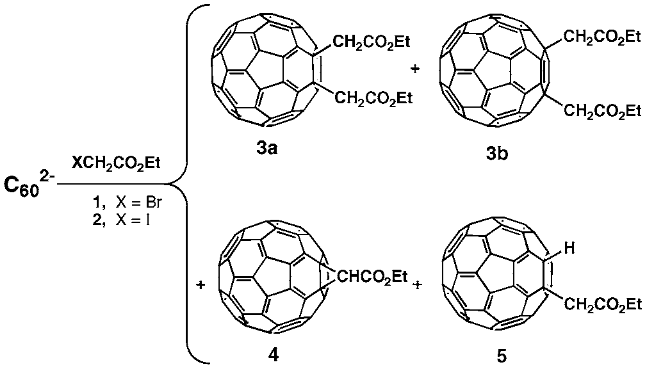
We now wish to report on the results of the reactions between C_{60}^{2-} anion and 2-haloacetates $XCH_2{-}CO_2Et$ **1** (X = Br) and **2** (X = I), α-bromoacetophenone $C_6H_5{-}CO{-}CH_2Br$ **6**, and the benzyl derivative *p*-$BrCH_2{-}C_6H_4{-}CH_2OH$ **13**. All the reactions were carried out in a glovebox.[12]

Reactions of ethyl bromoacetate $BrCH_2CO_2Et$ **1** or iodoacetate ICH_2CO_2Et **2** with C_{60}^{2-} have given rise to results that are slightly different from those observed from previous reactions of simple haloalkanes (Table 1, Scheme 1). As might be expected, the corresponding adducts $C_{60}(CH_2CO_2Et)_2$ have been obtained as a mixture of 1,2- and 1,4-regioisomers, respectively **3a** and **3b**, the latter still being the major product; however, other minor products, methanofullerene $C_{60}{>}CH{-}CO_2Et$ **4** and monosubstituted 1,2-dihydrofullerene $C_{60}(H)(CH_2CO_2Et)$ **5**, were also formed along with undefined polyadducts.

Table 1. Relative Formation Yields (%) of Compounds **3a**, **3b**, **4**, and **5** Starting from Esters **1** and **2**

starting ester	**3a**	**3b**	**4**	**5**
1 (X = Br)	1−2	10	2	1−2
2 (X = I)	1	16	4	traces

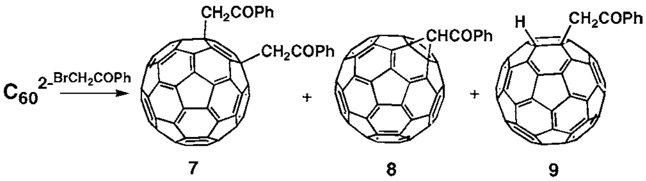
Scheme 1



The two regioisomers **3a** and **3b** are easily separated by column chromatography, such a separation being previously impossible in the case of dialkylated derivatives $C_{60}R_2$.[10,11] They have been unambiguously identified from ^1H NMR spectra, using the signals issued from the CH_2 groups bonded to the C_{60} core. In the 1,4-adduct **3b**, these two hydrogens are diastereotopic, thus providing an AB system, while a singlet is characteristic of both CH_2 groups in the 1,2-adduct **3a**. Compound **3b** has already been isolated and characterized by Komatsu et al. as a very minor product (ca. 1.8% yield) from a reaction involving C_{60}, Zn, and $BrCH_2CO_2Et$.[13]

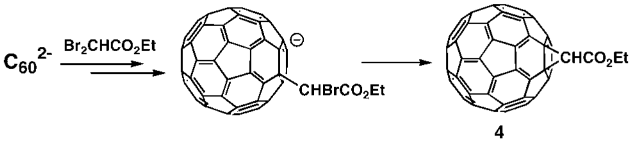
Similar results have been observed from reaction between C_{60}^{2-} and α-bromoacetophenone **6**, with the following compounds being isolated: the 1,4-adduct $C_{60}(CH_2COPh)_2$ **7** (ca. 25% yield) and a mixture of methanofullerene $C_{60}{>}CH{-}COPh$ **8** (ca. 5% yield) and monosubstituted dihydrofullerene $C_{60}H(CH_2COPh)$ **9** (ca. 10% yield). No 1,2-adduct could be detected (Scheme 2).

Scheme 2



The formation of methanofullerenes **4** and **8** appeared to be surprising, since such compounds are essentially reported to be obtained via the Bingel reaction. However, a careful analysis (GC-MS and ^1H NMR) of the commercially available ester $BrCH_2CO_2Et$ **1** revealed the presence of a very small amount of Br_2CHCO_2Et. Due to the large excess of ester **1** used in our process, methanofullerene **4** is likely to be formed from reaction of Br_2CHCO_2Et with C_{60}^{2-}. A similar reaction issued from various gemdihalo compounds has been described by Echegoyen et al.,[14] and we have effectively observed in a control experiment that reaction of pure Br_2CHCO_2Et with C_{60}^{2-} leads to compound **4** (Scheme 3). A similar explanation could hold for the formation of methanofullerenes from ester **2** and ketone **6**.

Scheme 3



The formation of dihydrofullerene **5** and **9** seems to be more difficult to explain. If we consider the mechanism proposed by Kadish et al.,[15] $[C_{60}(CH_2A)]^-$ (A = CO_2Et,

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[12] **General Experimental Conditions.** In a glovebox, an excess (10 equiv) of sodium methanethiolate was added to a carefully deoxygenated suspension of C_{60} (150 mg, 0.21 mmol) in dry acetonitrile (100 mL). The mixture was stirred at room temperature for 24 h. A deep red color developed progressively in the medium due to the formation of C_{60}^{2-} anion, which was usually achieved in 24 h. The reaction mixture was filtered off to eliminate unreacted C_{60} and excess sodium methanethiolate. Then, an excess (ca. 20 equiv) of halogenated derivative, either neat liquid or dissolved in dry acetonitrile when solid, was added to the resultant solution, which was stirred at room temperature overnight. After reaction, the obtained solid products were filtered off, washed with acetonitrile, isolated through column chromatography, and identified from MS and NMR analyses.

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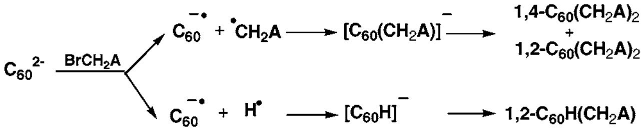
COPh) anion is formed in the first step. This ion could then lead to dihydrofullerenes **5**−**9** if a strong acid is added to the reaction medium as we have recently shown.[16] But, of course, such an acid cannot be available in this medium, and dihydrofullerenes thus cannot be formed.

Another possibility might be considered if $C_{60}H^-$ anion is first formed; in this case, a further reaction with XCH_2A (X = Br, I) should provide dihydrofullerenes. However, this ion is unlikely to come from an acid−base reaction between C_{60}^{2-} and XCH_2A since the basic character of C_{60}^{2-} has been estimated to be weaker than that of benzoate anion.[17] We put forward a new hypothesis. In the first stage the single-electron transfer between C_{60}^{2-} and $BrCH_2A$ could occur according two competitive pathways (Scheme 4), a major one leading as expected to $^{\bullet}CH_2A$ and $C_{60}^{-\bullet}$,[14] and a minor one leading to $H^{\bullet}$ and $C_{60}^{-\bullet}$ due to the strong polarity of the C−H bonds in XCH_2A (stronger than that in simple haloalkanes $R-CH_2X$ for instance).[18] Then, of course, the overall process will continue through coupling of the radical moieties, followed by the reaction with a second molecule of XCH_2A (Scheme 4).

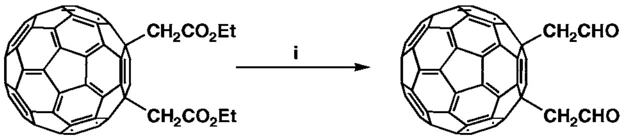
Scheme 4



Most of these new C_{60} derivative compounds possess great synthetic potential due to the presence of ketone and ester groups. Thus, the diester **3b** was easily reduced into the corresponding dialdehyde **10** (ca. 50% yield) upon reaction with DIBAL-H in toluene at low temperatures (−80 °C). This compound was isolated and characterized by NMR and mass spectrometry analyses. Unfortunately, further reactions of DIBAL-H, at different temperatures, versus dialdehyde **10** did not allow the isolation of the corresponding diol $C_{60}(CH_2CH_2OH)_2$, which could not be obtained from reduction of diester **3b** either.

Nevertheless, to obtain organo derivatives of C_{60} bearing two alcohol groups, we studied the reaction between C_{60}^{2-} and *p*-$BrCH_2-C_6H_4-CH_2OH$ **11**, this alcohol being easily obtained from reduction of the commercially available methyl ester *p*-$BrCH_2-C_6H_4-CO_2Me$. As expected, the reaction leads to the corresponding 1,4-adduct C_{60}(*p*-$CH_2-C_6H_4-CH_2OH)_2$ **12** (ca. 15% yield) (Scheme 6).

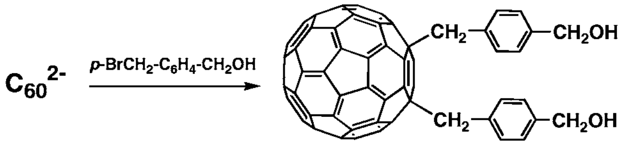
Scheme 5[a]



3b **10**

[a] Conditions: (i) excess DIBAL-H (20 equiv), toluene, 2 h, −80 °C, then acidic (aqueous 1 M HCl/MeOH) hydrolysis.

Scheme 6



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In conclusion, new functional organo derivatives of C_{60} were synthesized and characterized.[19] C_{60}^{2-} anion chemistry is thus emphasized, since the obtained compounds appear

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(18) This hypothesis may be related to the redox reactions of sodium or potassium with alcohols, the initial step being considered as a single-electron transfer from the alkali metal to the hydrogen atom of an OH group. This reaction appears to be strongly dependent on the polarity of the O−H bond, since the generation of hydrogen is very easy and even violent from primary alcohols but very sluggish from tertiary alcohols.

(19) **Selected Spectroscopic Data. Compound 3a:** ^1H NMR (500 MHz, $CDCl_3$) δ 4.68 (s, 4H), 4.47 (q, 4H, $J = 7.1$ Hz), 1.45 (t, 6H, $J = 7.1$ Hz); ^{13}C NMR (125.75 MHz, $CDCl_3$) δ 172.3, 156.2, 147.9, 146.6, 146.3, 146.0, 145.5, 145.4, 144.8, 143.3, 142.6, 142.2, 141.8, 141.4, 139.8, 136.2, 62.7, 61.8, 46.2, 14.3; ES-MS calcd for $C_{68}H_{14}O_4$ 894.089, found $M^{-\bullet}$ 894.086. UV−vis (hexane), λ_{max} [nm] 431, 307−308, 254, 214. **Compound 4:** ^1H NMR (500 MHz, CS_2/C_6D_6) δ 4.57 (s, 1H), 4.35 (q, 2H, $J = 7.1$ Hz), 1.40 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (125.75 MHz, CS_2/C_6D_6) δ 164.8, 148.5, 145.9, 145.7, 145.4, 145.4, 145.3, 145.3, 145.0, 144.9, 144.9, 144.8, 144.6, 144.2, 143.9, 143.6, 143.3, 143.3, 143.2, 143.0, 142.7, 142.5, 142.3, 142.2, 141.4, 141.2, 141.0, 136.6, 71.0, 62.3, 39.6, 15.0; MALDI-TOF MS calcd for $C_{64}H_6O_2$ 806.0, found $M^{+\bullet}$ 806.0; UV−vis (hexane), λ_{max} [nm] 425, 256, 214. **Compound 7:** ^1H NMR (500 MHz, $CS_2/CDCl_3$) δ 8.19 (d, 4H), 7.65 (t, 2H), 7.53 (t, 4H), 4.75 (d, 2H, $J = 15.8$ Hz), 4.72 (d, 2H, $J = 15.8$ Hz); ^{13}C NMR (125.75 MHz, $CS_2/CDCl_3$) δ 194.9, 155.9, 150.9, 148.3, 147.8, 146.9, 146.7, 146.7, 146.6, 145.2, 145.2, 144.9, 144.9, 144.5, 144.4, 144.2, 144.0, 144.0, 143.7, 143.6, 143.4, 142.9, 142.9, 142.8, 142.4, 142.0, 141.8, 141.6, 140.5, 138.6, 138.5, 136.6, 133.2, 128.6, 128.4, 55.1, 49.3; MALDI-TOF MS calcd for $C_{76}H_{14}O_2$ 958.1, found $M^{-\bullet}$ 958.1; UV−vis (*o*-dichlorobenzene) λ_{max} [nm] 443 (broad). **Compound 8:** ^1H NMR (500 MHz, $CS_2/CDCl_3$) δ 8.44 (dd, 2H, $J = 7.2$ Hz, $J' = 1.5$ Hz), 7.76−7.73 (m, 1H), 7.70−7.65 (m, 2H), 5.61 (s, 1H); MALDI-TOF MS calcd for $C_{68}H_6O$ 838.0, found $M^{-\bullet}$ 838.0. **Compound 9:** ^1H NMR (500 MHz, $CS_2/CDCl_3$) δ 8.36 (dd, 2H, $J = 7.2$ Hz, $J' = 1.5$ Hz), 7.76−7.73 (m, 1H), 7.70−7.65 (m, 2H), 6.72 (s, 1H), 5.20 (s, 2H); MALDI-TOF MS calcd for $C_{68}H_8O$ 840.0, found $M^{-\bullet}$ 840.0. **Compound 10:** ^1H NMR (500 MHz, CS_2/C_6D_6) δ 10.27 (t, 2H, $J = 1.8$ Hz), 3.98 (dt, 2H, $J = 1.8$ Hz, $J' = 16$ Hz), 3.93 (dt, 2H, $J = 1.8$ Hz, $J' = 16$ Hz); ^{13}C NMR (125.75 MHz, CS_2/C_6D_6) δ 195.8, 155.4, 150.4, 148.9, 148.2, 147.6, 147.2, 146.9, 145.8, 145.6, 145.0, 145.0, 144.8, 144.6, 144.6, 144.5, 144.4, 144.2, 143.8, 143.6, 143.4, 142.9, 142.5, 142.3, 139.1, 138.9, 54.3, 54.0; ES-MS calcd for $C_{64}H_6O_2$ 806.037, found $M^{-\bullet}$ 806.036. UV−vis (*o*-dichlorobenzene), λ_{max} [nm] 442 (broad). **Compound 12:** ^1H NMR (500 MHz, CS_2/acetone-d_6), δ 7.56 (d, 4H, $J = 7.9$ Hz), 7.43 (d, 4H, $J = 7.9$ Hz), 4.61 (d, 4H, $J = 5.6$ hz), 3.92 (m, 4H, $J = 13.7$ Hz), 3.90 (t, 2H, $J = 5.6$ Hz); ^{13}C NMR (125.75 MHz, CS_2/C_6D_6) δ 158.7, 152.6, 149.4, 149.2, 147.8, 147.8, 147.6, 147.5, 146.9, 146.1, 145.7, 145.5, 145.5, 145.4, 145.0, 144.9, 144.9, 144.7, 144.5, 144.4, 143.8, 143.7, 143.6, 143.3, 143.2, 143.1, 142.7, 142.6, 142.4, 141.1, 139.5, 138.6, 135.1, 131.5, 127.2, 64.4, 61.4, 48.9; MALDI-TOF MS calcd for $C_{76}H_{18}O_2$ 962.0, found $M^{-\bullet}$ 962.0; UV−vis (dichloromethane), λ_{max} [nm] 444 (broad), 327, 270.

to be difficult, if not even impossible, to prepare starting from C_{60} itself. In particular, dialdehyde **10** and diol **12** may constitute promising intermediates in synthesis of new triads, and this possibility is currently under study.

Acknowledgment. The CNRS is gratefully acknowledged for financial support.

Supporting Information Available: Experimental procedure for the preparation of dialdehyde **10** and alcohol **11** and ^{1}H NMR spectra of compounds **3a**, **3b**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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