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Preparation of Azafullerene $C_{59}NR_5$ and Fullerene Derivative $C_{60}NAr_5$ with a Pyridine Moiety on the Cage Skeleton

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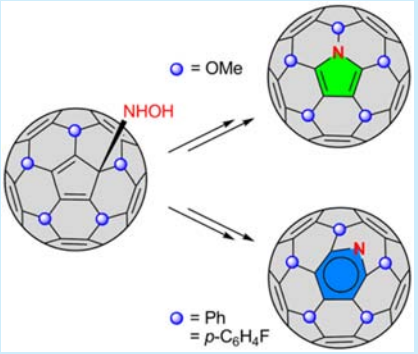
Supporting Information

ABSTRACT: [60]Fullerene hexaadducts $C_{60}R_5Cl$ (R = OMe or Ar) reacted with hydroxylamine to form $C_{60}R_5(NHOH)$ with the hydroxylamino group attached on the central pentagon as in the starting material. Further reactions including treatment with PCl_5 and basic alumina led to the insertion of the nitrogen atom into the fullerene cage skeleton and decarbonylation to form azafullerenes $C_{59}N(H)(OMe)_4$ and $C_{59}N(OMe)_5$. The fullerene derivatives $C_{59}N(CO)R_5$ and $C_{60}NAr_5$ with a pyridinone and a pyridine moiety on the cage skeleton, respectively, were also synthesized starting from the hydroxylamine adducts.



Partial replacement of the carbon atoms on the fullerene cage by one or more heteroatoms can generate numerous heterofullerenes.[1] A number of heterofullerenes have been predicted to be stable through theoretical calculations.[2] However, the preparation of heterofullerene is a challenging task due to their unique spherical structure and the still quite limited method suitable for selective fullerene skeleton modification. The "bottom up" synthesis of pristine C_{60} has been successfully achieved through well designed planar aromatic compounds as precursors.[3] A similar approach to synthesize heterofullerenes such as $C_{57}N_3$ has been proven to be possible[4] but still could not afford macroscopic quantity. Stepwise transformations of pristine fullerene to azafullerene appear to be the only practical method so far for the macroscopic preparation of heterofullerenes.[5] Isolation of endohedral azafullerenes have been reported in low yields from the soot of graphite arc evaporation containing rare earth metals.[6] Recently the water and hydrogen encapsulated azafullerenes $X@C_{59}N$ (X = H_2O, H_2) were prepared starting from C_{60} through organic reactions.[7] The chemical reactivity of azafullerene $C_{59}NR$ has been investigated extensively and both monoadducts $C_{59}NX$ (X = H, alkyl, or aryl)[8] and multiadducts such as $C_{59}NAr_5$ have been reported.[9] Possible applications for azafullerenes have been reported, such as the azafullerene acceptor $OQThC_{59}N$[10a] and $DPC_{59}N$[10c] in bulk heterojunction organic solar cell.[10]

Our previous studies of fullerene-mixed peroxides[11] have shown that hydroxylamine could add to open-cage fullerene which afforded azafullerene upon subsequent rearrangement and decarboxylation.[9c] To explore new methods for the preparation of azafullerene, we applied the hydroxylamine based approach to other more readily available fullerene derivatives such as the cyclopentadienyl fullerene derivatives **1a**−**c**. The work led to the preparation of both azafullerene and fullerene derivatives with a pyridinone or a pyridine moiety on the cage skeleton. In addition the results gave further insight into the mechanism of the hydroxylamine based method for the preparation of azafullerenes.

The methoxyl adduct **1a**[12] was prepared through an improved method, whereas the aryl adducts **1b**[13] and **1c**[14] were prepared following literature methods.[15] Yields of hexaadducts **1a**−**c** were more than 60% in two steps from C_{60}. Replacement of the chlorine atom for the aryl adducts **1b** and **1c** were straightforward by treating with hydroxylammonium sulfate and *N*,*N*-tetramethylethylenediamine (TMEDA) (Scheme 1). The same reaction for the methoxyl adduct **1a** was quite sensitive to the ratio of the reactants and the pH of the solution. The methoxyl groups in **1a** could be partially replaced under strong basic conditions thereby leading to a complicated mixture of products.[12,16] The optimized condition required excessive saturated aqueous hydroxylammonium sulfate solution relative to the base TMEDA. Treatment of the hydroxylamine adducts **2a**−**c** with PCl_5 afforded compounds *rac*-**3a**−**c** with a chlorine atom and an aziridine moiety on the central pentagon.

In an effort to substitute the newly formed chlorine atom on the center pentagon, we treated *rac*-**3a**−**c** with hydroxylamine

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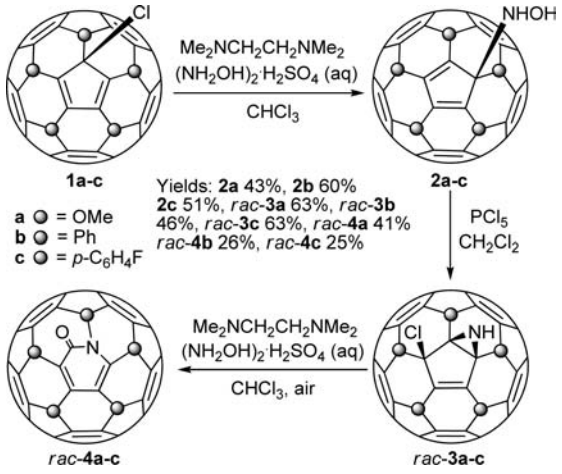
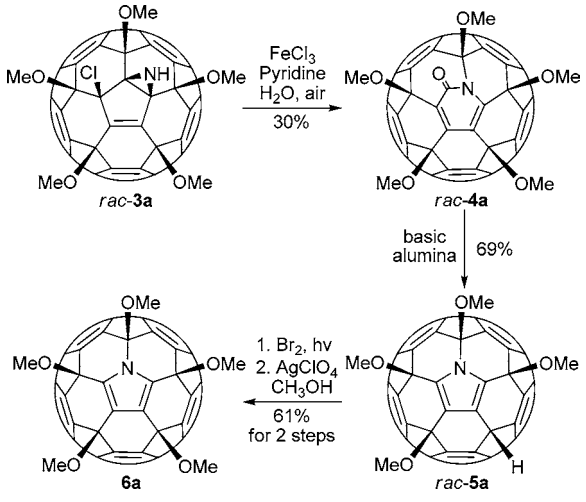
Scheme 1. Hydroxylamine Based Formation of Fullerene Derivatives with a Pyridinone Moiety



and TMEDA. However, instead of the expected substitution product, products *rac*-**4a**−**c** with a pyridinone moiety were obtained (Scheme 1). Even though the expected hydroxylamine substitution reaction did not take place, the combination of hydroxylammonium sulfate and TMEDA appeared to be the most effective reagents for the formation of *rac*-**4a**−**c**. TMEDA alone or other bases such as DABCO, DMAP, DBU, Na_2CO_3, KOH, and KO*t*Bu gave either complicated products or no reaction. The net result of the conversion from *rac*-**3a**−**c** to *rac*-**4a**−**c** is elimination of HCl and addition of an oxygen atom. In the formation of compounds **2a**−**c**, a S_N2' process should be operative since S_N1 would involve an unfavorable antiaromatic cation intermediate. Steric hindrance probably prevented compounds *rac*-**3a**−**c** from a similar S_N2' type substitution reaction. In agreement with this explanation, the ^{1}H NMR spectra of *rac*-**3a**−**c** showed broad signals due to hindered rotations.

To test the possibility of chloride loss as the first step in the conversion of *rac*-**3a**−**c** to *rac*-**4a**−**c**, we treated *rac*-**3a** with $FeCl_3$ and observed the formation of *rac*-**4a** (Scheme 2). To improve the yield we tested various conditions including different solvents and addition of organic bases. The optimized condition for the

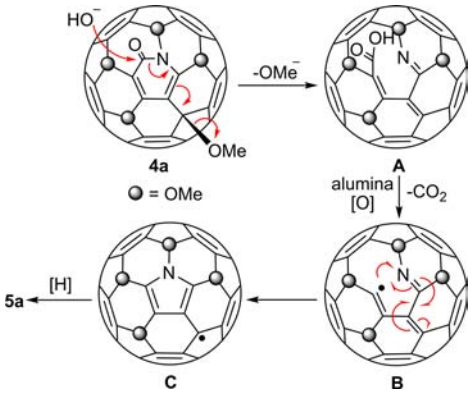
Scheme 2. Lewis Acid Initiated Insertion of Nitrogen Atom and Formation of Azafullerenes



formation of *rac*-**4a** is using pyridine as the solvent. In our previous study,[9c] we have reported the decarbonylation of the pyridinone moiety in a fullerene-mixed peroxide compound with analogous structure to *rac*-**4a**. Following the same procedure, we passed a solution of *rac*-**4a** through a basic alumina column. As expected decarbonylation of the methoxyl derivative *rac*-**4a** took place to form the azafullerene *rac*-**5a**. During the decarbonylation process a methoxyl group was replaced by a hydrogen atom. The hydrogen atom in *rac*-**5a** was converted into a methoxyl group to form the C_s symmetric **6a** through bromination followed by methoxylation. Bromination of *rac*-**5a** afforded both a monobrominated derivative and a bisbrominated derivative, both of which were unstable for full characterization but could be easily converted to the same product **6a**.

The arylpyridinone adducts *rac*-**4b**−**c** remained unchanged when treated with basic alumina. A possible pathway is shown in Scheme 3 for the decarbonylation process of *rac*-**4a**. The

Scheme 3. Proposed Mechanism for Decarbonylation of Pyridinone Moiety and Formation of Azafullerene



carbonyl group in the pyridinone moiety is not fully conjugated with the lone pair of the nitrogen due to ring strain and thus is prone to be attacked by a hydroxyl group to form intermediate **A**. The decarboxylation process from **A** to **B** probably takes place through interaction of the carboxyl group with aluminum ion on the alumina surface. The loss of methoxyl group is essential in the process. The aryl groups in *rac*-**4b**−**c** are not good leaving groups and thus failed to form analogous azafullerene derivatives. In our previous fullerene-mixed peroxide compound, a chlorine atom bound to the same fullerene carbon as the nitrogen atom acted as the leaving group and was replaced by a hydrogen atom.[9c]

Unlike the methoxyl adduct *rac*-**3a**, the aryl adducts *rac*-**3b**−**c** showed different reactivity toward $FeCl_3$. The pyridine containing products **7b**−**c** were isolated besides the expected products *rac*-**4b**−**c** in the reaction between aryl derivatives **3b**−**c** and $FeCl_3$ (Scheme 4). Compounds **7b**−**c** are stable in air for weeks without noticeable decomposition or oxidation. Treating **7b** with either *m*CPBA or H_2O_2 failed to produce *rac*-**4b** under both neutral and basic conditions. The pyridine moiety in **7b**−**c** could be reversibly protonated and deprotonated by TsOH and TMEDA. Heating **7b** in the presence of water and TsOH resulted in hydration of the pyridine moiety and formation of *rac*-**8b**, which slowly converted to *rac*-**4b** in the NMR tube (over a few weeks).

In an effort to optimize the selectivity, we tested other Lewis acids in place of $FeCl_3$. The stronger Lewis acid $AlCl_3$ reacted violently upon addition but compound *rac*-**3b** remained unchanged. The interaction between pyridine and $AlCl_3$ is

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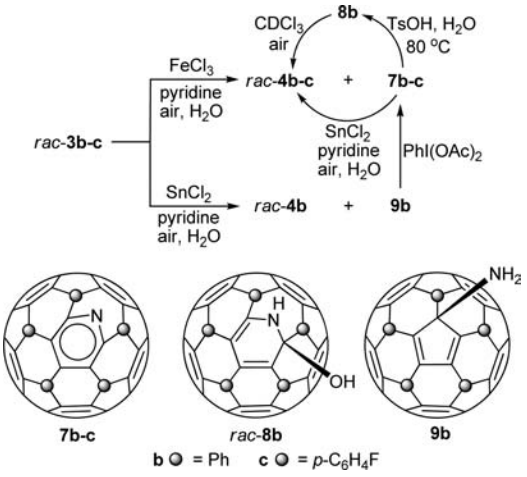
Scheme 4. Lewis Acids Induced Reactions[a]



[a]Yields: $FeCl_3$ reaction, *rac*-**4b** 32%, *rac*-**4c** 35%, **7b** 19%, **7c** 23%; $SnCl_2$ reaction with *rac*-**3b**, *rac*-**4b** 32%, **8b** 27%; $SnCl_2$ reaction with **7b**, *rac*-**4b** 67%; $PhI(OAc)_2$ reaction with **9b**, **7b** 48%; hydration of **7b**, **8b** 82%.

probably too strong thus preventing the interaction of $AlCl_3$ with *rac*-**3b**. There was no reaction with $BiCl_3$ and $SnCl_4$. When *rac*-**3b** was treated with $SnCl_2$, the new product **9b** was isolated besides the pyridinone products *rac*-**4b**. Treating **9b** with $PhI(OAc)_2$ resulted in removal of the hydrogen atoms on the amino group and insertion of the nitrogen atom into the central pentagon to form the pyridine moiety in compound **7b**. Compound **7b** could be effectively converted to *rac*-**4b** by $SnCl_2$ in pyridine under atmospheric condition, which explains the absence of **7b** in the reaction between $SnCl_2$ and *rac*-**3b**. Mechanisms for these Lewis acid induced reactions are not well understood.[17] Oxygen in the air must be involved in the formation of *rac*-**4a-c**. Under nitrogen atmosphere there is hardly any *rac*-**4a−c** even after prolonged reaction time.

Single crystals suitable for X-ray diffraction were obtained for *rac*-**3c** from a mixture of CS_2, $CHCl_3$, and EtOH (Figure 1). The

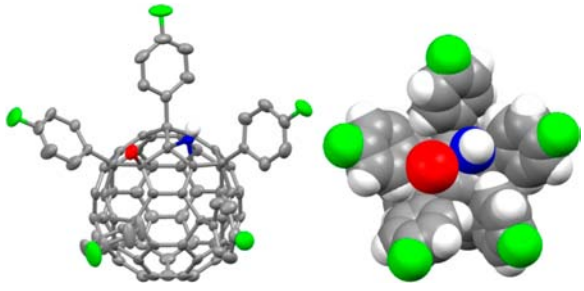


Figure 1. Single-crystal X-ray structure of compound *rac*-**3c**. Ellipsoids are set at 50% probability; hydrogen atoms on the 4-fluorinylphenyl groups in the left figure are omitted for clarity. Only one enantiomer is shown. Color scheme: C, gray; N, blue; F, green; Cl, red; H, white.

X-ray structure is disordered on the center pentagon because of the presence of two enantiomers. There are two sets of positions for the aziridine and the chlorine atom on the central pentagon. The crystal packing showed a head to head and tail to tail pattern. Such dimeric-like pattern has been reported before for a few cyclopentadienyl adducts.[9e,18]

Space-filling model of **3c** showed that rotation of the aryl groups is hindered in particular for the aryl groups adjacent to the chlorine and aziridine groups. In agreement with the structure the NMR spectra of *rac*-**3a−c** showed relatively broad signals for some sp^3 and sp^2 fullerene signals. As a result it is not possible to account for all the expected ^{13}C NMR signals for these three compounds. All the other compounds except *rac*-**3a−c** showed sharp NMR signals in agreement with the expected structures depicted in the Schemes. The C_s symmetric compounds **2a−c**, **6a**, **7b**, and **9b** exhibit the expected ^1H and ^{13}C NMR pattern. The pyridine containing derivative **7b** showed three sp^3 fullerene signals at 77.7, 60.4, and 59.7 ppm in 2:1:2 intensity ratio. There is a unique signal at 174.2 ppm, which can be assigned to the two carbon atoms connected to the nitrogen atom on the pyridine ring. NMR spectra of the pentamethoxyl azafullerene **6a** showed clearly the C_s symmetry, but the cage carbon atom bound to both nitrogen and the methoxyl group was not observed due to its low solubility in common organic solvents including *o*-dichlorobenzene.

The pyridinone containing compounds *rac*-**4a−c** are C_1 symmetric. On the ^{13}C NMR spectrum of *rac*-**4a** and *rac*-**4b**, there are five different sp^3 carbon signals connecting the five methoxyl and five phenyl groups. The pyridinone carbonyl carbon appears at 170.6 and 172.2 ppm for compounds *rac*-**4a** and *rac*-**4b**, respectively. The IR spectrum showed the carbonyl stretching band at 1754, 1744, and 1743 cm^{-1} for *rac*-**4a**, **4b**, and **4c**, respectively. Compound *rac*-**5a** showed the fullerenyl hydrogen at 5.75 ppm on the ^1H NMR spectrum, which is essentially the same as that in the analogous tetraarylmonohydro adduct $C_{59}N(H)Ar_4$ reported by Hirsch et al.[9e] Location of the hydrogen atom in *rac*-**5a** is based on its HMBC NMR data and comparison to the well-established structures of both C_1 symmetric isomers of $C_{59}N(H)Ar_4$. The HMBC spectrum of *rac*-**5a** showed two correlating signals to the sp^2 carbons on the pyrrole ring at 132.6 and 134.5 ppm. The other isomer with the hydrogen at the meta-position of the nitrogen should show just one correlating signal to one of the four sp^2 carbons on the pyrrole ring. As expected, compound *rac*-**8b** showed six sp^3 signals at 91.1, 73.0, 72.9, 61.5, 58.8, and 58.1 ppm.

Atomic nitrogen endohedral complex $N@C_{60}$ has been prepared through nitrogen plasma implantation.[19] Theoretical calculations indicate that a pyridine moiety is formed in the escape process of the encapsulated nitrogen atom.[19b,c] The pyridine moiety in these calculated results resembles the pyridine moiety in compounds **7b−c**. The structure of **7b** was optimized at the M06-2X/6-31G(d,p) theoretical level, which showed that the pyridine moiety is roughly planar with dihedral angles ranging from 10.3° to 11.6°.

In summary, hydroxylamine has been shown to be an effective reagent for the introduction of the nitrogen atom onto the fullerene skeleton. Suitable halofullerene derivatives can react with hydroxylamine to form halogen substituted products, which easily undergo further transformations to eventually form skeleton modified fullerene derivatives, such as the azafullerene and the pyridinone or pyridine containing fullerene derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00872.

Experimental details and selected characterization data for all new compounds (PDF)

Data for **3c** (CIF)

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Notes

The authors declare no competing financial interest.

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Scheme 3 was corrected on April 20, 2016.

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