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Exohedral Functionalization of [60]Fullerene by [4+2] Cycloadditions. Diels-Alder Reactions of [60]Fullerene with Electron Rich 2,3-Dioxy-substituted-1,3-butadienes.

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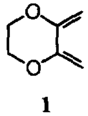
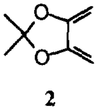
Key words: [60]fullerene, Diels-Alder reaction, 2,3-dioxybutadienes, acyloin
Abstract: The Diels-Alder reactions between [60]fullerene and 2,3-dimethylene-1,4-dioxane (**1**) or 4,5-dimethylene-2,2-dimethyldioxolane (**2**) are described. The C_{60}:**1** derivative was obtained under mild thermal conditions. The compound **2** necessitates the use of high pressure to perform the [4+2] cycloaddition and its hydrolysis yields the acyloin derivative **7**.

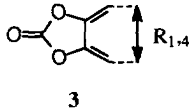
INTRODUCTION

Since the discovery and isolation in macroscopic quantities of C_{60}[1] numerous reactions have been developed to explore the potentially rich and diverse chemistry of this molecule.[2] The thermal and photochemical cycloadditions[3] constitute one of the most useful methods for accessing functionalized fullerene derivatives, as the C_{60} exhibits marked propensity to function as a 2π component. In this context, [2+2], [3+2], [4+2] and higher order cycloadditions have been successfully performed with this fascinating molecule.[2] The Diels-Alder reactions have been extensively used under thermal or high pressure conditions[4] to functionalize the fullerene surface obtaining mono- or polyadducts.[5] In any case, the success of the [4+2] cycloaddition is strongly dependent on the reactivity of the diene used, and the cycloreversion constitutes a competitive undesired pathway.[2]

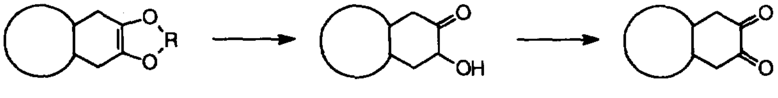
We report the study of the Diels-Alder reactions with 2,3-dioxy-substituted *cis*-fixed butadienes (**1**, **2**).







	1	**2**	**3**
$R_{1,4}$	322.6	338.5	340.9
reactivity	high	medium	low



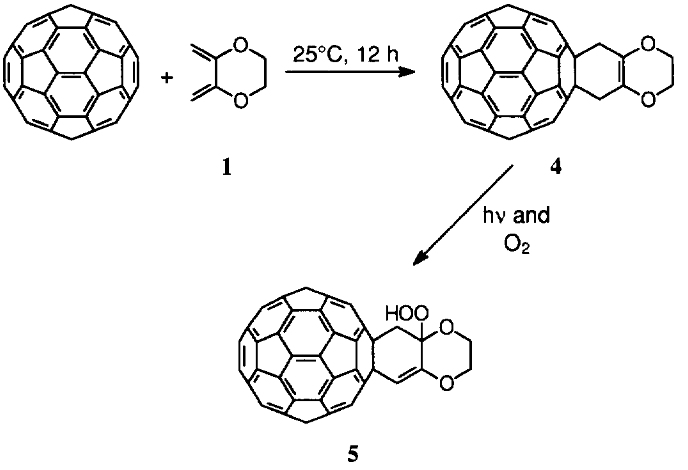
The cycloadducts obtained with these electron rich dienes (**1-3**) will be potential precursors of valuable functionalities like acyloin or diketone derivatives which can easily be further functionalized. The reactivity of these outer-ring dienes has been related to the distance between the methylene carbons in the butadiene moiety ($R_{1,4}$), the reaction rate is higher as the distance is shorter. Consequently the dioxolane systems (**2**, **3**) show lower diene reactivity in comparison with the dioxane **1**.[6]

RESULTS AND DISCUSSION

Diels-Alder reaction of C_{60} and 2,3-dimethylene-1,4-dioxane (1)

As we expected, the thermal [4+2] cycloaddition between 2,3-dimethylene-1,4-dioxane (**1**) and [60]fullerene provided the 1:1 cycloaddduct **4** as the major product (73 % yield based on consumed C_{60}).

The matrix assisted laser desorption ionization time of flight mass spectrum (MALDITOF MS) of this monoadduct displays a peak at 834 amu besides a base peak with m/e 721 due to the C_{60} fragment. The ^1H NMR spectrum of **4** presents only two singlets at 4.03 and 4.39 ppm, indicating that the rate of the ring inversion in the cyclohexene is faster than the NMR time scale at room temperature.[7] The ^{13}C NMR spectrum in the fullerene region contains 16 signals as well as a peak at 66.31 ppm characteristic of those quaternary sp^3-hybridized carbons that constitute the point of attachment of the cyclohexyl moiety. All these data support the predicted C_{2v} symmetry with 6-6 closed structure for this cycloadduct.

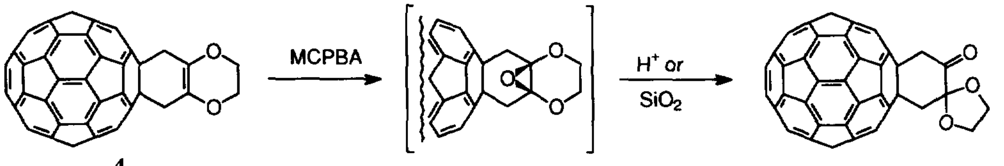


However, short exposure of a non-degassed solution of **4** to the ambient light causes a rapid decomposition yielding a more polar compound in the HPLC analysis. This oxygen and light sensitivity of **4** makes its isolation extremely difficult. Presumably the presence of a photosensitizer (the dihydrofullerene) and a photooxidizable group (the electron rich alkene in the cyclohexene moiety) in the monoadduct induces an ene reaction in the presence of singlet oxygen.

To confirm this hypothesis a toluene solution of **4** saturated with oxygen was irradiated (420 nm light). The new product presents a MALDITOF MS with a molecular ion peak at 865 amu (32 units more than the cycloadduct C_{60}:**1**). The ^1H NMR spectrum is extremely different, and selective decoupling experiments indicate that the dioxane ring still remains in the structure and the cyclohexyl fragment has no conformational flexibility (two doublets at 4.36 and 3.91 ppm), furthermore a new proton appears as a singlet at 6.58 ppm.

Due to the low solubility and the high asymmetry (C_1, 60 different fullerenic carbons) it was not possible to obtain a completely resolved ^{13}C NMR spectrum in the fullerene region, however all the data are in agreement with the hydroperoxide derivative **5**.

The high reactivity of the electron rich alkene in **4** prompted us to essay further derivatizations. We attempted an epoxidation of this double bond that subsequently could be hydrolyzed yielding a 1,2-diketone fused [60]fullerene. However, the epoxide obtained by treating the cycloadduct **4** with *m*-chloroperbenzoic acid (MCPBA) rearranges easily to the monoketal **6** under acid catalysis. Even the acid sites of the silica used during the chromatography produce the transposition.



4

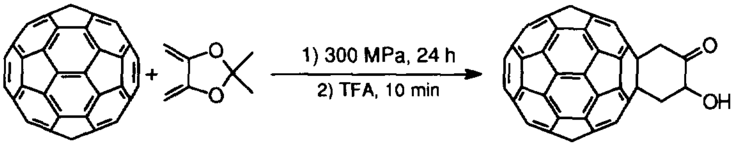
6

The ^1H NMR spectrum of **6** displays two singlets (4.10 and 4.72 ppm) and two multiplets (centered at 4.58 and 4.37 ppm) indicating that the energy of the barrier of inversion for the two boat forms of the molecule is very low. The ^{13}C NMR spectrum presents characteristic peaks for the carbonyl group (204.90 ppm) and the acetalic carbon (103.82 ppm) together with 28 signals (two lines seem to overlap incidentally) in the fullerene region indicating a C_s symmetry. The FT-IR spectrum shows diagnostic absorptions at 1735 (C=O) and 527 cm^{-1}. The mass spectrum using MALDITOF or electronic ionization (EI) techniques exhibits the molecular ion peak with m/e 849 and fragments at 735 and 721 amu. Nevertheless, any attempt to hydrolyze **4** with different acid catalysts failed.[8]

Diels-Alder reaction of C_{60} and 4,5-dimethylene-2,2-dimethyl-1,3-dioxolane (2)

In order to develop a monoadduct which is hydrolyzed easily, we attempted the Diels-Alder reaction with the diene **2**. However, the low diene reactivity of **2** makes the thermal [4+2] cycloaddition with [60]fullerene unsuccessful under usual reaction conditions.[9] Nevertheless, using high pressure conditions (300 Mpa) it is possible to avoid the cycloreversion and to obtain the acyloin derivative **7** after acid hydrolysis.

All efforts to isolate the primary adduct of the Diels-Alder reaction failed, and both silica or neutral alumina catalyze its hydrolysis probably due to steric hindrance between the fullerene surface and the methyl group in the dioxolane system.



2

7

The acyloin derivative **7** presents a ^1H NMR spectrum with two doublets (3.91 and 3.80 ppm) and an ABX system besides the hydroxy group (3.50 ppm). This chiral molecule does not undergo conformational exchange. The ^{13}C NMR confirms this supposition exhibiting a total of 58 carbons (52 lines, six with double integral) in the fullerene region. In the aliphatic region two signals due to the sp^3 carbons of the fullerene moiety (62.00 and 61.49 ppm) complete the 60 signals required. The FT-IR displays an intense signal (1729 cm^{-1}) due to the carbonyl group besides the characteristic bands for the fullerene skeleton and the -OH group. The MALDITOF MS shows a low intensity peak at m/e 807 in addition to the basis peak belonging to the C_{60} fragment (721) however, using a different matrix (9-nitroanthracene) it is possible to identify the molecular ion peak in high intensity. Other techniques like EI or DCI (NH_3 as reagent gas) were not useful.

EXPERIMENTAL

General: - FT-IR: Nicolet 5DXC FT-IR. - UV/Vis: Shimadzu UV-2100. - ^{1}H and ^{13}C NMR: Bruker AM 360 (360 MHz for ^{1}H and 90.5 MHz for ^{13}C), chemical shifts are given in ppm in values relative to $CDCl_3$ ($\delta = 7.24$ for proton and 77 ppm for carbon) as internal standard. - HPLC: Merck Hitachi L-6000 pump, Kontron HPLC detector 432 equipped with a Lichrosorb RP-18 column, eluent: toluene:acetonitrile (1:1), flow: 1.25 ml/min, detection wavelenght: 310 nm. - MALDITOF MS: 16 Kv, 337 nm, using 9-nitroanthracene or 1,8,9-trihydroxyanthracene as matrix. - EI MS: Finnigan MAT 312. - Column chromatography was performed on silica gel 60 (Merck, 63-200 µm) or neutral alumina (ICN Alumina N, Akt. I). - Irradiations were performed in pyrex tubes (10 ml) in a RPR 100 Rayonet Photochemical Chamber Reactor with RPR-4200 Å lamps. - Solvents: toluene, tetrahydrofuran, acetonitrile and *n*-hexane were *per analysis* quality, and used freshly distilled, diethyl ether was dried over KOH and distilled. - [60]Fullerene was used in *gold grade* quality (Hoechst, 99.4 %). - Dienes **1** and **2** were prepared according to literature procedures and stored in ethereal solutions at -77°C.[6]

1´,4´-Dioxa-1´, 2´, 3´, 4´, 5´, 6´, 7´, 8´-tetrahydronaphthalene[6´, 7´:1, 2][60]fullerene (4)

A mixture of C_{60} (101 mg) and 2,3-dimethylene-1,4-dioxane (**1**) (22.37 mg) in toluene (50 ml) was degassed with N_2, protected from light and stirred for 12 h. The solvent was evaporated under reduced pressure, and the resulting black powder purified by colummn chromatography (Al_2O_3, 85 g) with toluene:*n*-hexane (2:1, 500 ml) and toluene:acetonitrile (100:1, 750 ml), recovering C_{60} (32 mg) and 58 mg, (49%, 73 % based on consumed C_{60}) of **4** as a black powder.

- UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 327 (34974), 405 (sh, 4996), 431 (3747). - UV/Vis (toluene): λ_{max} (log ε) = 433 (3229), 547 (sh, 934), 640 (651), 704 (679). - FT-IR (KBr): ν_{max} (cm^{-1}) = 1510, 1318, 1234, 1181, 765, 552, 526. - ^{1}H NMR (CS_2:$CDCl_3$ (9:1)): $\delta = 4.03$ (s, 4H), 4.39 (s, 4H). - ^{13}C NMR (CS_2:$CDCl_3$ (9:1)): $\delta = 155.91$, 147.29, 146.21, 145.91, 145.41, 145.26, 145.14, 144.95, 144.38, 142.82, 142.32, 142.09, 141.79, 141.33, 139.89, 135.29, 118.59, 66.31, 65.66, 42.50. - MALDITOF-MS (1,8,9-trihydroxyanthracene): m/e (%) = 834 (22), 720 (100).

1´, 4´-Dioxa-8a´-hydroperoxy-1´, 2´, 3´, 4´, 6´, 7´, 8´, 8a´-tetrahydronaphthalene[6´, 7´:1, 2][60]fullerene (5)

A toluene solution of **4** (25 mg) was saturated with O_2 and irradiated with 420 nm lamps for 30 min. The solvent was evaporated under reduced pressure obtaining **5** in quantitative yield.

- UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 258 (49722), 328 (sh, 19456), 406 (7721), 434 (6485). - UV/Vis (toluene): λ_{max} (log ε) = 406 (6767), 435 (5451), 647 (1598), 707 (1318). - ^{1}H NMR (C_6D_6): $\delta = 6.58$ (s, 1H), 4,37 (dt, J = 2.6, 11.9, 1H), 4.36 (d, J = 14.3, 1H), 3.99 (dt, J = 3.1, 11.2, 1H), 3.91 (d, J = 14.3, 1H), 3.76

(dt, J = 2.6, 11.2, 1H), 3.44 (dt, J = 3.0, 11.9, 1H). - MALDITOF-MS (1,8,9-trihydroxyanthracene): m/e (%) = 865 (32), 849 (100), 832 (57), 721 (42).

1,2-Dihydro-1,2-(63,63-ethylendioxy-62-oxobutano)[60]fullerene (6)

A N_2 degassed and light protected toluene solution of C_{60} (120 mg, 50 ml) was mixed with 2,3-dimethylene-1,4-dioxane (**1**, 24.1 mg) and stirred for 12 h. A toluene solution (2 ml) of *m*-chloroperbenzoic acid was added (47 mg) and the resulting solution was stirred for 3 h, washed with water, dried and evaporated to dryness. The separation by column chromatography with Al_2O_3 (80 g) resulted in 58 mg of C_{60} (eluted with toluene) and 21 mg (28 % based on consumed C_{60}) of the compound **6**.

- UV/Vis (toluene): λ_{max} (log ε) = 406 (sh, 3558), 434 (2085), 540 (sh, 828), 639 (sh, 276), 705 (184). - FT-IR (KBr): ν_{max} (cm^{-1}) = 2849, 1735, 1462, 1182, 953, 770, 729, 579, 527. - ^1H NMR (CS_2:$CDCl_3$ (9:1)): δ = 4.57 (m, 2H), 4.47 (s, 2H), 4.38 (m, 2H), 4.10 (s, 2H) - ^{13}C NMR (CS_2:$CDCl_3$ (9:1)): δ = 204.90, 155.44, 154.28, 147.58, 147.52, 146.33, 146.25, 146.10, 146.08, 145.66, 145.47, 145.33, 145.31, 145.25, 144.56, 144.54, 144.46, 144.33, 143.08, 142.42, 141.94, 141.91, 141.71, 141.66, 141.51, 141.47, 140.06, 135.29, 135.16, 103.82, 66.29, 62.50, 60.41, 51.69, 47.92. - MALDITOF MS (1,8,9-trihydroxyanthracene): m/e (%) = 849 (60), 735 (100), 721 (12). - EI MS: m/e (%) = 720 (80), 721 (100), 722 (36), 734 (27), 848 (9), 849 (5).

1,2-Dihydro-1,2-(63-hydroxy-62-oxobutano)[60]fullerene (7)

An 1,2-dichlorobenzene solution (20 ml) of C_{60} (105 mg) and 4,5-dimethylene-2,2-dimethyl-1,3-dioxolane (**2**) (83 mg) was degassed with N_2 and introduced in a high pressure apparatus (300 MPa) for 24 h. To the dark brown solution was added TFA (500 μl), stirred for 1 h and evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column (70 g) with toluol and toluene:THF (100:1) as eluent recovering 45 mg of C_{60} and 20 mg of **7** (19 %, 33 % based on consumed C_{60}).

- UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 255 (90049), 309 (29858), 325 (sh, 27489), 407 (sh, 4265), 432 (3317).- UV/Vis (toluene): λ_{max} (log ε) = 407 (sh, 5592), 434 (4265), 537 (sh, 1232), 638 (sh, 616), 704 (379). - FT-IR (KBr): ν_{max} (cm^{1}) = 3435, 1729, 1423, 1267, 1095, 1026, 813, 526. - ^1H NMR (CS_2:$CDCl_3$ (9:1)): δ = 5.13 (dd, J = 5.72, 10.01, 1H), 3.91 (d, J = 16.7, 1H), 3.80 (d, J = 16.7, 1H), 3.50 (brs, 1H), 3.43 (dd, J = 5.72, 13.83, 1H), 3.37 (dd, J = 10.01, 13.83, 1H). - ^{13}C NMR ($Cl_2DCCDCl_2$): δ = 209.61, 154.92, 154.83, 154.75, 154.62, 147.60, 147.55, 146.35, 146.32 (2C), 146.26, 146.14 (2C), 146.11 (2C), 145.56, 145.54, 145.50, 145.49, 145.41, 145.35, 145.28, 145.26 (2C), 145.24, 145.10, 144,62, 144.60, 144.55, 144.37 (2C), 144.27, 143.95, 143.06, 143.01, 142.52, 142.45, 142.44, 142.39, 142.02, 141.94, 141.88 (2C), 141.84, 141.62, 141.60, 141.55, 141.47, 141.42, 141.39, 141.38, 140.27, 140.23, 140.14, 140.04, 135.21, 134.92, 134.85, 134.19, 74.70, 62.00, 61.49, 50.43, 43.91. - MALDITOF MS (1,8,9-trihydroxyanthracene): m/e (%) = 721 (100), 735 (37), 807 (17). - MALDITOF MS (9-nitroanthracene) m/e (%) = 721 (65), 736 (29), 792 (72), 807 (100).

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8. The hydrolysis of **4** has been attempted in two phases: toluene:HCl (2N), toluene:H_2SO_4 (2N), toluene:$HClO_4$ (30%), in one phase: toluene:THF and HCl (2N), H_2SO_4 (2N) or $HClO_4$ (30%), toluene:TFA or p-TsOH, under neutral conditions: toluene:PPTS or using anhydrous conditions: $CHCl_3$:$(CH_3)_3SiI$ without results.
9. The thermal Diels-Alder has been tested increasing the **2**:C_{60} ratio from 1 to 20, and from 0° to 80° C, all the reactions under N_2 atmosphere and protected from light, but only traces of the monoadduct were detected by HPLC.

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