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[4+2] Cycloaddition of C_{60} to 2-(thi)oxo-4,5-bis(methylene)-1,3-dithioles : en Route to the *bis*-Linking of Tetrathiafulvalene to C_{60}

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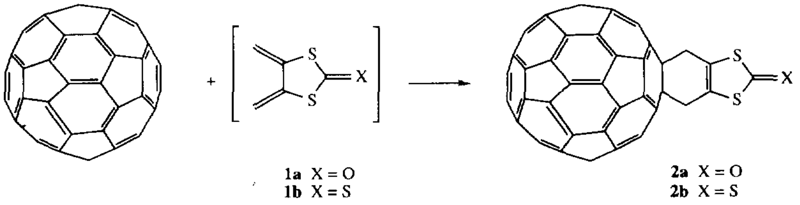
Abstract : The title reaction carried out from S-propargyl xanthate **3** or 2-(thi)oxo-4,5-bis(bromomethyl)-1,3-dithioles **4a** and **4b** with C_{60} is presented and some conversions of the synthesized cycloadducts **2a** and **2b** in several 1,3-dithiole derivatives are described.

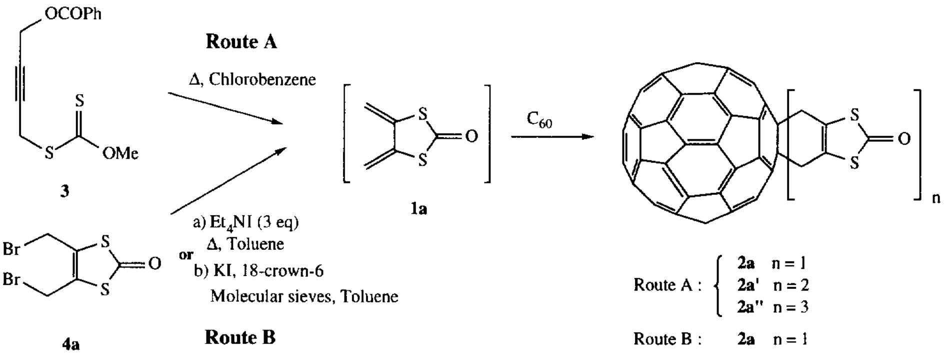
Since the discovery[1] of C_{60} and its large scale preparation,[2] much work has been devoted[3] to this new exceptional π-acceptor and to the exciting superconducting properties of its alkali metal-doped forms.[4] There is also an obvious interest to use tetrathiafulvalene (TTF) as the antagonistic π-donor of C_{60} : charge transfer complexes endowed with interesting electroconductive properties may be expected, and to date some new related attempts can be found.[5, 6] A recent report by Martín and Seoane[7] on the linking of thiophene onto C_{60} using 2,3-bis(methylene)benzo[*b*]thiophene prompts us to publish some preliminary results on our quest to perform the *bis*-linking of TTF to C_{60}. We present here the [4+2] Diels-Alder cycloaddition of 2-(thi)oxo-4,5-bis(methylene)-1,3-dithioles to C_{60}, the cycloadducts thus produced constituting interesting synthetic intermediates in the fields of the chemistry of 1,3-dithioles,[8] TTFs[9] and 1,3-dithiolato complexes.[10]

Because of the pronounced dienophilic character of its 6-6 bonds, [4+2] cycloaddition is one of the most powerful approach for the C_{60} functionalization, and accordingly, the main step in our synthesis of target molecules **2** (scheme 1) lies in the Diels-Alder reaction[3,11] of C_{60} with 2-(thi)oxo-4,5-bis(methylene)-1,3-dithioles **1a** and **1b**.



Scheme 1

First, in order to generate the 2-oxo intermediate **1a**, we compared two alternative pathways (scheme 2) : the thermal rearrangement of S-propargyl xanthate **3** (Route A)[12] and the reductive 1,4-elimination of the corresponding 2-oxo-4,5-bis(bromomethyl)-1,3-dithiole **4a** (Route B).[13]

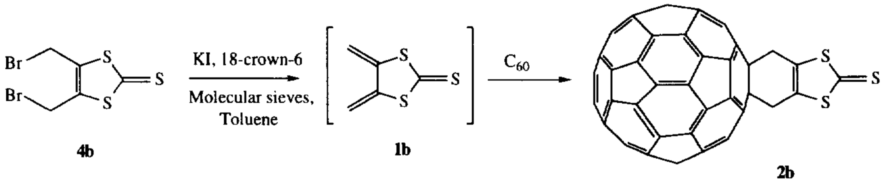


Scheme 2

In route A, compound **3** (292 mg, 1.04 mmol) was heated in dry chlorobenzene (400 mL) in the presence of 1.035 g (1.44 mmol) of C_{60} under a nitrogen atmosphere for 2 h. After silica gel column chromatography (CS_2 then toluene as eluents), the mono, bis, and tris-adducts were separated respectively in 60%, 5-10% and < 5% yields.

Route B, which uses tetraethylammonium iodide[13] to *in situ* generate diene **1a**, only afforded the required monocycloadduct of C_{60} in 16% yield. Furthermore, the [4+2] cycloaddition could readily be achieved by treatment with potassium iodide in the presence of 18-crown-6.[7,11,14] A mixture of C_{60} (100 mg, 0.14 mmol), dried potassium iodide (50 mg, 0.30 mmol) and 18-crown-6 (300 mg, 1.13 mmol) in dry toluene (100 mL) was stirred in the presence of molecular sieves 4Å under a nitrogen atmosphere for 6 h. After addition of compound **4a** (42 mg, 0.14 mmol), the reaction mixture was stirred at room temperature for 3 days. After work up and similar chromatography, cycloadduct **2a** was isolated in 30% yield.

In order to reach the corresponding cycloadduct **2b**, we considered the application of route B to the 2-thioxo series (scheme 3). In contrast to the synthesis of **4a**,[13] all attempts to convert 2-thioxo-4,5-dimethyl-1,3-dithiole[15] into 2-thioxo-4,5-bis(bromomethyl)-1,3-dithiole **4b** using NBS were unsuccessful. However, **4b** could be prepared from the 2-oxo derivative **4a** (1 mmol) by classical treatment with phosphorus pentasulfide (1.5 mmol) in refluxing xylene (6 mL) for 2 h. Column chromatography (CH_2Cl_2/cyclohexane : 1/1) afforded this target compound in 25% yield. Similarly, the application of the method with KI and 18-crown-6 to **4b** gave adduct **2b** in 36% yield.



Scheme 3

The structure of each isolated cycloadduct was clearly established by spectral investigations.[16] Thus the FAB(-) mass spectra of **2a** exhibited the molecular ion peak at *m/z* 864 with the base peak at *m/z* 720. The bis and tris-cycloadducts **2a'** and **2a"** respectively showed the sequences *m/z* 1008, 864, 720 and *m/z* 1152, 1008, 864, 720 resulting from successive retro-Diels-Alder reactions. The structure of **2a** was further confirmed by ^1H nmr, the methylene protons appearing as a singlet at δ 4.50 ppm. Furthermore, the UV-Vis peaks at 434 and 700 nm are typical of a C_{60} mono-adduct at the 6-6 ring junction.[17]

The FAB (-) mass spectrum of **2b** exhibited the expected molecular ion peak at *m/z* 880 together with a base peak at *m/z* 720 while the ^1H nmr spectrum also revealed the presence of a singlet at δ 4.30 ppm, and the ^{13}C nmr spectrum showed (δ ppm) 14 peaks between 136 and 155 (C_{60} moiety and SC=CS), 66.2 (junction carbons), 210.8 (C=S) and 40.9 (CH_2). The UV-Vis spectrum of this monoadduct also presented the typical absorption bands at 435 nm and 700 nm.

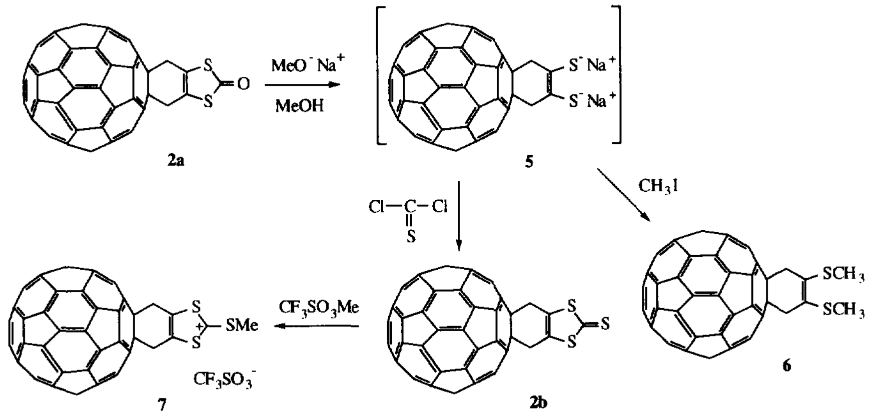
The cyclovoltammetric data in the table show that, as expected, the first three reversible reduction peaks of C_{60} undergo a negative shift (from 30 to 180 mV).

compound	Epc1	Epc2	Epc3	Epc4
C_{60}	- 0.72	- 1.12	- 1.56	- 2.19
2a	- 0.80	- 1.20	- 1.74	- 2.17
2b	- 0.78	- 1.15	- 1.70	- 2.05

1.5 mM in *o*-dichlorobenzene-*n*-Bu_4NPF_6 0.1 M, v = 100 mVs^{-1}, Epc in V/SCE

Table : Cyclovoltammetric data

The basic cleavage of the 2-oxo-1,3-dithiole cycle of **2a** was cleanly achieved by treatment with a sodium methoxide solution.[10] Disodium dithiolate **5** thus generated was trapped with either an excess of iodomethane to afford **6** or with thiophosgene leading to **2b**. In addition, **2b** was readily converted into **7** by treatment with methyl trifluoromethanesulfonate (scheme 4). Compounds **6** and **7** were characterized by FAB(-) and FAB(+) mass spectra respectively.[16] Moreover, the UV-Vis peaks at 434 and 700 nm were effectively present.



Scheme 4

Of course, attempts to convert **2a** and **2b** into the attractive corresponding TTFs doubly attached to one or two C_{60} were run. Unfortunately, the usual trialkyl phosphite mediated symmetrical couplings, as well as the dissymmetrical couplings involving other 2-(thi)oxo-1,3-dithioles, could not succeed.[18] Therefore, efforts are now currently developed aiming to achieve such conversions by using either other coupling reagents or another classical multistep pathway.

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    2a : ^{1}H nmr (*o*-dichlorobenzene-d_4) δ 4.33 ppm; ^{13}C nmr (*o*-dichlorobenzene-d_4) δ 40.99 (CH_2), 66.53 (sp^3 C atoms of C_{60}), 136.21, 140.69, 142.09, 142.54, 142.64, 143.07, 143.52, 145.06, 145.24, 145.96, 146.02, 146.13, 146.74, 147.03, 148.18, 155.27 (sp^2 C atoms of C_{60} and SC=CS), 191.45 (C=O); FAB(-) MS *m/z* (I%) : 864 ($M^{\cdot -}$, 39), 720 (100); Rf (toluene) = 0.62 (0.90 for C_{60}); IR (KBr) : 1600-1720 cm^{-1} (large and decomposed band C=O).

    2a' : FAB(-) MS *m/z* (I%) : 1008 ($M^{\cdot -}$, 24), 864 (16); 720 (100); Rf (toluene) = 0.40 .

    2a" : FAB(-) MS *m/z* (I%) : 1152 ($M^{\cdot -}$, 16); 1008 (17); 864 (13); 720 (100); Rf (toluene) = 0.07.

    2b : ^{1}H nmr (*o*-dichlorobenzene-d_4) δ 4.30 ppm; ^{13}C nmr (*o*-dichlorobenzene-d_4) δ 40.93 (CH_2), 66.22 (sp^3 C atoms of C_{60}), 136.16, 139.31, 140.70, 142.09, 142.54, 142.58, 143.09, 145.04, 145.12, 146.02, 146.74, 147.05, 148.18, 154.99 (sp^2 C atoms of C_{60} and SC=CS), 210.82 (C=S); FAB(-) MS *m/z* (I%) : 880 ($M^{\cdot -}$, 18), 720 (100); Rf (CS_2) = 0.34 (0.90 for C_{60}); IR (KBr) : 1050 cm^{-1} (C=S).

    6 : FAB(-) MS *m/z* (I%) : 866 ($M^{\cdot -}$, 20), 720 (100); Rf (toluene) = 0.68.

    7 : FAB(+) MS *m/z* (I%) : 895 (M^+, 37), 720 (100).
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