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Oxidation of 3-Alkyl-Substituted 2-Pyrazolino[60]fullerenes: A New Formyl-Containing Building Block for Fullerene Chemistry

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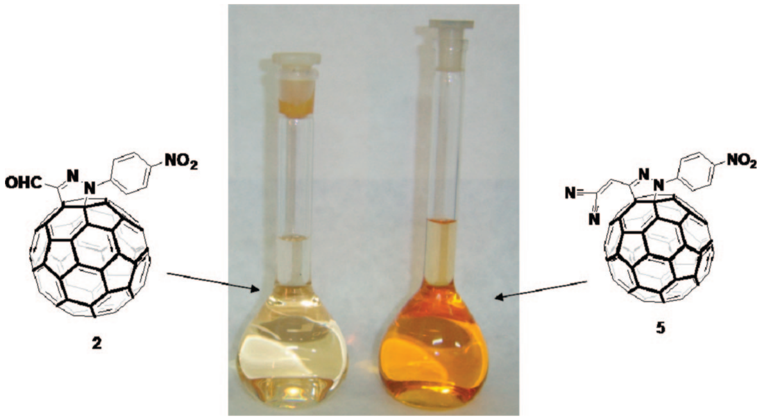
ABSTRACT



A new building block for fullerene chemistry, endowed with a formyl group on C-3 of the 2-pyrazoline ring, has been prepared in a simple two-step synthesis by oxidation of readily available 3-alkyl-substituted 2-pyrazolino[60]fullerenes; the new building block paves the way for the preparation of new light-harvesting fullerenes.

Recent studies on the retro-cycloaddition process of a variety of fullerene cycloadducts, namely, pyrrolidino[3′,4′:1,2][60]-fullerenes[1] and isoxazolino[4′,5′:1,2][60]fullerenes,[2] have shown the usefulness of these reactions as a new protection-deprotection protocol that has been successfully used in the isolation of endohedral metallofullerenes.[1] In contrast to the former studies, the retro-cycloaddition reaction of related 2-pyrazolino[4′,5′:1,2][60]fullerenes afforded, in addition to the expected pristine fullerene, a side product whose nature was not determined.[3]

Studies have stimulated an interest in this new fullerene derivative, and in this Letter we report on its unambiguous structural determination as well as the improvement carried

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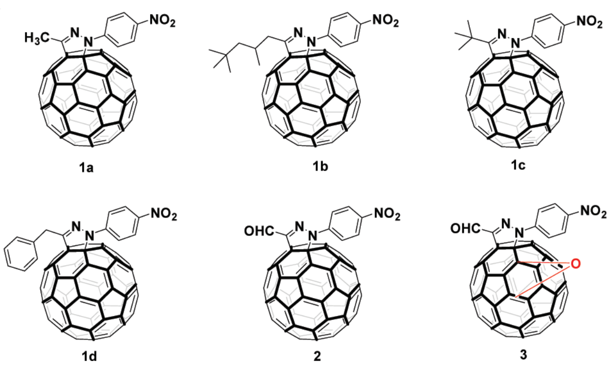

Figure 1. *C*-Alkyl-*N*-aryl-2-pyrazolino[60]fullerenes investigated (**1a**−**d**).

out on its synthetic preparation. Moreover, in order to investigate the interest of the new compound as a building block in fullerene chemistry, it has been used as starting material for the preparation of a new fullerene derivative strongly absorbing in the visible region. Thus, we have carried out new reactions on a variety of 2-pirazolinofullerene derivatives (**1a**−**d**) bearing different substituents on the pyrazoline carbon atom.

Reactions of **1a** and **1b** under standard retro-cycloaddition conditions[3] were monitored by HPLC, and [60]fullerene and the unknown fullerene-based compounds were isolated by column chromatography (toluene). A thorough study of this new compound was performed by using different spectroscopic techniques (FT-IR, ^{1}H and ^{13}C NMR, UV−vis, MS). The results of these analyses clearly indicate that both derivatives (**1a,b**) yield the same side compound endowed with a formyl group on C-3 of the 2-pyrazoline ring, and whose structure corresponds to compound **2**. The study of both reactions by HPLC showed the formation of a small shoulder in addition to aldehyde **2** (Figure S1, Supporting Information), its UV−vis spectrum showing the typical features of another fullerene-based compound with a ^{1}H NMR spectrum very similar to that observed for **2**(Figure 2).

MS analysis revealed that oxidation of a double bond of the fullerene cage takes place, forming an epoxy group on the fullerene sphere, affording the new compound **3**. Thus the peak at 911.8 amu for compound **2**, as well as the peak at 928.8 amu (M + 16) for compound **3** are observed in the MS.

It is important to note that oxidations of alkyl chains in fullerene cycloadducts are not studied, despite their synthetic availability and interest for further chemical transformations

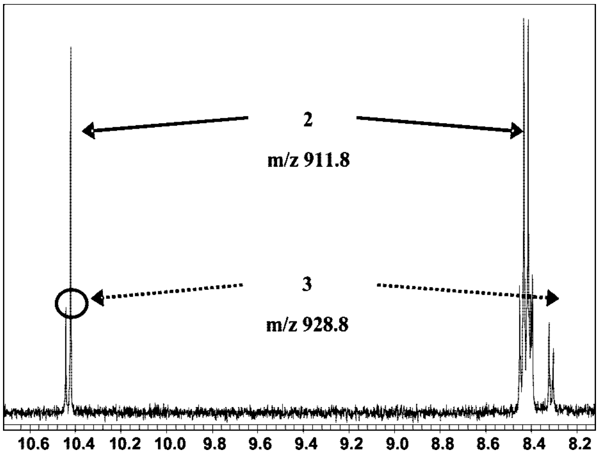

Figure 2. ^{1}H NMR spectrum of compounds **2** and **3**.

For a better understanding of this singular allylic-type oxidation process involving Cu(II) and to evaluate its possible scope, we synthesized two new *C*-Alkyl-*N*-(4-nitrophenyl)-2-pyrazolino[60]fullerene derivatives **1c,d** (Table 1). These molecules bearing a *tert*-butyl group (**1c**) and a benzyl unit (**1d**) were synthesized by 1,3-dipolar cycloaddition of the corresponding nitrile-imines, which were in turn generated from the corresponding hydrazones.[4]

Table 1. Experimental Conditions used for the Retro-cycloaddition Reaction of 2-Pyrazolino[60]fullerenes **1c,d**[a] and Formation of Pristine C_{60} (%) Determined by HPLC

entry	experiment	1c	1d
1	*o*-DCB, 24 h	59	10
2	*o*-DCB, 48 h	60	19
3	MA, 24 h	53	20
4	MA, 48 h	78	24
5	$CuTf_2$, 24 h	83	77
6	$CuTf_2$, 48 h	92	82
7	MA, $CuTf_2$, 24 h	84	36
8	MA, $CuTf_2$, 48 h	96	70

[a] All reactions were performed in *o*-DCB at reflux; MA = 30 equiv of maleic anhydride; $CuTf_2$ = 1 equiv of copper triflate.

The highest efficiency for the retro-cycloaddition process to afford pristine C_{60} (96%) was obtained for derivative **1c**, where formation of compound **2** or **3** was not detected. Derivative **1d** showed a similar trend, and only the retro-cycloaddition process was observed. It is important to note, however, that the retro-cycloaddition rate observed for both derivatives is higher than that observed for other *C*-alkyl-*N*-(4-nitrophenyl)-2-pyrazolino[60]fullerenes.[3]

These experimental findings support the existence of an additional allylic-type oxidation process, which occurs

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simultaneously with the retro-cycloaddition reaction. For **1a** and **1b** both processes take place, and the result (by HPLC) is the formation of compound **2** and C_{60} in an almost 1:1 ratio (see Supporting Information). The behavior observed for **1d** resembles that observed for *C*-aryl-*N*-(4-nitrophenyl)-2-pyrazolino[60]fullerenes, where only the retro-cycloaddition process was detected. Derivative **1c**, which lacks the allylic hydrogen, gives the highest efficiency for the retro-cycloaddition process (96%).

In order to shed some light on the allylic-type oxidation process, we carried out a number of experiments under different conditions. Thus, using the same protocol described above, derivative **1a** was stirred with a catalytic amount (6 % w/w) of copper triflate in refluxing *o*-DCB for 24 h. HPLC analysis showed that compound **1a** did not undergo any oxidative process under these conditions, and only the thermal retro-cycloaddition was observed.

It is worth mentioning that no other catalyst except for copper(II) triflate such as $CuCl_2$, $Cu(OAc)_2$, KTf, or $LaTf_3$ with different anions or metalic cations afforded aldehyde **2** (HPLC) (see Supporting Information).

Interestingly, reaction of compound **1a** under standard conditions in argon atmosphere and using dry *o*-DCB (dried over calcium hydride) as solvent led to the formation of only aldehyde **2**, and no evidence of compound **3** was observed. This result allowed us to conclude that atmospheric oxygen could play a role in the oxidation of the double bond on the fullerene cage to form **3**.

We performed new experiments with **1a** and **1b** under argon atmosphere in order to fully characterize the isolated aldehyde **2**. Both reactions were monitored by HPLC, and evolution of the process revealed the competition between the oxidation and retro-cycloaddition reactions. Once the reaction was completed (by HPLC), we isolated compound **2** and carried out its full structural characterization. Analysis by X-ray diffraction of a single crystal obtained by slow diffusion of hexane vapor into a solution of **1a** in chlorobenzene[5] evidenced the chemical structure of compound **2**, where the formyl group is responsible for the existence of different weak interactions that contribute to stabilize the supramolecular network. Hydrogen bonds ($C-H\cdots O-N$) between nitro and formyl groups (d = 2.377 Å) and $\pi-\pi$ stacking between *p*-NO_2-phenyl units (d = 3.095 Å) led to the formation of fullerene dimers in the crystal (Figure 3).

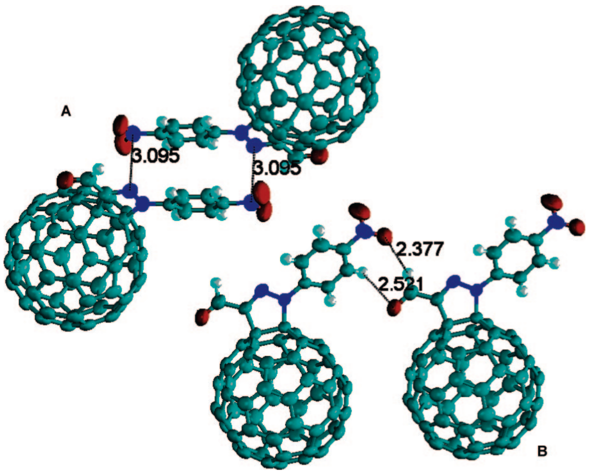

Figure 3. X-ray crystal structure of **2**:[5] (A) $\pi-\pi$ stacking interactions and (B) hydrogen bond interactions.

A plausible explanation for the formation of aldehyde **2** is that the oxidation of **1a** and **1b** takes place through coordination of copper either to the N sp^2 or the C=N in the 2-pyrazole ring and to a neighbor C=C of the C_{60} sphere.[6] Although the mechanism of this oxidation is not yet clear, copper(II) triflate is the reagent that produces the oxidation by assisting the allylic-type oxidation through the formation of Cu/O complexes, which upon formation undergo a rapid decomposition to yield compound **2**.[7] To the best of our knowledge, this unexpected reaction represents the first example of an allylic-type oxidation accomplished in the presence of copper(II) triflate, without using classical oxidants.[8]

To improve the allylic-type oxidation, we carried out the reaction of **1a** with SeO_2 as a classical reagent used in related allylic oxidations. Compound **1a** was heated at reflux in the presence of an excess of selenium dioxide under argon atmosphere, and the reaction was monitored by HPLC. In this case, the reaction was completed in 24 h, and almost no retro-cycloaddition was detected, thus forming compound **2** in 60% yield.

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(5) Crystal data: $C_{68}H_5N_3O_3{\cdot}1.5(C_6H_5Cl)$, M_r = 1080.07, red thin plate (0.6 × 0.6 × 0.04 mm^3), triclinic, space group *P*-1, a = 9.9093(8) Å, b = 10.0293(8) Å, c = 24.979(2) Å, α = 80.616(2)°, β = 85.699(1)°, γ = 62.232(1)°, V = 2167.2(3) Å^3, Z = 2, ρ_{calcd} = 1.655 g cm^{-3}, $F(000)$ = 1089, μ = 0.191 mm^{-1}, $2\theta_{max}$ = 50.0°, T = 296(2) K, 7567 unique reflections [R(int) = 0.1106], $R1$ = 0.0510, $wR2$ = 0.1454 (all data), GOF($F2$) = 0.957, N0/NV = 7567/769, highest residual electron density 1.289 e Å^{-3}. X-ray diffraction data were measured on a Bruker Smart CCD diffractometer, with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 35 mA. The intensity data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure of 20 s covered 0.3 in ω. Reflection range for the data collection were 1.65° < θ < 25.0°. The first 100 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. Structure solution and refinement: The structure was solved by direct methods. The refinement was done by full matrix least-squares procedures on *F*2 (SHELXTL version 5.1). The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated at their geometrical positions and refined as riding on their respective carbon atoms except H2 bonded to C2 atom (from formyl group) which was located from Fourier synthesis difference and the coordinates were refined. CCDC 687339 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

(6) To shed light on the influence of the fullerene unit, we performed the same experiments on a similar 2-pyrazolino-based molecule, 3-methyl-1-phenylpyrazole without the fullerene moiety. TLC analysis of reaction of this compound with copper(II) triflate in *o*-DCB at reflux for 2 days revealed that this derivative does not undergo any oxidation process.

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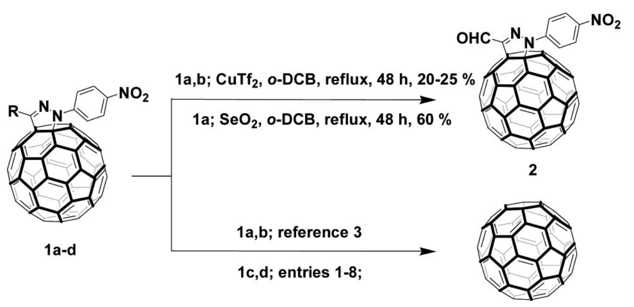
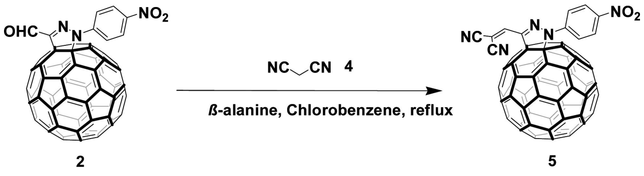
Scheme 1



Compound **2** bearing a formyl group on the pyrazoline ring is suitably functionalized to carry out a wide variety of further chemical transformations affording new and appealing derivatives. As an immediate application of **2**, we have carried out its Knoevenagel condensation with malononitrile (**4**) to form the dicyanovinylene derivative (**5**) in moderate yield (31%) (Scheme 2). The structure of **5** was determined by spectroscopic measurements (UV−vis, FTIR, ^{1}H and ^{13}C NMR, MS). Thus, the presence of the conjugated cyano groups was confirmed by the intense band at 2222 cm^{-1} in the FT-IR spectrum. The ^{1}H NMR spectrum of **5** shows, in addition to the aromatic protons as two doublets centered at 8.44 and 8.50 ppm, the diagnostic presence of the vinyl proton at 8.07 ppm. Interestingly, the organic addend on the fullerene sphere results in a push−pull moiety due to the electron-accepting ability of the dicyanovinyl unit.

The UV−vis spectrum of compound **5** reveals the strong influence of the dicyanovinylene group on the electronic properties. Thus, in contrast to compounds **1a** and **2** that show similar absorption properties with λ_{max} at around 370 nm, compound **5** presents a strong shift to the visible region with a λ_{max} at 492 nm, with the onset reaching 600 nm (Figure 4). This dramatic change in the electronic properties results in orange-colored solutions of **5** in organic solvents. This finding is very important to prepare new colored fullerenes with stronger absorption properties in the visible region, which are a key issue in the search for new light-harvesting materials for the construction of organic solar cells.

Scheme 2



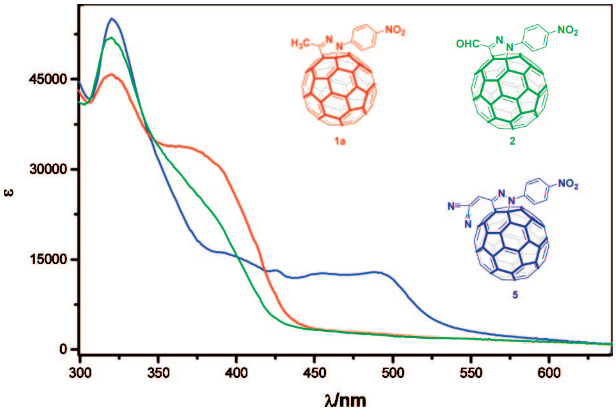


Figure 4. UV−vis spectra of **1a**, **2**, and **5** recorded in methylene chloride (1 × 10^{-5} M).

In summary, in contrast to previous studies on fullerene derivatives, copper(II) triflate is able to oxidate moderately alkyl-substituted 2-pyrazolino[60]fullerenes to form a formyl group through an allylic-type oxidation process whose mechanism is not completely understood. The yield of formyl-containing fullerene is significantly improved by using SeO$_2$ as oxidant reagent. The new compound **2** can be considered an appealing building block that open the way to the preparation of colored fullerenes of interest in PV applications.

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Supporting Information Available: Synthetic procedures and characterization details for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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