Heterofullerenes

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Fullerene Doping: Preparation of Azafullerene $C_{59}NH$ and Oxafulleroids $C_{59}O_3$ and $C_{60}O_4$**

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Dedicated to Professor Chunhui Huang on the occasion of her 80th birthday

Controlled cleavage of fullerene skeleton bonds and replacement of fullerene cage carbon atom(s) with other heteroatoms is a rational fullerene doping process that could generate many novel spherical compounds with interesting properties for practical applications.[1] The first heterofullerenes, borafullerenes $C_{60-n}B_n$ ($n = 1$–6), were formed by laser vaporization of a graphite/boron nitride composite disk.[2] Certain nitrogen-containing fullerene derivatives were converted into azafullerene ions in the gas phase during mass spectroscopic analysis.[3] Other elements, such as O,[4] As,[5] P,[6] and Si,[7] have also been reported to form doped fullerenes. Furthermore, the transition metals Fe, Co, Ni, Rh, Ir,[8] and Pt[9] can also be doped into fullerenes to form species such as $C_{59}Pt^+$ and $C_{58}Pt^-$. All of these heterofullerenes except the azafullerene were only observed in the gas phase and were characterized by mass spectroscopy.

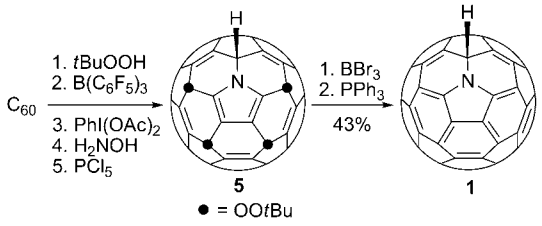
To date, macroscopic preparation of heterofullerene is limited just to azafullerenes, despite numerous studies. In 1995, Wudl reported the first macroscopic synthesis of azafullerene $C_{59}N(R)$ and the dimer $(C_{59}N)_2$ using a ketolactam fullerene derivative as the precursor.[10] Soon after, Hirsch reported a second synthetic method starting from a bisazafulleroid.[11] Based on the chemistry of fullerene-mixed peroxides, we have reported the preparation of azafullerene peroxide derivatives $C_{59}N(R)(OOtBu)_4$ (R = H, OH, Br).[12] Endohedral azafullerenes $M_2@C_{79}N$[13a,c] (M = Tb, Y, Gd) and $La_3N@C_{79}N$[13b] were isolated from the soot of a composite graphite rod containing the corresponding metal oxide.

In theory, a number of heterofullerenes containing one or more heteroatoms have been investigated, such as B,[14] Si,[15] Ti,[16] N,[17] O,[18] S,[19] and Xe,[20] among which oxygen-doped fullerenes have been relatively more intensively studied. The neutral $C_{59}O$ and positive species $C_{59}O^{2+}$ were predicted to have cage-opened and cage-closed structures, respectively.[19] Various isomers of $C_{60-x}O_y$ ($x = 0$–2, $y = 0$–4)[18] were calculated to investigate the oxidation products of C_{60} fullerite by interstitial oxygen. The mixed heterofullerenes $C_{56}X_2Y$ (X = N, P; Y = O, S)[21] are shown to be as chemically stable as C_{60}.

We have reported the preparation of a series of fullerene-mixed peroxides $C_{60}(O)_x(OOtBu)_y$ ($x = 0$, 1; $y = 2$, 4, 6).[22] Further investigation of the reactivity of these peroxides indicates that they are excellent precursors for selective fullerene skeleton bond cleavage. A number of open-cage fullerene derivatives, some of which have a orifice large enough to encapsulate a water molecule, were prepared starting from either $C_{60}(O)(OOtBu)_4$ or $C_{60}(OOtBu)_6$.[23] Herein we report the preparation of the compounds $C_{59}NH$ (**1**), $C_{59}O_3$ (**2**), and $C_{60}O_4$ (**3**,**4**) through peroxide-mediated reactions and selective formation of $C_{58}O_2$ in the gas phase.

The azafullerene derivative **5** was prepared as previously reported.[12] Presence of the *tert*-butylperoxo groups provides excellent solubility and rich chemistry for such oxygen-rich azafullerenes. However, the facile reactivity of the peroxo groups hinders further investigation for materials applications, such as solar-cell devices. To remove the peroxo groups and prepare the parent azafullerene, we tried many unsuccessful methods including exhaustive reduction by excess Na/K metal. Inspired by the BBr_3-mediated efficient cleavage of ethers under mild conditions,[24] we then treated **5** with BBr_3. The reaction was complete within a few minutes. The solution was then quenched with water. Further treatment of the solution with PPh_3 afforded the hydroazafullerene **1** (Scheme 1).

Encouraged by the successful preparation of azafullerene **1**, we then extended the BBr_3 reaction to the furan-embedded fullerene derivative **6**, which was prepared from C_{60} in three steps (Scheme 2).[25] Both the peroxo and hydroxy groups



Scheme 1. Synthesis of azafullerene (**1**). See the Supporting Information for details.

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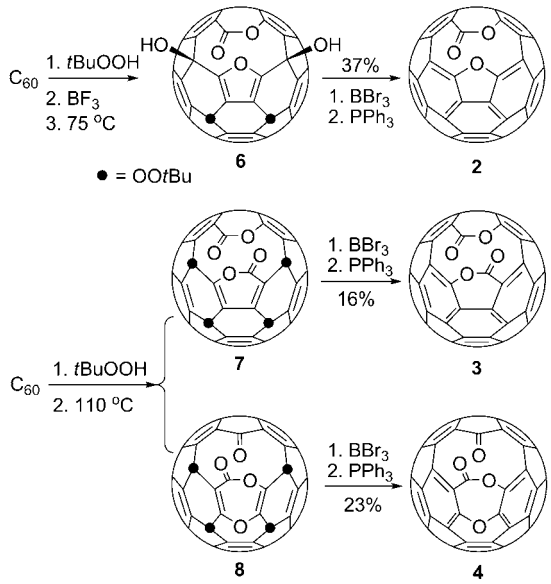
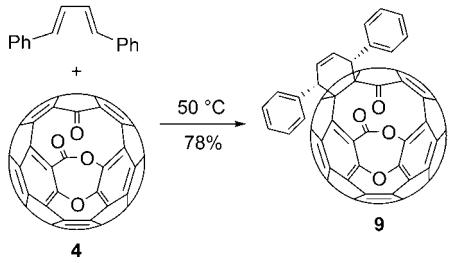


Scheme 2. Synthesis of oxafulleroids. See the Supporting Information for details.

were removed from the cage under the conditions used. Similarly, the isomeric compounds **7** and **8** with lactone and/or ketone moieties, both of which were prepared from C_{60} in two steps from the same reaction,[26] could react with BBr_3/PPh_3 to form the oxafulleroids **3** and **4**, respectively. It is noteworthy that the lactone moiety is inert towards BBr_3 and the aqueous acidic condition during subsequent water quenching. Heating a sample of oxafulleroid **3** in dichlorobenzene at 180 °C for 30 minutes resulted in little change. The oxofulleroids **2**–**4** can be stored under normal atmospheric conditions for weeks without noticeable change.

Spectroscopic data of the new compounds are in agreement with the structures depicted in Schemes 1 and 2. The MS and ^{1}H NMR spectra of the azafullerene **1** are the same as those reported in the literature.[10] The characteristic C=O stretching bands of the oxafulleroids **2**–**4** in the IR spectra showed little change compared to their corresponding precursors **6**–**8**, which indicates that removal of the *tert*-butylperoxo and hydroxy groups does not change the skeleton structure significantly. For example, the C=O stretching bands of the oxafulleroids **6** and **2** appear at 1775 and 1781 cm^{-1}, respectively. The ^{13}C NMR spectrum also showed a similar phenomenon. Beside disappearance of the sp^3 carbon signals, other fullerene signals of oxafulleroids **2**–**4** are quite similar to those of their precursors. The unique carbonyl signal of oxafulleroid **4** appears at 196.1 ppm as compared to that of its precursor **8** (193.5 ppm). The ^{13}C NMR spectrum of the bis(lactone) derivative **3** shows a C_2-symmetric pattern with 30 signals in the range from 118 to 156 ppm.

To obtain more conclusive data about the structural assignments, we tried to grow single crystals for the new compounds but were unsuccessful. In our previous studies, we have verified the structure of precursors **5**–**8** by single X-ray crystal structures of their closely related derivatives.[12,25,26] By using the same strategy, we converted compound **4** into the



Scheme 3. Diels–Alder addition reaction of **4**.

Diels–Alder derivative **9** (Scheme 3). The reaction was almost quantitative based on converted starting material. The excellent regioselectivity should be due to the strong electron-withdrawing effects of the ketone and lactone carbonyl groups. The *endo* isomer was obtained exclusively as in most Diels–Alder reactions. In contrast to the facile reaction of **4**, the dilactone oxafuleroid **3** did not react with 1,4-diphenylbutadiene under similar conditions.

Single crystals of **9** were obtained by slow evaporation of its toluene solution at room temperature. The X-ray diffraction analysis (Figure 1) confirmed the structure proposed above. A total of four molecules, as two enantiomeric pairs,

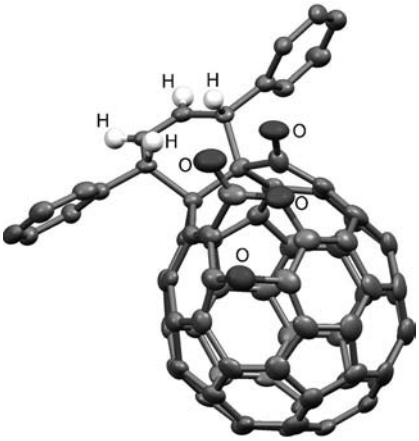
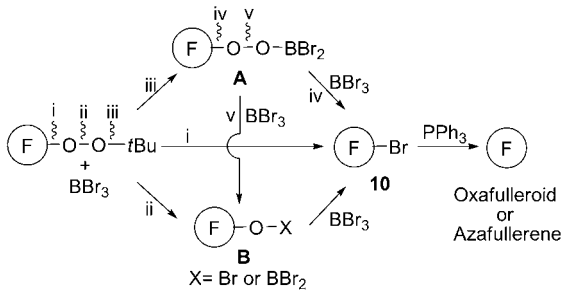


Figure 1. Single-crystal X-ray diffraction structure of **9**. Ellipsoids are set at 50% probability; H atoms on the phenyl groups are omitted for clarity.

were present in the unit cell. The fullerene-fused cyclohexadiene ring adopts a boat conformation with the two phenyl groups in the equatorial positions. The distance between the two fullerene carbons bound to the same ether oxygen atom is 2.134 Å, which clearly rules out the presence of an epoxy moiety. This is in agreement with the lack of sp^3 carbon signal for the fullerene skeleton in the ^{13}C NMR spectra of **4** and **9**. The bonding distances of the carbonyl C=O and the lactone C=O are 1.245 and 1.206 Å respectively.

A possible mechanism for the BBr_3-assisted removal of peroxo groups is shown in Scheme 4. In our previous studies, we have shown that any of the three single bonds in the C_{60}–O–O–*t*Bu moiety could be cleaved in the presence of Lewis acids, such as BF_3 and $FeCl_3$.[22,23] The selectivity depends on



Scheme 4. Possible mechanism of the BBr_3 reaction with fullerene-mixed peroxides.[27]

the reaction conditions and the local structure of the fullerene-mixed peroxides. Cleavage of the C_{60}–O will give the bromo derivative **10** in one step; cleavage of the O–O and O–*t*Bu bonds will results in the intermediates **A** and **B**, respectively. Presence of a large excess of BBr_3 makes it possible for both intermediates **A** and **B** to react further with BBr_3 to form the bromo derivative **10**. Thus all three pathways could lead to the formation **10**.[27]

Formation of molecular bromine was observed in the BBr_3 reaction. To reduce the bromine, we quenched the solution with aqueous $Na_2S_2O_3$ in the preparation of **2**–**4**. BBr_3 is known to generate molecular bromine upon reaction with certain quinone derivatives.[28] Removal of bromo addends from **10** with PPh_3 is analogous to the dehalogenation of halofullerene derivatives with PPh_3.[29]

It was not possible to fully characterize the bromo derivative **10** owing to its facile reactivity, which presumably involves replacement of Br by OH and related reactions. Compound **10** obtained from **5**, the precursor for the hydroazafullerene **1**, has signals in the mass spectrum corresponding to the presence of a bromine atom added to the cage. In the preparation of the oxafulleroid **2**, we isolated the bromo derivative **10**, which showed a clear signal for $C_{58}O_2$ at *m*/*z* 728 along with the major signal from **2** (*m*/*z* 756.1) in the MALDI-TOF mass spectrum (Figure 2). A number of isomers are possible for the formula $C_{58}O_2$. The dioxafullerene isomer shown in Figure 2 with analogous structure to C_{60} was the most stable isomer among the four isomers considered for $C_{58}O_2$ according to theoretical calculations by Gutsev et al.[18] Considering the structure of compound **6** and fragmentation pattern of the lactone moiety, we believe that the signal at *m*/*z* 728.1 corresponds to the pure isomer with the two oxygen atoms at a 6,6-junction, as shown in Figure 2.

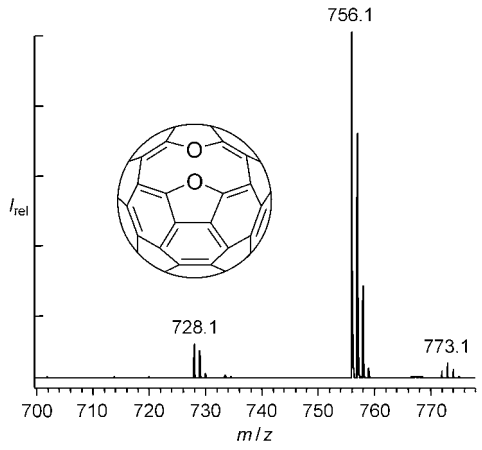


Figure 2. MALDI-TOF mass spectrum of **10** from **6** (see Scheme 4).

The signal at *m*/*z* 773.1 in Figure 2 corresponds to the addition of OH to **2**, which is probably due to hydrolysis of the lactone moiety. Thus a possible pathway for the formation of $C_{58}O_2$ is hydrolysis of the lactone moiety followed by decarboxylation. Interestingly, the mass spectrum of pure **2** showed the molecular ion peak at *m*/*z* 756 as the only signal under the same conditions. The mass spectrum of the peroxide **6** did not show recognizable peak for $C_{58}O_2$ either;[25] therefore, the bromo addends in **10** must play an important role in the formation of $C_{58}O_2$. Presence of bromo addends in **10** may alternate the local strain around the furan lactone, facilitating extrusion of the carbonyl carbon. Furthermore, the bromo addends can be easily removed from the cage, unlike the OH and peroxo groups in **6**. A detailed study is still needed to elucidate the mechanism for $C_{58}O_2$ formation.

Fullerene oxides $C_{60}O_n$ have been extensively studied.[30] Many methods have been reported for their synthesis. The mass spectra of $C_{60}O_n$ usually show quite rich fragmentation products. In the LDI-FTMS of $C_{60}O_2$, a signal corresponding to $C_{58}O_2$ was observed as a minor peak among many other more intense fragmentation products.[31] The ozonolysis product of C_{60} also leads to a minor signal for $C_{58}O_2$ in the SALI-MS (surface analysis by laser ionization).[32] Collision-induced dissociation of $C_{60}O_{2-4}^-$ in the gas phase yielded $C_{60-x}O_{n-x}^-$, and in particular $C_{59}O^-$.[33] The present work provides a unique precursor for the selective formation $C_{58}O_2$ in the gas phase under MALDI-TOF conditions.

In summary, synthetic procedures for the preparation of azafullerene and oxafulleroids have been developed involving BBr_3-mediated removal of peroxo addends as a key step. The oxafulleroids are potential precursors for the preparation of oxafullerenes as shown by the mass spectrum. Preliminary results indicate that the lactone moiety of the oxafulleroids show moderate reactivity towards nucleophiles, such as anilines. Replacement of the oxygen atom with other heteroatoms, such as sulfur, can also be envisioned based on the present results. Further work is in progress to prepare the dioxafullerene $C_{58}O_2$ and other heterofullerenes.

Experimental Section

2: BBr_3 (0.08 mL, 0.8 mmol) was added to a stirred solution of compound **6**[25] (44.8 mg, 0.0463 mmol) in toluene (10 mL) at room temperature. Toluene (40 mL) was added after about 15 min, and then the reaction was quenched by adding $Na_2S_2O_3$ aqueous solution. The organic layer was separated and treated with PPh_3 (45 mg, 0.17 mmol), and the solvent was removed under vacuum. The residue was chromatographed on silica gel, eluting with toluene/CS_2 (1:1). The first yellow-green band was collected and evaporated to give compound **2** (13 mg, 37%). ^{13}C NMR (125 MHz, CS_2/C_6D_6; all signals represent 1C except as noted): $\delta = 164.07$, 160.96, 159.42, 150.25, 148.21, 147.52, 147.23, 147.07, 147.04, 146.79, 146.77 (2C), 146.69, 146.63, 146.55, 146.32, 146.23 (4C), 146.22, 146.07, 146.01 (2C),

145.98, 145.80, 145.42, 145.01, 144.07, 143.81, 143.68, 143.53, 143.50, 143.45, 143.20, 142.91, 142.66, 142.52, 142.46, 142.38, 142.30, 142.29, 141.88, 141.86, 141.17, 140.58, 140.56, 138.40, 137.93, 137.78, 135.92, 135.49, 133.95, 132.79, 131.99, 131.42, 128.75, 127.03, 121.09 ppm. FTIR (microscope): 1781, 1557, 1510, 1425, 1368, 1297, 1283, 1229, 1163, 1128, 1082, 1049, 1012, 909, 782 cm^{-1}. MALDI-TOF: $C_{59}O_3$ calcd 756.0, found 756.1.

Crystal data for **9**: Crystal size, $0.25 \times 0.23 \times 0.21$ mm^3, monoclinic, space group $P2_1/n$, $a = 17.005(4)$, $b = 15.102(3)$, $c = 19.160(5)$ Å, $\beta = 114.948(3)$, $V = 2342.8(8)$ $Å^3$, $Z = 4$, $d_{calcd} = 1.612$ $g\,cm^{-3}$; $T = 173(2)$ K; 30348 reflections collected, 10217 independent ($R_{int} = 0.0701$) included in the refinement; min/max transmission = 1.000 and 0.6863; refinement method: full-matrix least-squares on F^2. Final R indices $[I > 2\sigma(I)]$ $R1 = 0.1444$, $wR2 = 0.3589$, R indices (all data) $R1 = 0.1660$, $wR2 = 0.3749$.

CCDC 872700 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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