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Selective preparation of 18-membered open-cage fullerene with one imino and five carbonyl groups on the rim of the orifice

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ABSTRACT

2,6-Diisopropylaniline reacts with an open-cage fullerene derivative with a 11-membered orifice and forms an open-cage derivative containing one imino group on the rim of the expanded orifice. Further treatment with Lewis acids leads to open-cage fullerenes with an 18-membered orifice. Instead of the direct addition process observed before for less bulky anilines, an electron transfer process takes place in the initial step in the present reaction with bulky 2,6-diisopropylaniline. As a result, the chemo-selectivity is completely different affording the mono imino open-cage derivative selectively.

Open-cage fullerenes are fullerene derivatives formed through partial cleavage of the fullerene skeleton carbon-carbon bonds [1-3]. The size of the orifice in open-cage fullerenes are usually defined by the number of atoms on the rim of the orifice. Cleavage of one 5,6-bond on C_{60} forms a 9-membered orifice, whereas one 6,6-bond forms a 10-membered orifice. Consecutive cleavage of three 6,6-bonds around the same pentagon leads a 18-membered orifice. Insertion of a heteroatom such as nitrogen [4], oxygen [5] and sulfur [6] on the rim of orifice has been reported to expand the size of the orifice. Open-cage fullerenes serve as unique molecular containers because of their fully covalent bonded cage structure. Various neutral guest molecules have been inserted into the cavity of open-cage fullerenes with a suitable orifice size including He [7], O_2 [8], HF [9,10], HCCH [11] and CH_3OH [12]. Recently halide anions [13] and LiF and $[BeF]^+$ [14] have been inserted into open-cage fullerene derivatives.

Preparation of open-cage fullerenes is a challenging task due to their unique spherical structure. Classical organic carbon-carbon bond breaking reactions usually results in complicated mixtures of products when applied to fullerenes. It is not uncommon that fullerene chemistry shows special reaction pathways [15-18]. The first open-cage fullerene derivative has a 11-membered orifice, which was reported back in 1995 by Wudl *et al.* [4]. Since then several methods have been reported for the preparation of open-cage fullerenes [1]. Singlet oxygen oxidation is one of the frequently used method, which results in two carbonyl groups on the rim of the orifice per singlet oxygen addition step. The fullerene-peroxide mediated cage-opening method has generated a number of open-cage fullerenes with a relatively large orifice [19,20]. Anilines are very effective reagents for orifice expansion through complicated rearrangement processes [21]. Most of the reported methods were found through serendipity. Based on the reported methods, it is still not possible to rationally design the synthesis of open-cage fullerenes with a specific size of orifice and special functional groups around the rim of the orifice for functional studies. More information is still needed to selectively cleave the fullerene skeleton bonds and prepare open-cage fullerenes for practical application exploration. In the present work, we report the formation of 18-membered open-cage fullerene derivatives through a selective aniline mediated orifice expansion reaction.

In our previous study we have shown that compound **1** react with anilines to form the 14-membered and the 18-membered open-cage fullerene derivatives **2** and **3** depending on the amount of anilines added (Scheme 1) [22,23]. The bis-imino derivative **3** were formed readily in the presence of excess anilines. To obtain the mono-imino derivative **2**, we had to add the aniline very carefully to avoid the formation of the bis-imino derivative **3**. The imino groups in compound **3** are very stable towards hydrolysis. It was not possible to hydrolyze these imino groups into carbonyl groups. We tried to convert **2** into the mono imino analogue of

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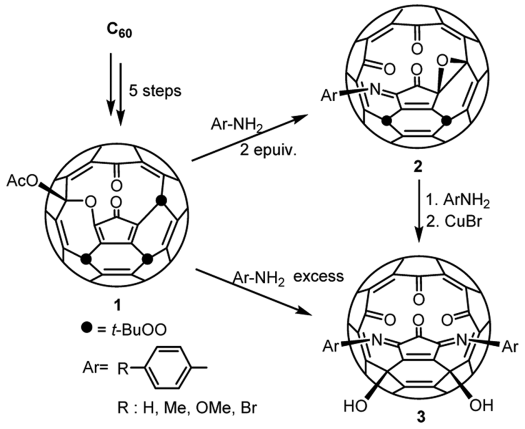
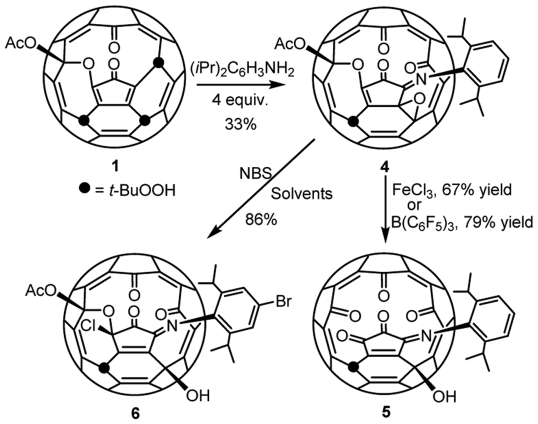


Scheme 1. Reactions of compound **1** with less hindered aniline derivatives.

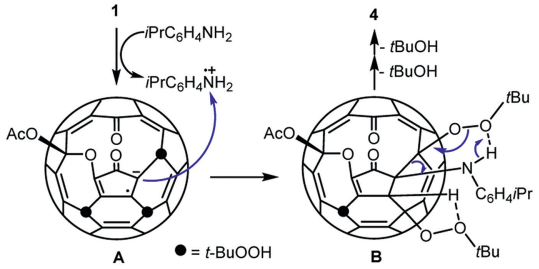


Scheme 2. Reaction of **1** with 2,6-diisopropylaniline and subsequent reactions with NBS and Lewis acids.

compound **3** under various conditions, but only observed decarbonylation derivatives.

All the anilines used previously has little steric hindrance because the substituent is located at either the *para* or *meta*-position on the benzene ring (Scheme 1). In an effort to make mono imino analogue of compound **3**, we tested the reaction of **1** with 2,6-diisopropylaniline which is quite sterically hindered. Instead of the orifice expanded derivative **2** for less hindered anilines, we isolated compound **4** as the major product (Scheme 2). As expected the more sterically hindered 2,6-diisopropylaniline was much less reactive and there was no bis-imino derivative detected even in the presence of four equivalent of 2,6-diisopropylaniline. Interestingly the purity of compound **1** was quite important for the formation of **4**. We had to remove all the impurities by repeated preparative thin layer chromatography (PTLC) purification. Impurities present in compound **1** severely affected the yield of **4**.

Compound **4** has a 15-membered orifice including the oxygen atom on the rim of the orifice. To further expand the orifice, we tried various conditions to hydrolyze the acetal moiety. Both $B(C_6F_5)_3$ and $FeCl_3$ were effective at removing the acetyl group to form compound **5**. The epoxy moiety was converted into a hydroxyl group along with the shift of the C=C double bond on the lifted pentagon ring. This double bond shift also took place in the epoxide opening process with *N*-bromosuccinimide (NBS) to form compound **6**. The phenyl group was also brominated at the 4-postion during the reaction with NBS. The imino group remains unchanged under both the conditions for the formation of **5** and **6**. Surprisingly there is a chloro atom on the lifted pentagon instead of the bromine atom. The original bromine atom was apparently replaced by a chlorine atom from chloride impurities such HCl in the solvents during the chromatography purification procedure. Silica gel could be another possible source for chloride. Flood *et al.* has reported that chloride on silica gel was extracted into their chloride recognition molecule [24].

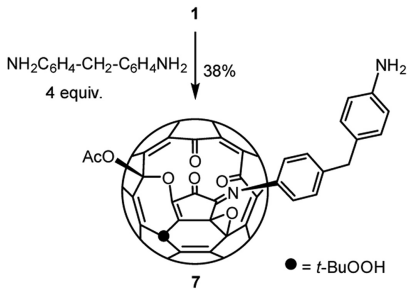


Scheme 3. Proposed mechanism for the reaction between 2,6-diisopropylaniline and compound **1**.

The structure of **4** is quite different from that of **2**. The acetyl group is still present in **4**. A possible mechanism is shown in Scheme 3 for the formation of **4**. Unlike the less hindered anilines which act as nucleophilic reagents and attack the acetyl group in the first step, the present sterically hindered 2,6-diisopropylaniline acts as an reductant in the first step. The initial electron transfer process forms intermediate **A**. Among the various resonance forms, structure **A** is the most favored because the negative chrge is next to the electron withdrawing carbonyl group, and the radical can form conjugation with the C=C double bond (an ally radical). The other alternative structure with the negative charge also next to the carbonyl group but on the oxygen bonded carbon is less favorable because the electron donating ether oxygen would make it less stable. The charged nature of the aniline radical cation and the radical anion **A** provides driving force for the formation of intermediate **B** even though steric hindrance is still quite high. The cleavage of the fullerene C–C bond may take place through the six-membered transition state shown in **B**. Cleavage of the *t*butylperoxo O–O bond helps to reduce the steric hindrance around the bulky 2,6-diisopropylanilino group. It is possible that the *t*butylperoxo O–O bond was cleaved before the fullerene C–C bond.

The above electron transfer pathway is further supported by the reaction between **1** and 4,4′-methylenedianiline, the major product of which is compound **7** analogous to compound **4**. Presence of the two amino groups facilitates electron transfer process. In addition, the methyleneanilino group is also a bulky group and may prevent direct addition through interactions with the *t*butylperoxo groups. Only after the electron transfer process to form the charged radical ions, the enhanced attractions between the charged radical species can overcome the steric hindrance. The remaining anilino group in **7** showed limited reactivity towards **1**. There was no dimeric product detected. Steric hindrance of the fullerene cage and the addends on it apparently makes the aniline moiety in compound **7** unreactive towards another molecule of **1**.

All the new compounds are C_1 symmetric. Their NMR spectra agree with the structures shown in Schemes 2 and 4. The phenyl group in the 2,6-diisopropylaniline derivatives **4**, **5** and **6** showed two sets of distinct signals for the two isopropyl groups, *i.e.*, two multiplets for the two tertiary C–H protons and four doublets for the four CH_3 protons. So the rotation is restricted for both the N-Ar and the ^{i}Pr-Ar single bonds. The phenyl group in the 4,4′-methylenedianiline derivative **7** showed free rotation, each of the phenyl rings showed just two doublets for the four protons. The carbonyl groups showed the expected number of signals above 177 ppm on the ^{13}C NMR spectra. The two dimensional HMBC spectra of compounds **6** and **7** revealed the acetyl carbonyl carbon



Scheme 4. Reaction between compound **1** and 4,4′-methylenedianiline.

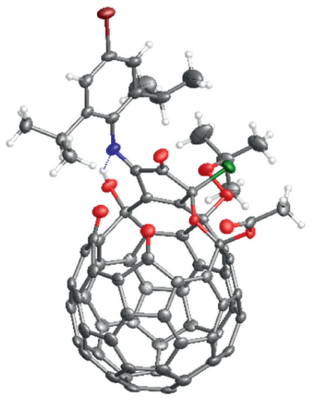


Fig. 1. Single-crystal X-ray structure of **6**. Ellipsoids were drawn at the 50% level. Color key: gray, carbon; red, oxygen; blue, nitrogen; green, chlorine; wine red, bromine. Dashed blue line indicates H-bond.

at 167.30 and 167.68 ppm respectively. The imino carbon is difficult to assign conclusively because its chemical shift is similar to the fullerene skeleton carbon signals. The expected molecular ion signals were observed on the mass spectra. The mass spectrum of **6** showed clearly the presence of one Cl and one Br atom.

The structure of compound **6** is further confirmed by single crystal X-ray diffraction analysis (Fig. 1). The unit cell contains two pairs of enantiomers. The hydroxyl group forms H-bond with the imino nitrogen atom. The N···H-O distance is 2.861 Å. The phenyl ring is almost perpendicular to the lifted pentagon ring, leaving the two isopropyl groups away from the adjacent carbonyl oxygen atom on the pentagon. Space-filling model indicates that rotation of the phenyl group is hindered mainly by the carbonyl oxygen group. The C=O bond distance (1.191(4) Å) of the carbonyl group on the lifted pentagon is slightly shorter than those of the other two carbonyl groups (1.208(4), 1.203(4) Å), as a result of less distortion by the spherical cage structure.

In conclusion, steric effect plays an important role in the reaction between aniline and open-cage fullerene derivative **1**. Less hindered anilines act as nucleophiles and directly attack less crowded electron positive positions around the rim of the orifice. The bulky aniline follows an electron transfer pathway as the first step to form ionic radical intermediates, which than interact with each other to form an aniline derivative. As a result of their different reaction mechanism, the structure of the aniline added derivatives can be quite different. Unlike the less hindered anilines which easily form open-cage fullerenes with two imino groups, bulky anilines gave open-cage fullerenes with just one imino group, which is quite stable towards hydrolysis. Further work is underway to explore the chemical reactivity and the application of open-cage fullerene as ligands for metal complexes [25].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Linlin Yu: Investigation. **Xueli Liu:** Investigation. **Rui Gao:** Investigation. **Jialin Ming:** Funding acquisition. **Yi Qiu:** Investigation. **Jie Su:** Investigation. **Liangbing Gan:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110382.

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