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Functionalization of [60]fullerene through the anionic route

Jack Cousseau [*], Emmanuel Allard, Stéphanie Chopin

Laboratoire CIMMA, UMR CNRS 6200, Faculté des Sciences, Université d'Angers, 2, boulevard Lavoisier, 49045 Angers cedex 01, France

Abstract

The reactivity of C_{60}^{2-} anion, easily generated upon chemical reduction of the C_{60} core by sodium methanethiolate, has been systematically investigated versus a great number of saturated halogenated compounds RX or X–CH$_2$–R′–CH$_2$–X (X = I or Br), while these halo-compounds are unreactive with C_{60} itself. Various C_{60}-derivatives in the series of bis-adducts R_2C_{60} and fused cycloadducts R′(CH$_2$)$_2$C$_{60}$ are thus obtained in fair to good yields, the R or R′ groups bearing functionalities such as ethylenic double bond, halogen, ketone, alcohol, or ester moieties. On the other hand a judicious utilization of the overall mechanism of the reaction between C_{60}^{2-} anion and well chosen different RX and R′X compounds allow to extend this methodology to the preparation of mixed adducts RR′C$_{60}$. Functional adducts in the series R_2C_{60} and R′(CH$_2$)$_2$C$_{60}$ are new attractive building blocks in C_{60} chemistry, and can lead to novel highly functionalized C_{60}-based molecules. Some examples of such covalent ensembles are presented, the specific physical properties of which are typical of organic materials. ***To cite this article: J. Cousseau et al., C. R. Chimie 9 (2006).***

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1. Introduction

As shown from electrochemical studies, [60]fullerene is easy to reduce and can accept up to six electrons in six well separated one-electron reduction steps, leading at maximum to the hexaanion C_{60}^{6-} [1]. This electronegative character, associated with the very specific structure of the C_{60} core in which each hexagon is described at best as a cyclohexatriene ring rather than a benzene ring, gives [60]fullerene the reactivity of an electron-deficient polyolefin. As a consequence, functionalizing the C_{60} core has been carried out in most cases through cycloaddition reactions and nucleophilic additions [2]. In this context, two processes, namely the

Prato reaction ([3 + 2] cycloaddition of azomethine ylides) [3] and the Bingel [4] reaction (cyclopropanation of C_{60} with a dialkyl bromo(iodo)malonate in the presence of a strong base) are particularly used. They allow to obtain a wide variety of compounds in two different families, respectively, fulleropyrrolidines and methanofullerenes, under simple experimental conditions and in good yields.

Electrophilic reagents, of course, are not expected to easily react with the C_{60} core because of its electronegative character. However, using such reagents might be considered if the starting fullerene moiety is in C_{60}^{n-} anionic form, these anions being likely to react as potential nucleophiles. This strategy may open up new attractive ways for functionalizing [60]fullerene, and increase to some extent the field of [60]fullerene organo-derivatives. In this case, some conditions are

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[*] Corresponding author.

*E-mail address:* jack.cousseau@univ-angers.fr (J. Cousseau).

expected to be fulfilled in order to make this approach as fruitful as possible: (i) a specific anion C_{60}^{n-}, possessing a defined charge, should be easily obtained, and readily used in subsequent reactions; (ii) the electrophilic moieties prone to react with C_{60}^{n-} should allow to obtain new [60]fullerene derivatives very difficult, or even impossible, to be prepared through more usual methods starting from C_{60} itself.

As part of this research, we have studied the reaction of chemically generated C_{60}^{2-} anion towards various halogenated organic compounds. We have thus prepared new [60]fullerene derivatives, some of them being able to act as building blocks in C_{60} chemistry and to give rise to novel compounds in the field of organic materials. These results are summarized in this account.

2. Formation of C_{60}^{2-} anion

Kadish et al. have first shown that C_{60}^{2-} anion can react with saturated iodo or bromo derivatives RI or RBr, giving rise to corresponding bis-adducts R_2C_{60} [5,6]. Interestingly, these results established that new [60]fullerene organo-derivatives could be obtained from C_{60}^{2-}. However the electrochemical formation of this ion, as reported in these studies, appeared to be a somewhat limiting factor for a development of this methodology on a preparative scale.

A forward step was accomplished when the formation of dianion C_{60}^{2-} was observed to be performed through chemical reduction of C_{60} upon reaction with an alcanethiolate anion RS^-, this ion being then formed in situ from a mixture of an alcanethiol RSH and K_2CO_3 in acetonitrile under nitrogen atmosphere [7]. The reaction is slow, due to the weak solubility of the carbonate salt in the reaction mixture which limits to some extent the formation of the RS^- K^+ salt. Besides, J. Chen et al. have obtained C_{60}^{n-} ($n = 1-3$) salts in the series $A_nC_{60}(THF)_m$ after reduction of C_{60} upon reaction of corresponding stoichiometric amounts of alkali metal A (K, Na) with 1-methylnaphthalene in THF at room temperature [8].
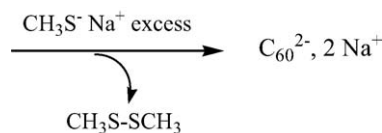
Scheme 1.

We have found a more simple and efficient process, which also avoids using a very ill-smelling alcanethiol. In this case the reducing agent is the commercially available sodium methanethiolate CH_3S^- Na^+. We observed that this latter salt easily reduces [60]fullerene in acetonitrile at room temperature, and gives rise to the sole C_{60}^{2-} anion within a few hours (Scheme 1) under inert atmosphere. C_{60}^{2-} anion is unambiguously identified from near-IR spectroscopic studies of the acetonitrile medium where it is perfectly soluble, giving an intense dark red color to this solution [9]:

Another chemical process has been reported, in which C_{60}^{2-} anion is produced in benzonitrile medium by treating dihydrofullerene $C_{60}H_2$ with tetrabutylammonium hydroxide [10].

3. Reaction of C_{60}^{2-} anion with functional halo-derivatives

### 3.1. Formation of symmetrical bis-adducts R_2C_{60}

A great variety of saturated mono-halo derivatives RX has been reacted with C_{60}^{2-} in acetonitrile, at room temperature, usually for 24 h.

Some general features characterize the observed results from these halo derivatives [9,11]. The overall yield of the addition, versus the starting amount of C_{60}, lies in the 10–70% range, the lowest yields being generally observed when R is a long chain, while the reactivity of the halo-derivatives decreases in the order RI > RBr > RCl, the chloro-derivatives being able to react only in the case of strongly activated structures, such as benzyl chloride [12].

On the other hand, a mixture of two regio-adducts R_2C_{60} is generally formed, namely the 1,2- and 1,4-isomers **1** and **2** (Scheme 2). The regioselectivity of this
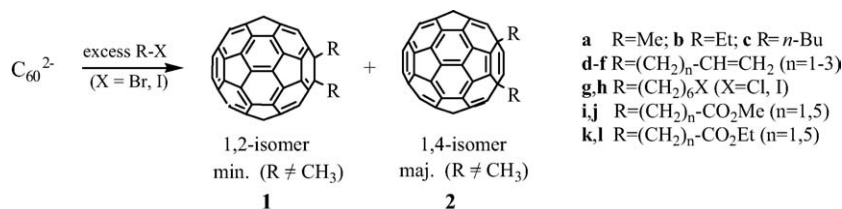
Scheme 2.
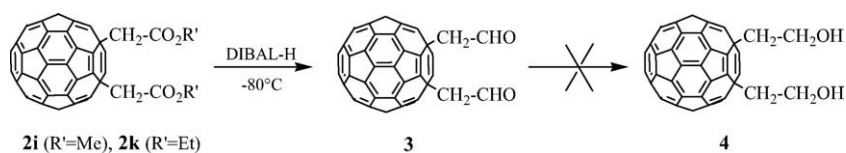
Scheme 3.

reaction is high, the relative molar ratio **1/2** being ca. 9/1 when R = CH$_3$ and 1/9 in other cases (Scheme 2).

The regiochemistry of this reaction is accounted for by the steric hindrance due to both R groups in the 1,2-positions when R ≠ CH$_3$, whereas theoretical calculations predict a better reactivity of the 2-position compared to the 4-one of the intermediate [RC$_{60}$]$^-$ anion which is first formed whatever the nature of the R group.
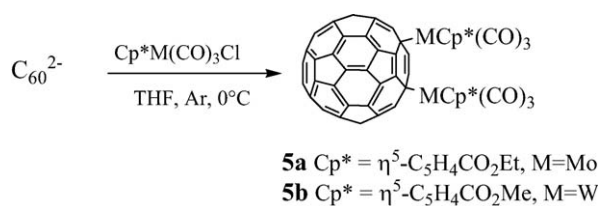
The reaction with haloacetates X–CH$_2$–CO$_2$R^1 (X = Br, I; R′ = Me, Et) gives rise to particular results [13]. Whereas it is generally quite difficult to separate both 1,2- and 1,4-adducts being formed, major 1,4-(CH$_2$CO$_2$R^1)$_2$C$_{60}$ **2i** and **2k** derivatives are easily isolated as pure compounds through column chromatography. We also observed that these bis-esters can be reduced in good yield (50%) into corresponding bis-aldehydes 1,4-(CH$_2$CHO)$_2$C$_{60}$ **3** through reduction by DIBAL-H at –80 °C. However, a further reduction to alcohols 1,4-(CH$_2$CH$_2$OH)$_2$C$_{60}$ **4** failed, no definite compound being obtained in this case (Scheme 3).

On the other hand, unexpected results have been observed about the electron affinity of the C$_{60}$ core in these bis-esters **2i** and **2k**. Whereas C$_{60}$-derivatives are usually known to be reduced at more negative potentials (average $\Delta E \sim -100$ mV) than C$_{60}$ itself [14], these 1,4-adducts are characterized by a first reduction potential which remains very close to the one observed for pristine C$_{60}$.

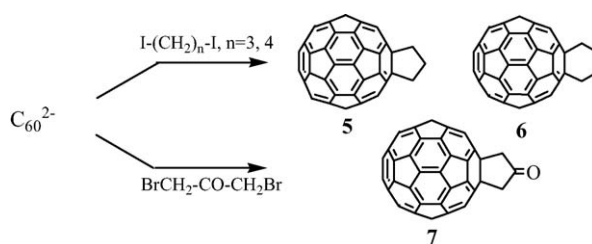This methodology of functionalization has also been extended to the reaction of organometallic halides with C$_{60}$$^{2-}$ issued from reduction of C$_{60}$ by potassium/1-methylnaphtalene in THF. Thus, Zhu et al. [15] have obtained two σ-bonded [60]fullerene transition metal derivatives, respectively (μ-C$_{60}$)Mo$_2$(η^5-C$_5$H$_4$CO$_2$Et)$_2$ **5a** and (μ-C$_{60}$)W$_2$(η^5-C$_5$H$_4$CO$_2$Me)$_2$ **5b**. These compounds are identified as 1,4-adducts (Scheme 4).
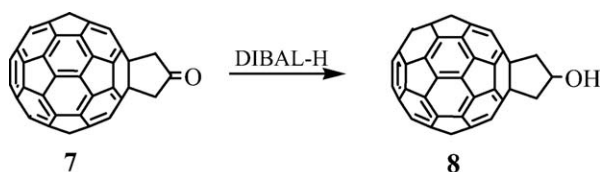
3.2. Formation of cycloadducts

Diiodoalkanes I–(CH$_2$)$_n$–I constitute an important class of reagents when $n = 3$ or 4, since they lead to cycloadducts **5** or **6** in very good yields (~80%). These

5a Cp* = η^5-C$_5$H$_4$CO$_2$Et, M=Mo
5b Cp* = η^5-C$_5$H$_4$CO$_2$Me, M=W
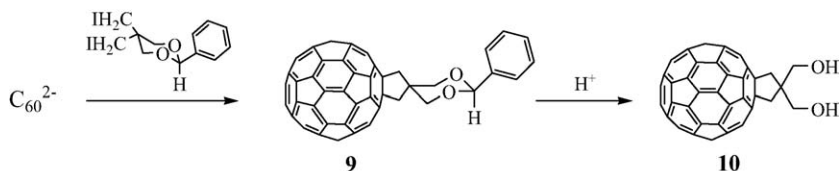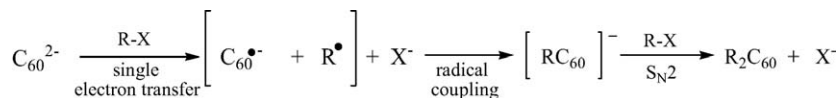
Scheme 4.

Scheme 5.

Scheme 6.

results prompted us to extend this reaction to functionalized 1,3-dihalopropane derivatives in order to obtain in one step new cyclopentanofused [60]fullerene able to act as attractive building blocks in further syntheses of multifunctional C$_{60}$-based covalent assemblies [9]. Thus, the reaction of 1,3-dibromopropan-2-one easily gave rise to the ketone **7** (20% yield) (Scheme 5) [11].

Furthermore, we observed that ketone **7** was easily reduced at room temperature by DIBAl-H into the corresponding alcohol **8** (50% yield) (Scheme 6) [11]. As will be indicated later, alcohol **8** was proven to be a fruitful building block for the synthesis of novel [60] fullerene-based organic materials.
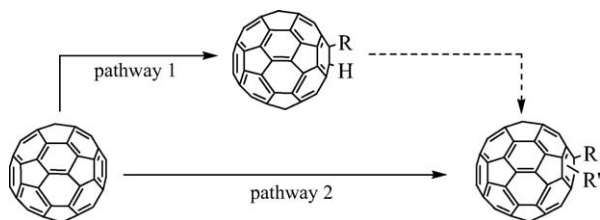
These results led us to search for the synthesis of the diol **10**, a relatively few examples of C$_{60}$ derivatives bearing two alcohol groups being known. From our previous results, the simplest pathway seemed to allow to react C$_{60}$$^{2-}$ anion with the 1,3-diiodopropan-2-ol

Scheme 7.

Scheme 8.

Scheme 9.

ICH_2–$CHOH$–CH_2I. However, no definite compound could be isolated from this latter reaction. The diol **10** was finally obtained in good yields in two steps (~50% in each step) starting from the diiodo acetal **9** derived from pentaerythritol [16] (Scheme 7).

3.3. Formation of functional mixed bis-adducts $RR'C_{60}$ ($R \neq R'$)

The easy formation of various symmetrical bis-adducts R_2C_{60} starting from C_{60}^{2-} anion prompted us to check if the same methodology could be extended to the preparation of functional mixed bis-adducts $RR'C_{60}$.

Previously, only one C_{60} adduct bearing two different alkyl groups (t-C_4H_9)(C_6H_5–CH_2)C_{60}, was reported to be obtained from C_{60}^{2-} anion [17]. In the same work, the authors have studied in detail the reaction kinetics of C_{60}^{2-} anion with various halo-derivatives RX, from which they have proposed the overall following mechanism in three successive steps (Scheme 8).

On this basis, the reaction of C_{60}^{2-} with t-C_4H_9I is considered to stop when the $[(t$-$C_4H_9)C_{60}]^-$ anion is formed, the size of this t-butyl group preventing further fixation of a second one on the C_{60} core, even in a 4-position. In this case, the introduction of benzyl bromide in the reaction medium allows to add the less bulky benzyl group in the third step, giving rise to (t-C_4H_9)(C_6H_5–CH_2)C_{60}.

From the above mechanism, it appears that the RX derivative is involved in two quite different steps, a single electron transfer and a S_N2 nucleophilic substitution. It thus appeared to be likely to take advantage of these mechanistic differences if we were able to stop the overall process after the radical coupling, irrespective of any steric effect as shown by the t-butyl group.

Two possibilities can be considered:

- if the RX compound is very reactive, the two first steps will be very rapid. At this stage, the process may be stopped upon addition of a strong acid in order to form then isolate a $R(H)C_{60}$ derivative (pathway 1). The final $RR'C_{60}$ will be obtained in a second stage;
- if the RX compound is weakly reactive, the two first steps will be slow, and the third one still slower. In this case the $RR'C_{60}$ final derivative may be obtained in a "one pot" overall process, provided a second $R'X$ compound, much more reactive than RX, is added after the radical coupling (pathway 2) (Scheme 9).

3.3.1. Formation of $R(H)C_{60}$ compounds

Very reactive halo-derivatives were chosen in the alkyl halo-acetates series, XCH_2–CO_2R^1 **11**. Following the progress in the reaction with C_{60}^{2-} is easy, due to the color change of the solution from red associated to C_{60}^{2-} to dark emerald-green characteristic of a $[RC_{60}]^-$ anion [18]. As expected, the formation of the $[(R^1O_2C$–$CH_2)C_{60}]^-$ anion is very rapid, and a further addition of an excess of CF_3CO_2H leads instantaneously to the corresponding dihydrofullerene 1,2-$(R^1O_2C$–$CH_2)(H)C_{60}$ **12** (Scheme 10).

We observed that RHC_{60} **12a–b** were formed in 35% yield when CF_3COOH is added after 2–3 min reaction at room temperature between C_{60}^{2-} anion and corresponding $XCH_2CO_2R^1$ **11** (100 mg C_{60}, 75 ml
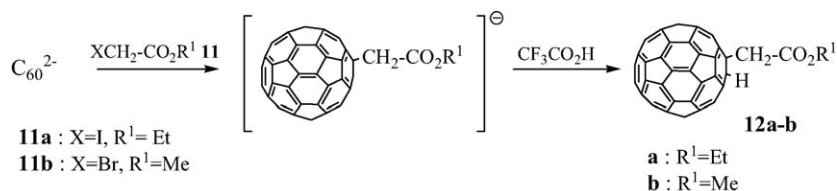
Scheme 10.
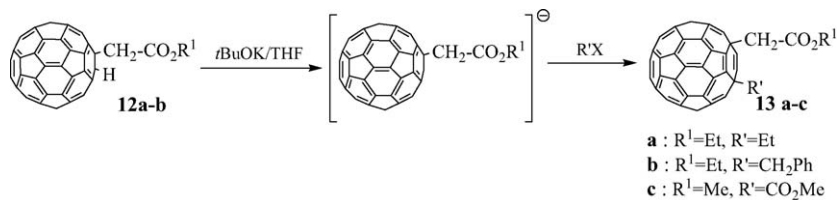
Scheme 11.

acetonitrile, 20 eq. RX) [19]. By comparison, under strictly identical experimental conditions, the bis-adducts $(CH_2CO_2R^1)_2C_{60}$ **2i–k** were obtained in 15–20% yield after 24-h reaction.

A comparable procedure was reported by Meier et al., C_{60}^{2-} anion being generated in this case by treating 1,2-dihydro[60]fullerene $C_{60}H_2$ by tetrabutylammonium hydroxide. Various alkyl bromides RBr were used (R=Ph$_2$CH, PhCH$_2$, HC≡C–CH$_2$, CH$_2$=CH–CH$_2$), and gave rise to the corresponding R(H)C$_{60}$ derivatives in fair to good yields (21% from propargyl bromide, 60% from diphenylmethyl bromide) after an immediate quenching of the reaction mixture by acetic acid [10].

3.3.2. Formation of RR′C$_{60}$ compounds

A simple process consists of using functional 1,2-(R)(H)C$_{60}$ **12** previously obtained. These compounds are first transformed into their anions $[RC_{60}]^-$ upon reaction with *t*BuOK, then a further reaction of these anions with a second halo derivative R′X allows to easily obtain the expected RR′C$_{60}$ derivative (Scheme 11).

Derivatives **13a–c** are obtained in 50–60% yield. Furthermore, it has to be mentioned that the regiochemistry of the second addition is very selective, since in these three adducts both CH$_2$CO$_2$R^1 and R′ groups are only in the 1,4-positions on the C$_{60}$ core [19].

As already indicated, functional mixed RR′C$_{60}$ compounds might also be obtained according to another strategy, if the first RX derivative is weakly reactive. In this case, the nature of the halogen may be considered. Since the first step of the whole process is a single electron transfer associated with a departure of X$^-$ anion, its rate is expected to be slower with X = Cl and faster with X = I. A good candidate is benzyl chloride C$_6$H$_5$CH$_2$Cl,
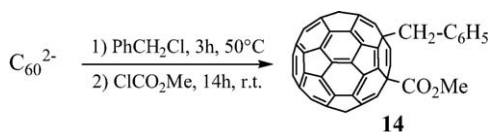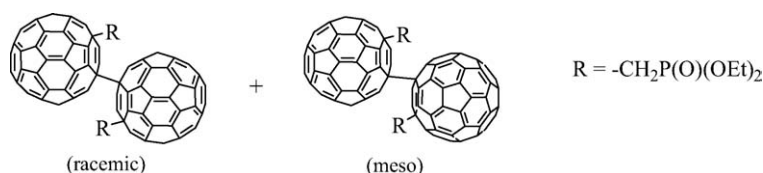

Scheme 12.

which was already shown to be a weak reagent towards C_{60}^{2-} anion in THF [12]. Thus, we observed in a test experiment that the $[(C_6H_5CH_2)C_{60}]^-$ anion is produced in acetonitrile between C_{60}^{2-} anion and benzyl chloride upon heating at 50 °C for 3 h. A further addition of excess methyl chloroformate ClCO$_2$Me, a priori more reactive than benzyl chloride, allowed to obtain the pure 1,4-(CH$_2$–C$_6$H$_5$)(CO$_2$Me)C$_{60}$ **14** derivative in 15% yield [19] (Scheme 12).

Another particular result was observed by Komatsu's group. After reaction of C_{60}^{2-} anion with diethyl iodomethylphosphonate ICH$_2$P(O)(OEt)$_2$, the $[C_{60}(CH_2P(O)(OEt)_2]^-$ anion does not add a second CH$_2$P(O)(OEt)$_2$ group at room temperature because of its bulkiness, but can react with I$_2$, thus leading to a singly bonded C$_{60}$ dimer as a mixture of two inseparable isomers [20] (Scheme 13).

4. Optoelectronic properties

Due to their good reduction ability (see Table 1), the bis-esters 1,4-(CH$_2$–CO$_2$R^1)C$_{60}$ **2i** and **2k** appeared as potential candidates as acceptor partners in organic solar cells. In this purpose, the photovoltaic characteristics of different donor–acceptor mixtures have been studied, the donor being poly[2-methoxy-5-(2′ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). The results show that, for the same w/w donor–acceptor ratio (1/2), the

R = -CH₂P(O)(OEt)₂

(racemic)   (meso)

Scheme 13.

Table 1
Voltammetric data [$E_{1/2}$ (V) vs. Fc$^+$/Fc, o-DCB, Pt, 100 mV s^{-1}]

| Compound	$E_{1/2}^{red1}$	$E_{1/2}^{red2}$	$E_{1/2}^{red3}$
[60]Fullerene	−1.11	−1.49	−1.92
Bis-ester **2i**	−1.13	−1.58	−2.03
Bis-ester **2k**	−1.14	−1.58	−2.03

energy conversion efficiency η associated to compounds **2i** (0.27%) and **2k** (0.4%) is slightly lower, although in the same order of magnitude, than when the acceptor is PCBM (0.7%), the weaker solubility of the bis-esters **2i** and **2k** in 1,2-dichlorobenzene (ODCB) preventing to work with the more usual w/w donor–acceptor ratio 1/5 [21].

From alcohol **8**, two C_{60}-TTF-based diads **21a–b** were synthesized. Their third-order non-linear optical susceptibilities have been measured in conventional solution (THF) [22] and in nematic liquid crystal [23] (Scheme 14).

The photophysical properties of **21a–b** have also been investigated, and radical ion pairs $C_{60}^{\bullet-}$/TTF$^{\bullet+}$ have been characterized from photoinduced electron-transfer processes. The longer lifetime of the ion-pair is associated to the longer spacer between C_{60} and TTF moieties ($N = 10$) [24].

More recently, starting from diol **10** we have prepared the triad **22**, which includes one C_{60} unit and two TTF moieties. The study of its photophysical properties indicates that the photoinduced charge separation is likely to take place via the excited triplet state of the C_{60} moiety, giving rise to a longer lifetime of the radical ion-pair state in non-polar solvents [25] (Scheme 15).

In these C_{60}-TTF-based diads **21a–b** and triad **22** the electrochemical HOMO–LUMO gap follows the sequence **22** (1.17 eV) < **21b** (1.21 eV) < **21a** (1.25 eV).

n=1: **21a**; n=10 : **21b**
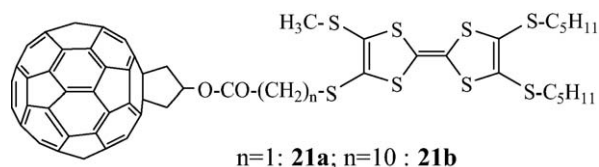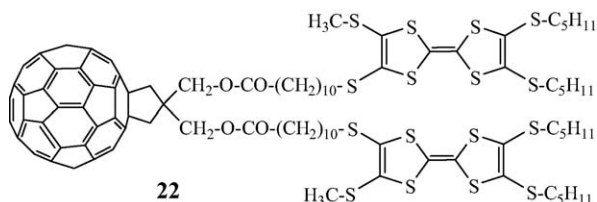
Scheme 14.

Scheme 15.

5. Conclusion

The reactivity of C_{60}^{2-} anion has been studied towards a great number of halogenated compounds. The [60]fullerene derivatives issued from these reactions evidenced the interest of this methodology. In particular functional halo-derivatives, thanks to the numerous structures they can offer, greatly enlarge the range of derivatization of the C_{60} core which can be performed in a few steps. Among these results, we established that a judicious choice of the halo-derivatives and the experimental conditions allows to obtain various functional mixed dihydrofullerenes RR′C_{60}. We have also shown that some of these novel [60]fullerene derivatives are promising building blocks in C_{60} chemistry, which open up the way to new covalent ensembles in the field of organic materials.

Acknowledgements

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