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LETTERS

Chemical Generation and Reactivity of C_{60}^{2-}. High-yield and Regioselective Alkylation of [60, I_h] Fullerene

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Abstract. Chemical generation of the dianion of C_{60} followed by the reaction of monoiodo- or α,ω-diiodo-alkanes leads to the high-yield and regioselective formation of 1,2- and 1,4- dialkyl C_{60} or 1,2-fused ring C_{60} adducts. ^{13}C NMR studies including proton-carbon correlations were used to ascertain the geometry of the products while the new closed adducts were also characterized by MS, UV-vis and voltammetric measurements. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Owing to its outstanding physical and chemical properties, [60, I_h] fullerene[1] (C_{60}) has proven to be an attractive unit in the field of new materials. In particular much work has been devoted to its covalent functionalization with various groups, mainly through cycloaddition methodology and the Bingel reaction.[2] An alternative strategy might be achieved by the reaction of the stable and easily formed C_{60}^{2-} anion with electrophilic reagents. Recent studies have shown that the C_{60}^{2-} anion, generated electrochemically[3] or chemically,[4] reacts with alkyl bromides or iodides in large excess, leading to the expected adducts $C_{60}R_2$ (R = alkyl) in fair yields (40-60%). However, to our knowledge, this strategy has not been exploited on a large preparative scale, and we have decided to check the scope and limits of this methodology as a synthetic tool, our first objective being the chemical generation of C_{60}^{2-} through the most simple way.

In this note we report a very simple, effective, high-yield and regioselective preparation of open adducts $C_{60}R_2$ (R = alkyl) 1-3 as well as the unprecedented closed adducts of the type $C_{60}(CH_2)_n$ (n = 3, 4) 4 and 5.

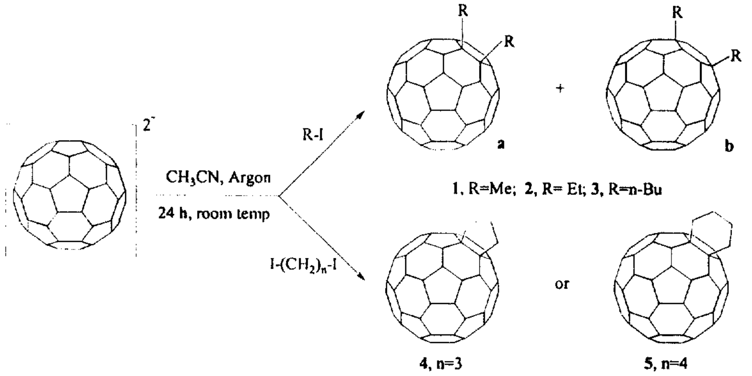

Figure 1. Reaction of C_{60} dianion with iodoalkyl derivatives

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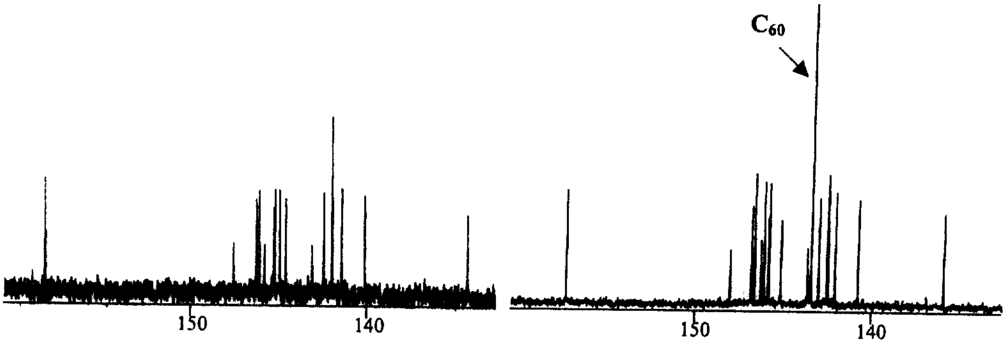
Following Kadish's finding that C_{60}^{2-} can be generated from C_{60} and propanethiol in the presence of potassium carbonate,[5] we found that this dianion can also be selectively, and very easily, formed by the reaction (*via* reduction) of C_{60} with excess (*ca.* 10 eq.) commercial sodium alkanethiolate $R'S^- Na^+$ (R' = Me, n-Pr, n-Bu) in acetonitrile or DMF at room temperature under argon. The formation of C_{60}^{2-} is clearly demonstrated by vis-NIR monitoring of the solution thanks to the characteristic absorption of C_{60}^{2-} at 829 and 945 nm.[5] After the generation of the anion (dark red colour in solution), an excess of neat iodo derivative RI or $I\text{-}(CH_2)_n\text{-}I$ (n = 3, 4) added to the mixture leads to alkylation of C_{60} which is usually complete within 24 h when the colour has disappeared.

In all of the cases studied, apart some residual amount of unreacted C_{60}, HPLC analysis of the resulting reaction mixtures revealed the presence of one major product and several minor compounds. Micro and semipreparative HPLC separation was performed, which led to pure samples of the main adducts.[6] The structures of compounds **1-5** were unambiguously determined from NMR analyses, either of the unseparated reaction products or of the pure samples ; these conclusions were made using a combination of ^1H and ^{13}C NMR evidence, as well as 2D correlations (Figures 2 and 3).

In the series of diadducts **1-3**, formed in 65-90% yield,[7] the ^1H spectra showed the expected signals from the alkyl groups. Furthermore, the decoupled ^{13}C spectra exhibited patterns consistent with either C2 (17 expected fullerene peaks) or C1 symmetry (32 expected fullerene peaks).[8] This behaviour is in full agreement with the addition of two alkyl groups to C_{60} in the 1,2- or 1,4-positions, respectively corresponding to isomers **a** and **b**. HMBC experiments fully confirmed these assignments. Thus the two isomers **1a** and **1b** of $C_{60}(CH_3)_2$ were clearly identified, and the molar ratio **1a**/**1b** = 9/1 showed a very high regioselectivity of the methylation of C_{60}^{2-}. Previously, after reaction between CH_3I and C_{60}^{2-} electrochemically generated, these isomers were differentiated by comparison of the relative intensities of the methyl signals in the ^1H spectrum of the mixture and the heats of formation of these isomers issued from semiempirical calculations, and the molar ratio **1a**/**1b** = 1.4/1.[3a] On the contrary, the other two

Figure 2. Downfield part of ^{13}C NMR spectra : a) pure compound **1a** ;
b) compound **5** mixed with unreacted C_{60}



adducts, $C_{60}(C_2H_5)_2$ (Fig. 3) and $C_{60}(n\text{-}C_4H_9)_2$, essentially consisted of the 1,4-isomer, namely **2b** and **3b**, the **2a**/**2b** and **3a**/**3b** molar ratios being 1/9 and ≈0/100 respectively. These results can be related to the case of dibenzyl derivative $C_{60}(CH_2\text{-}C_6H_5)_2$, which was formed exclusively as the 1,4-diadduct as a consequence of the size of the benzyl groups.[4a] Furthermore, the 1,4-adducts **2b** and **3b** are also identified by ^1H NMR, owing to the presence of diastereotopic hydrogens in the CH_2 groups bonded to C_{60}.

Regarding the reaction of α,ω-diiodo derivatives $I\text{-}(CH_2)_n\text{-}I$ ($n = 3, 4$) with C_{60}^{2-} to give 1,2-([1',3']propano)[60]fullerene **4** and 1,2-([1',4']butano)[60]fullerene **5**,[1] respectively, these products were formed in high yield (≈80-90%),[7] and provide ^{13}C spectra which are very similar to that of the 1,2-isomer **1a** of $C_{60}(CH_3)_2$, as shown in Fig 2. 2D correlations are also consistent with an addition of the $-(CH_2)_n-$ moiety through a ring closure, across a 6-6 double bond of the fullerene, thus leading to 1,2-type adducts **4** and **5** with C2 symmetry. The presence of an adduct formed *via* a 1,4 ring closure could not be detected.

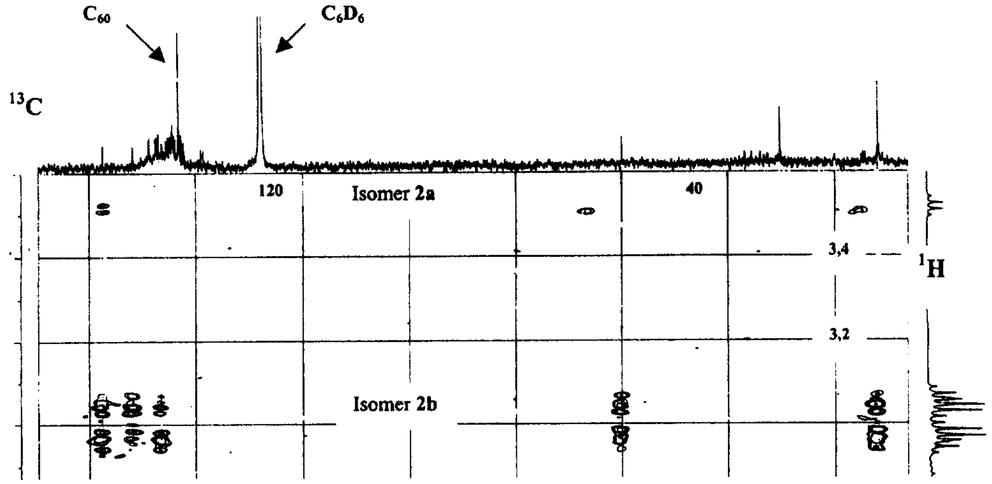
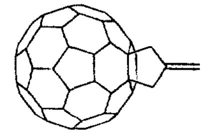


Figure 3 . HMBC NMR spectrum for crude $C_{60}(C_2H_5)_2$ **2** mixed with unreacted C_{60} .

Cyclic voltammetry was performed on pure samples of derivatives **4** and **5**.[9] The cyclic voltammograms exhibit at least three sets of waves indicative of three consecutive reversible one-electron transfers (*i.e.* reductions). The reversible $E_{1/2}$ are slightly more negative than that of C_{60} at $E_{1/2} = -1.11, -1.48, -2.04$ V (compound **4**) and $E_{1/2} = -1.10, -1.50, -2.05$ V (compound **5**) *vs.* Ag/AgCl as reference electrode. This is in agreement with the saturation of one double bond on the carbon cage and with data previously obtained on similarly saturated compounds.[10b] On the other hand, UV absorption maxima were detected in cyclohexane at 253 nm, 306 nm and 431 nm for compound **1a**, 256 nm, 316 nm and 428 nm for compound **4** and 256 nm, 317 nm and 432 nm for compound **5**. In all of these three cases the small maximum around 430 nm compares favorably with previous measurements on derivatives of C_{60} where an addition has occured accross a 6-6 bond.[11]

In summary, we have shown that controlled, highly regioselective and high yield formation of simple alkyl adducts of C_{60} could be achieved in a simple two-step procedure, the yields appearing clearly higher than those reported so far for similar alkylations and the regioselectivity of the methylation being increased to a great extent. More importantly, this procedure was also successfully applied to yield a new class of derivatives consisting of fullerene C_{60} bearing a closed chain. All compounds were unambiguously identified with the help of NMR studies, and this is the first example whereby 2D correlations have shown to be particularly useful in assigning the structures, in which the regioselectivity could be ascertained in all cases. The latter new molecules appear to be a promising starting point for the functionalization of fullerenes. In particular, it is worth noting that these products provide an original way of grafting chosen single or multiple functionalities onto C_{60} Thus, as an example, TMM-C_{60} **6**, previously obtained in a 25-30% yield *via* palladium-catalyzed [3 + 2] cycloadditions,[10] was easily formed in 70% yield [7] by our procedure through alkylation with $(ICH_2)_2C{=}CH_2$.



TMM-C_{60} **6**

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1. We use here the nomenclature recommended by IUPAC, *Pure and Applied Chem.*, **1997**, *69*, 1411-1434.
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6. Analytical, micro and semiprep HPLC separations were performed on a 4.6 x 250 mm or a 10 x 250 mm Cosmosil Buckyprep column from Nacalai Tesque. Pure toluene was used as the eluent.
7. These yields are based on the amount of reacted C_{60} as evaluated from HPLC analyses.
8. Selected Data. Compound **1a**: ^1H NMR (500 MHz, C_6D_6/CS_2) δ 3.14 (s, 6H). ^{13}C NMR (125.75 MHz, C_6D_6/CS_2) δ 29.51, 61.45, 134.35, 140.22, 141.54, 142.10, 142.57, 143.23, 144.74, 145.10, 145.36, 145.44, 145.95, 146.24, 146.42, 147.74, 158.57. Compound **1b**: ^1H NMR (500 MHz, C_6D_6/CS_2) δ 2.73 (s, 6H). Compoud **2a**: ^1H NMR (500 MHz, C_6D_6/CS_2) δ 1.78 (t, 6H, ^3J = 7.4 Hz), 3.51 (q, 4H, ^3J = 7.4 Hz). Compoud **2b**: ^1H NMR (500 MHz, C_6D_6/CS_2) δ 1.76 (t, 6H, ^3J = 7.4 Hz), 2.96 (dq, 2H, ^2J = 13.5 Hz, ^3J = 7.4 Hz), 3.05 (dq, 2H, ^2J = 13.5 Hz, ^3J = 7.4 Hz). ^{13}C NMR (125.75 MHz, C_6D_6/CS_2) δ 12.12, 37.01, 60.18, 138.73, 139.18, 142.37, 142.68, 142.89, 143.38, 143.98, 144.22, 144.32, 144.49, 144.61, 144.95, 145.09, 145.39, 145.69, 146.51, 147.09, 147.42, 147.69, 148.82, 148.96, 151.96, 157.63. Compound **3b**: ^1H NMR (500 MHz, C_6D_6/CS_2) δ 1.09 (t, 6H, ^3J = 7.3 Hz), 1.64 (m, 4H), 2.24 (m, 4H), 2.90 (m, 2H), 2.98 (m, 2H). Compound 4: HRMS 762.21642 ($M^{+)}$ calc. :762.048043 ; ^1H NMR (500 MHz, C_6D_6/CS_2) δ 2.81 (m, 2H), 3.58 (m, 4H). ^{13}C NMR (125.75 MHz, C_6D_6/CS_2) δ 25.71, 45.11, 71.05, 135.71, 140.44, 142.09, 142.29, 142.54, 142.83, 143.38, 144.76, 145.50, 145.53, 145.92, 146.28, 146.43 , 147.49, 157.26. Compound **5**: HRMS 776 .06644 (M^+) calc.776.06626 ; ^1H NMR (500 MHz, C_6D_6/CS_2) δ 2.66 (m, 4H), 3.33 (m, 4H). ^{13}C NMR (125.75 MHz, C_6D_6/CS_2) δ 21.13, 35.77, 64.37, 135.75, 140.65, 141.95, 142.37, 142.41, 142.89, 143.53, 145.04, 145.72, 145.75, 146.01, 146.18, 146.55, 146.73, 147.94, 157.35.
9. Cyclic voltammograms were performed on a Pt electrode in acetonitrile/toluene mixture (60/40) with 0.05 M tetrabutylammonium tetrafluoroborate at 200 mV/s or 500 mV/s scan rates.
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