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Novel C_{60}-Based Building Blocks Derived from C_{60}^{2-} Anion

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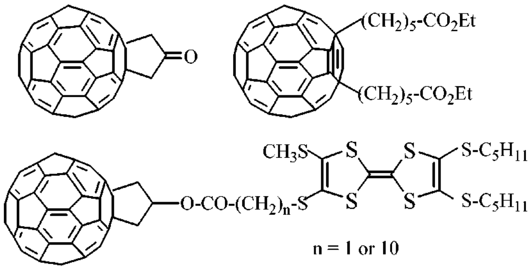
ABSTRACT



Reactions of chemically generated C_{60}^{2-} dianion with halo derivatives bearing a second functional group (halo, ester, ketone) give rise to new organo C_{60} derivatives. Thus, the regioselective formation of 1,2- and 1,4-adducts is observed from long-chain halo derivatives, whereas using 1,3-dihaloalkanes leads to 1,2-fused ring C_{60} adducts. Such adducts may be used as new synthons in C_{60} chemistry, thus leading to new C_{60}-based dyads, as exemplified by two examples.

The chemical reactivity of C_{60}^{2-} dianion is a priori very attractive as a result of the potential properties of this ion as an electron donor, a nucleophile, or a Brönstedt base, as exemplified in a recent review.[1] Furthermore, C_{60}^{2-} appears as a very good complement to C_{60}, since C_{60} mainly reacts as an electron acceptor or an electrophile, as well as in various cycloaddition processes.[2] Therefore, C_{60}^{2-} may play an important role in the search for new functionalized C_{60} derivatives. However, so far the chemistry of C_{60}^{2-} dianion has been mainly devoted to its alkylation through reaction of various halo derivatives RX.[3]

We have recently shown that, after generation of C_{60}^{2-} via a chemical reduction of C_{60} using sodium propanethiolate $C_3H_7S^-Na^+$ in acetonitrile, the alkylation reactions of C_{60}^{2-} exhibit the following features:[4] (i) The formation of 1,2- and 1,4-dialkyl adducts $C_{60}R_2$ obtained from R−I derivatives (R = Me, Et, *n*Bu) 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, this regiochemistry appearing to be much more selective than when C_{60}^{2-} dianion is electrochemically generated.[3a] (ii) With diiodo derivatives I-$(CH_2)_n$-I ($n = 3$ or 4), only the cyclic 1,2-adducts $C_{60}(CH_2)_3$ or $C_{60}(CH_2)_4$ are formed in high yields (ca. 80%).[4]

These results have prompted us to study an extension of this process starting from halo-derivatives that possess a second functional group, to check if this method may open up a new way for functionalizing fullerene C_{60}. Here we

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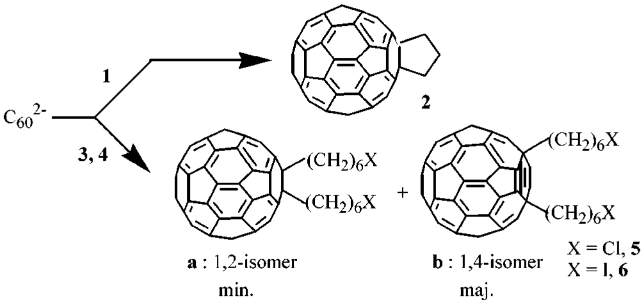
report the results that we have obtained from α,*ω*-dihaloalkanes, haloketone, and haloester derivatives.

At first we studied the reaction of 1-chloro-3-iodopropane $Cl(CH_2)_3I$ **1** with C_{60}^{2-}, expecting to obtain the adduct $C_{60}[(CH_2)_3Cl)]_2$ because of the poorer leaving group ability of Cl compared to I. In fact only the formation of cyclic adduct $C_{60}(CH_2)_3$ **2** in very good yield was observed. According to the mechanism proposed by Kadish et al.,[3b,c] this result suggests that the final S_N2 reaction, which follows the formation of the intermediate anion $[C_{60}(CH_2)_3Cl]^-$, is a fast intramolecular ring closure, owing to favorable entropic factors, instead of a reaction with a second molecule of $Cl(CH_2)_3I$ **1** (Scheme 1).

Scheme 1



However, in the same experimental conditions,[5] longer chain α,*ω*-dihaloalkanes such as $Cl(CH_2)_6I$ **3** or $I(CH_2)_6I$ **4** lead (ca. 20−30% yield) to the expected adducts $C_{60}[(CH_2)_6Cl]_2$ **5** and $C_{60}[(CH_2)_6I]_2$ **6**, the 1,4-compound being largely predominant (molecular ratios **5b**/**5a** and **6b**/**6a** ≥ 90/10) (Scheme 1).

The structures of 1,2- and 1,4-isomeric adducts were unambiguously assigned from NMR spectra of the corresponding mixtures (**5a** + **5b**) and (**6a** + **6b**). In 1,4-adducts, the hydrogen atoms of CH_2 groups bonded to the C_{60} core are diastereotopic and characterized by an AB system in ^IH spectra due to the chirality of C1 and C4 atoms in C_{60}.[3d] On the opposite, in 1,2-adducts C1 and C2 atoms are equivalent, and a single triplet is then ascribed to the same CH_2 groups (see Figure 1). These structural assignments were confirmed by $^1H-^{13}C$ 2D correlations, as previously observed.[4]

From these latter results, our interest has focused on the reaction of halo derivatives bearing another function such as a ketone or an ester group. To compare the results, the molecular frames of these halo derivatives were chosen to be similar to those of compounds **1** and **3**−**4**. Thus C_{60}^{2-} anion was reacted with 1,3-dibromo-propanone $BrCH_2-CO-CH_2Br$ **7** and with ethyl halo-hexanoates $X-(CH_2)_5-CO_2Et$ **9** (X = Br) and **10** (X = I).

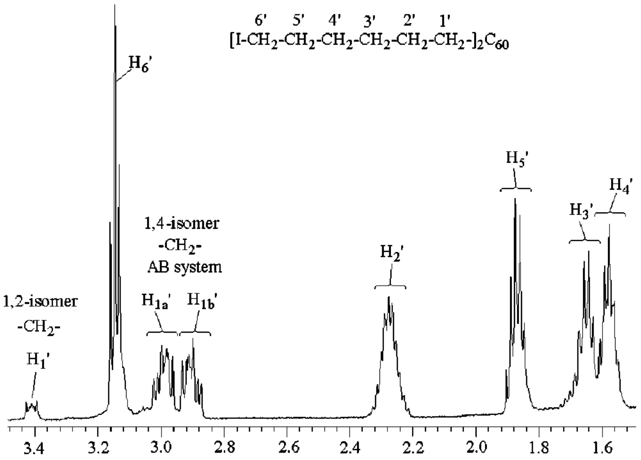
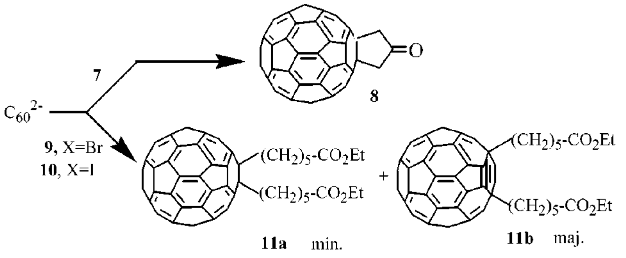


Figure 1. ^1H NMR spectrum of the mixture **6a** + **6b**.

The reactions occurred as expected, respectively leading (Scheme 2) to the cyclic ketone **8** (ca. 25% yield) [6] and to the diesters **11** (ca. 15% yield, molecular ratio **11b**/**11a** > 90/10 determined from NMR as for adducts **5** and **6**); both esters **9** and **10** give rise to identical results.

Scheme 2



All new C_{60} adducts (mixtures of isomers **5**, **6**, **11** or ketone **8**) were isolated by column chromatography, and their purity was confirmed by ^{13}C spectra (no detection of pristine C_{60}). (See Figure 2)

The adducts **8** and **11** offer further possibilities in synthesis as a result of the presence of the ketone and ester groups. In this field, our first results come from ketone **8**, which was easily reduced into the corresponding alcohol **12** (ca. 50% yield) upon reaction with DIBAL-H in toluene at room

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(5) **General Experimental Conditions.** Nitrogen is bubbled for 1 h in a suspension of 50 mg of C_{60} in 40 mL of dry acetonitrile, then excess $C_3H_7S^-Na^+$ is added in this medium, and the whole mixture is stirred under nitrogen at room temperature for 24 h. A deep red color is progressively developed in the liquid phase during this period as a result of the generation of C_{60}^{2-}. Halo derivative in large excess, previously degassed, is then added through a syringe into the reaction mixture, which is stirred at room temperature under nitrogen for a further 24 h period. The reaction mixture is filtered off, and the remaining solid is washed with diethyl ether. This crude solid is analyzed by TLC (eluent, carbon disulfide), HPLC (eluent, toluene), and ^1H NMR (solvent, $CS_2-C_6D_6$ or $CDCl_3$). The adducts were separated and purified by column chromatography.

(6) Commercially available 1,3-dibromopropanone **7** must be carefully purified (distillation) before use to separate 1-bromopropanone and 1,1-dibromopropanone, which may be present in minor proportions (5−10%). In particular, we have noticed that, in addition to cyclic ketone **8**, the methano-derivative $C_{60}{>}CHCOCH_3$ is formed up to ~15% from the commercial 1,3-dibromopropanone but only as traces (1−3%) from the distilled one. The formation of this methano-derivative is likely to be ascribed to reaction of 1,1-dibromopropanone with C_{60}^{2-} (see Boulas, P., Zuo, Y., Echegoyen, L. *Chem. Commun*. **1996**, 1547−1548).

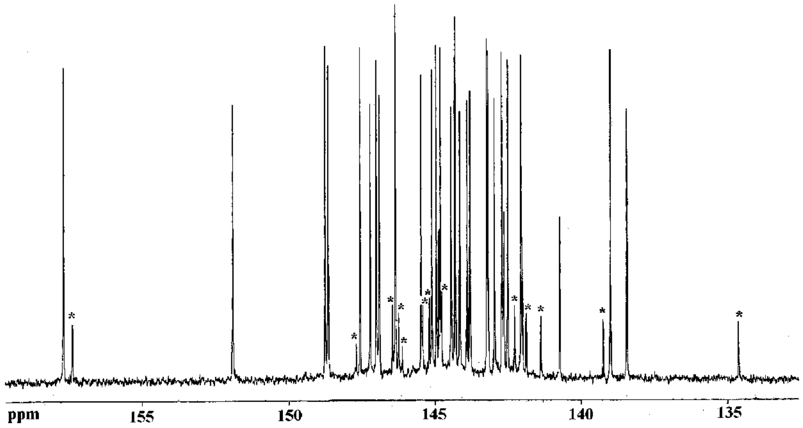
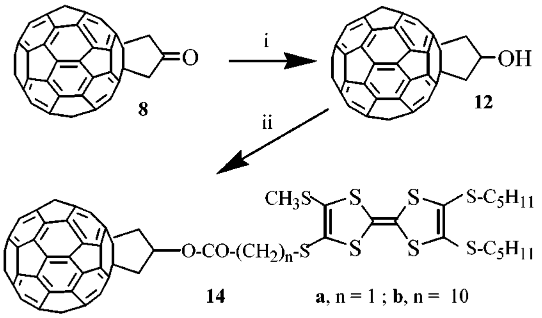


Figure 2. ^{13}C spectrum (C_{sp2} range) of the mixture **11a*** + **11b**.

temperature, as already observed from a 1,2-fused cyclohexanone-C_{60} derivative.[7]

This alcohol **12** readily reacted with a tetrathiafulvalene (TTF) analogue bearing a carboxylic acid function in a short or a long chain, respectively **13a** or **13b**,[8] leading to very good yields (80%) of the corresponding dyads **14a** and **14b** (Scheme 3).

Scheme 3[a]



[a] (i) excess DIBAl-H (10 equiv), toluene, 24 h, rt, then acidic (aq HCl 1 M) hydrolysis; (ii) **13a** or **13b**, toluene, DMAP, DCC, rt, 24 h.

The redox properties of the new compounds **5**, **6**, **8**, **12**, and **14** were studied electrochemically in *o*-dichlorobenzene or toluene/acetonitrile solutions. Well-resolved and reversible cyclic voltammograms were observed in all cases.

As expected, compounds **5**, **6**, **8**, and **12** exhibit more negative reduction potentials than C_{60} because of the loss of a carbon−carbon double bond.[9] The same trend is observed in the case of dyads **14a** and **14b**, their reduction potentials being identical and apparently not dependent on the moiety attached to the C_{60} core. However, these two dyads exhibit more positive oxidation potentials than the parent TTFs **13a** and **13b**, whereas other comparable C_{60}-TTF dyads were reported to display the same oxidation potentials as their starting TTFs.[10] Despite this particular result and by comparison with other studies,[10,12a] any important electronic interaction is unlikely to be considered in dyads **14a** and **14b** in their ground state, as can also be expected from their cyclic voltammograms showing usual characteristic patterns for C_{60} and TTF units (see Figure 3, **14a**).

Table 1. Cyclic Voltammetry Data at Room Temperature for C_{60} Derivatives **5**, **6**, **8**, and **12**, TTF Analogues **13a** and **13b**, and Dyads **14a** and **14b**[a]

compound	E1	E2	E3	E4
C_{60}			−1.15	−1.52[b]
			−1.0	−1.42[c]
5			−1.27	−1.69[b]
6			−1.26	−1.67[b]
8			−1.22	−1.59[b]
12			−1.25	−1.60[b]
13a	0.34	0.09[c]		
13b	0.32	0.09[c]		
14a	0.41	0.19	−1.06	−1.47[c]
14b	0.38	0.16	−1.05	−1.47[c]

[a] Experimental conditions: *o*-dichlorobenzene or toluene/MeCN (3/1) as indicated, working electrode, Pt, $E_{1/2}$ (V) vs Fc^+/Fc, $^nBu_4PF_6$ (0.05 M), 100 mV s^{-1}. [b] *o*-Dichlorobenzene. [c] Toluene/MeCN.

In conclusion, these results clearly show the importance of C_{60}^{2-} dianion as a starting compound for functionalizing C_{60}. The high versatility of this ion versus various halo derivatives strongly emerges from this work, giving rise to new organo-C_{60} derivatives **5**, **6**, **8**, and **12**, which are difficult

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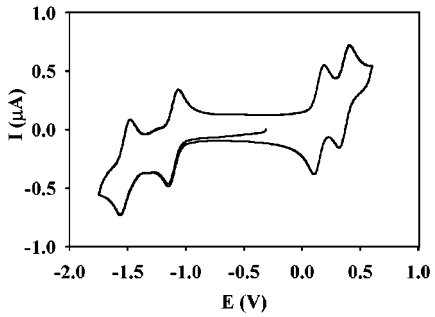

Figure 3. Cyclic voltammogram of the dyad **14a**.

to prepare by other ways.[11] In particular, compounds **8** and **12** may be considered as promising new building blocks in C_{60} chemistry, especially in the design of new C_{60}-based materials. Thus, from compound **12**, new C_{60}-based dyads **14** are readily obtained, which indicates that our methodology may complement other synthetic strategies in this field.[10,12] Photophysical properties of these dyads **14** are currently under study, as well as their NLO properties.

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(11) **Selected Data**. Compound **5b**: MALDI-TOF MS 958.0 ($M^{-\bullet}$), calcd 958.13; ^{1}H NMR (500 MHz) δ 1.61−1.65 (m, 8H), 1.81 (m, 4H), 2.29 (m, 4H), 2.90 (m, 2H), 2.99 (m, 2H), 3.46 (t, 4H, $J = 6.4$ Hz); UV−vis ($C_6H_4Cl_2$) 443 nm (broad). Compound **6b**: MALDI-TOF MS 1141.95 ($M^{-\bullet}$), calcd. 1142.0; ^{1}H NMR (500 MHz) δ 1.55−1.59 (m, 4H), 1.61−1.68 (m, 4H), 1.87 (m, 4H), 2.27 (m, 4H), 2.89 ((m, 2H), 2.99 (m, 2H), 3.14 (t, 4H, $J = 6.9$ Hz); UV−vis ($C_6H_4Cl_2$) 441 nm (broad). Compound **8**: MALDI-TOF MS 776.03 ($M^{+\bullet}$), calcd 776.03; ^{1}H NMR (500 MHz) δ 4.17(s); ^{13}C NMR (125.75 MHz) δ 49.6, 64.5, 135.1, 140.5, 142.2, 142.3, 142.4, 143.0, 143.5, 144.9, 145.4, 145.7, 145.8, 146.1, 146.6, 146.6, 147.9, 155.9, 207.9; UV−vis ($C_6H_4Cl_2$) 433 nm. Compound **12**: MALDI-TOF MS 778.02 ($M^{+\bullet}$), calcd 778.04; ^{1}H NMR (500 MHz) δ 1.89 (broad s, 1H), 3.63−3.70 (m, 4H), 5.28 (m, 1H); UV (CH_2Cl_2) 431 nm; ^{13}C NMR (125.75 MHz) d 51.5, 69.9, 73.0, 135.1, 136.5, 140.3, 141.9, 142.2, 142.3, 142.4, 142.4, 142.8, 143.4, 144.7, 144.9, 145.5, 145.5, 145.7, 145.8, 145.9, 146.0, 146.1, 146.2, 146.3, 146.4, 146.4, 147.5, 157.5, 157.5. Compound **14a**: MALDI-TOF MS 1304.03 ($M^{+\bullet}$), calcd 1304.02; UV (CH_2Cl_2) 430, 300, 255 nm; ^{1}H NMR (500 MHz/$CDCl_3$) δ 0.9 (t, 6H), 1.28−1.39 (m, 8H), 1.54−1.60 (m, 4H), 2.44 (s, 3H), 2.72−2.76 (m, 4H), 3.69 (s, 2H), 3.91 (dd, 2H), 4.07 (d, 2H), 6.27 (s, 1H). Compound **14b** : MALDI-TOF MS 1429.9 ($M^{+\bullet}$) calcd 1430.1; UV (CH_2Cl_2) 430, 300, 255 nm; ^{1}H NMR (500 MHZ/$CDCl_3$) d 0.9 (t, 6H), 1.23−1.40 (m, 20 H), 1.60−1.64 (m, 6H), 1.81 (m, 2H), 2.40 (s, 3H), 2.58 (t, 2H), 2.76−2.84 (m, 6H), 3.92 (dd, 2H), 3.96 (d, 2H), 6.24 (s, 1H).

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