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Electrochemical and H/D-Labeling Study of Oxazolino[60]Fullerene Rearrangement

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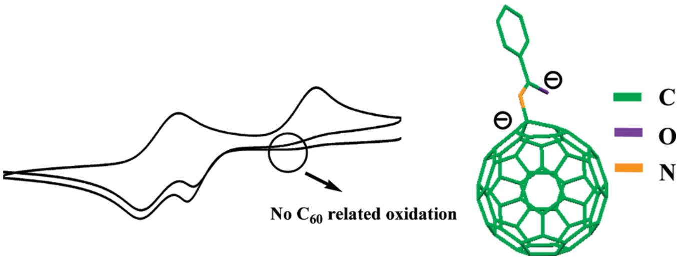

Isomerization of an oxazoline cycle from a [6,6]- to [5,6]-junction on the C_{60} sphere of dianionic [60]fullero-oxazoline ($\mathbf{1}^{2-}$) during a 1,4-addition is studied by electrochemistry and a stepwise addition of $PhCH_2Br$ and $PhCD_2Br$. Cyclic voltammerty of the in situ generated $\mathbf{1}^{2-}$ shows a very unusual positive shift for the anodic peak corresponding to the oxidation of $\mathbf{1}^{2-}$, indicating that the C_{60} cage of dianionic **1** bears only one unit negative charge due to the heterolytic cleavage of the $C_{60}-O$ bond. Further study with a stepwise addition of $PhCH_2Br$ and $PhCD_2Br$, which are used to differentiate the aryl groups added at each step onto dianionic **1**, shows explicitly there is an exclusive selectivity of the C−O bond for the ring-opening and ring-closure during the isomerization of the heterocycle. A reaction mechanism is proposed on the basis of the experimental results and computational calculations.

Introduction

Isomerization of cyclic functional groups on fullerene spheres between the [5,6]- and [6,6]-junctions has attracted intense interest,[1] since it reveals the unique reactivity of fullerenes. Echegoyen and co-workers have reported an electrochemically induced "moonwalking" of cyclopropane rings over the C_{60} sphere, which involves the consequential migration of a singly bonded malonate between the [5,6]- and [6,6]-junctions.[1c] Migration from the less stable [5,6]-junction to the more stable [6,6]-junction is typical, and has been recorded during the early days of fullerene study,[1a,b] while the unusual migration from [6,6]- to [5,6]-junction has been shown until recently for the cases of $Y_3N@$N-ethylpyrrolidino-C_{80}[1f] and aziridinofullerenes.[1g] The rearrangement of the cyclic functional groups on fullerene spheres is closely related to the important retrocycloaddition reactions,[2] where the remaining singly bonded linkage during the isomerization process is further cleaved and the addends are completely

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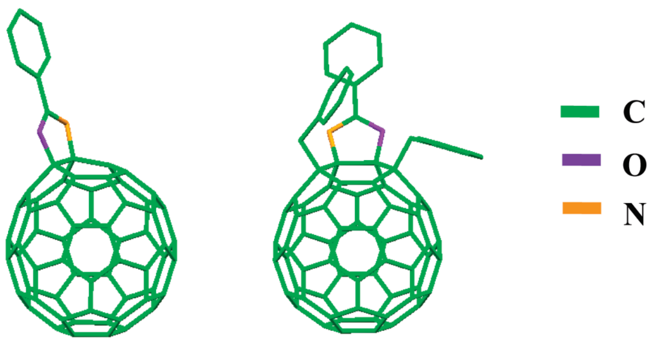
SCHEME 1. **Illustrated Structures of 1 and 2**[a]



1 **2**

[a] The hydrogen atoms are omitted for clarity.

removed from the C_{60} sphere. However, different from the retrocycloaddition reactions, where cyclic structures including cyclopropane,[2a,b] pentagonal pyrrolidino,[2c,d] isoxazolino,[2e] pyrazolino,[2f] and cyclopentadiene[2g] have been reported, the isomerizations of organofullerenes are mostly limited to the cyclopropane rings,[1a−e] with only few examples of other cyclic structures.[1f,g] In addition, details of the isomerization process remain elusive due to the difficulty of following the reaction.

We have recently reported the synthesis of a five-membered heterocyclic C_{60} derivative, 1,2-cyclic phenylimidate C_{60} (**1**, Scheme 1) and a *cis*-1 1,4-dibenzyl-2,3-cyclic phenylimidate C_{60} (**2**, Scheme 1).[3] Notably, the pentacyclic oxazoline ring undergoes an unusual migration from the [6,6]- to [5,6]-junction from **1** to **2** upon 1,4-addition of benzyls. Such a migration is quite intriguing because it is the first example of isomerization involving an oxazolino structure for organofullerenes, and it makes one wonder if there is a selectivity for the migration.

Fukuzumi and co-workers have shown that the addition of organic halides to dianionic C_{60} is a stepwise process, where the reaction is initiated by a single-electron transfer (SET) process, followed by an S_N2 reaction.[4] More importantly, it has been demonstrated that the addition of addends can be controlled by taking advantage of the stepwise nature of the reaction, which leads to the formation of organofullerenes having different addends by adding various organic halides with a time interval.[4,5] Inspired by such results, we employed the stepwise reaction of dianionic **1** with benzyl bromide ($PhCH_2Br$) and benzyl bromide-α,α-d_2 ($PhCD_2Br$) to study the isomerization mechanism of the oxazoline ring during the transformation from **1** to **2**.

Results and Discussions

Electrochemical Study of 1 and 1^{2-}. Dianionic **1** was generated electrochemically by reducing **1** at −1.10 V vs SCE in benzonitrile containing 0.1 M TBAP (tetra-*n*-butylamonium perchlorate), and the stability of dianionic **1** was examined by in situ cyclic voltammetry. Figure 1 shows the cyclic voltammogram of the in situ generated dianionic **1** along with the cyclic voltammograms of the neutral **1** for comparison. As for the neutral compound, the first redox is a reversible one-electron transfer process with an $E_{1/2}$ of −0.44 V, which is almost identical to the value of C_{60}, but different from the typical 100−150 mV negative potential shift observed for C_{60} derivatives,[6] suggesting that the addend is rather electronegative. As for the second reduction, it shows a very interesting and unusual redox process. The compound is cleanly reduced with an E_p^{red} at −0.86 V, which is also very similar to that of C_{60}. However, as the potential is reversed, the anodic peak corresponding to the oxidation of this dianionic species, which is usually about 60−100 mV more positive with respect to the E_p^{red}, is completely missing in the expected potential region. Instead, a small anodic peak appears around −0.54 V, followed by a reversible anodic peak corresponding to the oxidation of monoanionic **1** at −0.39 V. It indicates that the heterocycle is still on the C_{60} cage of dianionic **1**, and no decomposition of dianionic **1** to C_{60} occurs, otherwise the anodic peak due to the oxidation of dianionic C_{60} would appear around −0.80 V; however, a heterolytic cleavage of one $C_{60}-X$ (X = O or N) bond occurs when compound **1** receives two electrons, consistent with previous report on C_{60} heterocycles upon reduction.[7] The heterolytic cleavage results in the bearing of only one unit of negative charge on the C_{60} cage in dianionic **1**, with the other charge located on the heteroatom. Consequently, dianionic **1** will not be oxidized at a potential suitable for removing one electron from the C_{60} core having two electrons, and the oxidation peak around −0.54 V should correspond to the electron removal from the addend. Such a charge redistribution has been proposed for anionic malonated fullerenes to

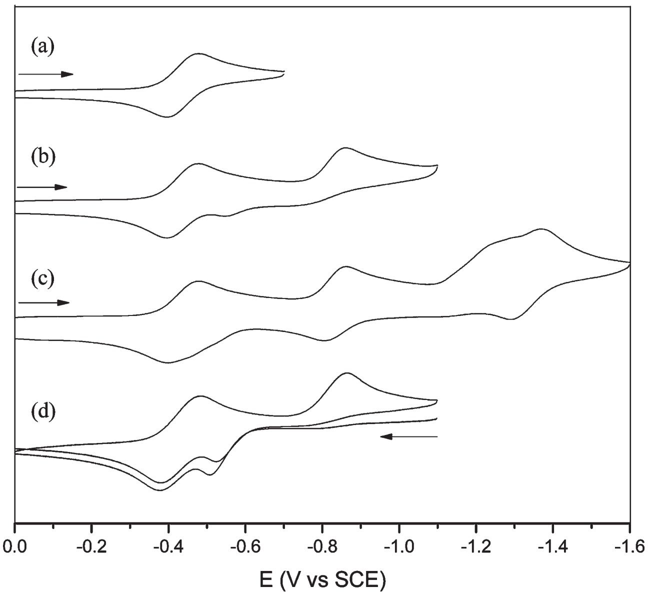


FIGURE 1. Cyclic voltammograms of **1** in benzonitrile containing 0.1 M TBAP at a scan rate of 0.1 V·s^{-1}. (a), (b), and (c) are for neutral **1**, while (d) is for the in situ generated dianionic **1**.

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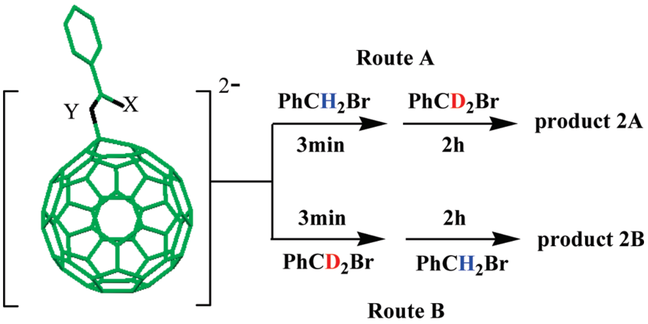
account for the retroaddition mechanism,[8] but no such electrochemical behavior has been recorded. It is noteworthy that such a charge redistribution between the C_{60} cage and addend is unlikely to occur without a heterolytic cleavage of the C_{60}−X bond, since the C_{60} core of $\mathbf{1}^-$ would be more electronegative than the heterocycle as evidenced by the reduction potentials (−0.86 V vs SCE for $\mathbf{1}^-/\mathbf{1}^{2-}$; −2.49 V vs SCE for an oxazoline reduction[9]). The result therefore asserts that there is a ring-opening via heterolytic cleavage for dianionic **1**, and the appendage is singly bonded to the C_{60} cage in this intermediate, however, it is not known at this stage which bond, C−O or C−N, is cleaved.

As the potential is further scanned to the third reduction as shown in Figure 1c, multiple reduction waves appear in the region, indicating that the remaining C_{60}−Y (Y = O or N) bond in dianionic **1** is further cleaved, and the heterocycle is removed completely to afford C_{60}. The observed anodic peaks are likely due to the decomposed product of C_{60}, especially the one around −0.80 V, which is absent in Figure 1b, confirming that **1** decomposes to C_{60} completely upon acquiring three electrons. The decomposition is further evidenced by the broadening of the first oxidation peak (around −0.39 V vs SCE), which should consist of the oxidation of both $\mathbf{1}^-$ and $C_{60}{}^-$. In the meantime, it corroborates that the dianionic **1** is indeed stable without decomposition to C_{60} under the experimental conditions. Figure 1d shows the cyclic voltammogram of the in situ generated dianionic **1**, which is similar to the CV shown in Figure 1b, with no oxidation wave appearing around −0.80 V, consistent with the formation of a singly bonded appendage intermediate. Compared with Figure 1b, the anodic peak around −0.53 V is much more prominent, and the height of current is almost identical to that of the second reduction, indicating that it is indeed the oxidation process countering the one reduced at −0.86 V. As for the reason for a smaller current of this anodic peak exhibited in Figure 1b, it is likely caused by dianionic **1** diffusing away, the generation of which was only in tiny amounts by cyclic voltammetry, from the electrode. Notably, this peak was used previously as an indicator to monitor the formation of C_{60} oxazolines even though the origin of it was not fully understood at that time.[3,11] Due to the unusual positive shift of this wave potential, it indicates that the oxidation likely originates from a process where the electron is taken away from the hetero addend directly rather than from the C_{60} cage. In addition, judging by the reversibility of the subsequent oxidation wave ($\mathbf{1}^-/\mathbf{1}$), it indicates that compound **1** is fully recovered at the stage of $\mathbf{1}^-$, i.e., the C_{60}−X bond is formed upon giving up an electron from $\mathbf{1}^{2-}$.

The stability of dianionic **1** in PhCN was further confirmed by oxidizing the species back to neutral at 0 V vs SCE. HPLC analysis of the obtained crude product showed the full recovery of **1** with only trace amount of C_{60} formed (see the Supporting Information). The result is different from that obtained in DMF,[10] where the dianionic **1** undergoes a significant decomposition, probably due to the difference of solvent polarities.

SCHEME 2. **Reaction of $PhCH_2Br$ and $PhCD_2Br$ with Dianionic 1**



Stepwise Addition of $PhCH_2Br$ and $PhCD_2Br$ and HMBC NMR. Scheme 2 illustrates the reaction procedures of the stepwise addition of $PhCH_2Br$ and $PhCD_2Br$ to dianionic **1**, where X and Y are used to denote the heteroatoms, and X stands for the atom that is heterolytically cleaved from C_{60}, while Y stands for the one that remains bonded to the C_{60} core. Two different routes in which $PhCH_2Br$ and $PhCD_2Br$ were added in opposite order were employed with the purpose to obtain a complete picture of the reaction. Equivalent amounts of $PhCH_2Br$ and $PhCD_2Br$ (molar ratio to **1** = 5:1) were used to eliminate the concentration effect, and the chemicals were added separately with a time interval of 3 min. The products obtained from route A and route B are respectively designated as **2A** and **2B**.

Compound **2A** or **2B** was purified by HPLC eluted with toluene over a Buckyprep column with an isolated yield of ~50%. Only one fraction for each product was obtained, even though both compounds consist of actually an isotopic mixture containing both hydrogen and deuterium benzyls as indicated by NMR characterizations. The identification of the compound has been confirmed with positive ESI FT-ICR MS (Electrospray Ionization Fourier Transform Ion Cyclotron resonance Mass Spectrometry) and NMR spectroscopy (see the Supporting Information). In the mass spectrum of **2A**, two $[M + H]^+$ peaks at 1022.15520 and 1024.16514 are shown, which correspond to the $C_{81}H_{20}NO$ and $C_{81}H_{18}D_2NO$; and in the mass spectrum of **2B**, the $[M + H]^+$ peak appears at 1024.16457, corresponding to $C_{81}H_{18}D_2NO$.

The ^1H and ^{13}C NMR of **2A** are in good agreement with the data reported previously.[3] Two AB quartets centered at 4.10 ppm (ABq, $\Delta\nu_{AB} = 324$ Hz, $J_{AB} = 13.2$ Hz) and 4.06 ppm (ABq, $\Delta\nu_{AB} = 258$ Hz, $J_{AB} = 13.2$ Hz) are shown in the ^1H NMR. As expected, the intensity of one of the two AB quartets is decreased due to the presence of excessive $PhCD_2$−, which facilitates the assignment of the correlated doublets within each quartet. The AB quartet in the lower field has shown a higher intensity, implying that the corresponding benzyls should bear more methylene hydrogen atoms, indicating that this quartet is likely to originate from the benzyls added in the first step, since $PhCH_2Br$ was used in the first step. The AB quartet in the upper field shows a reduced intensity, and it is therefore likely to originate from the benzyls that were added to dianionic **1** during the second step. Notably, the intensity reduction is only about 25%, less than the ideal situation where one of the AB quartets should completely disappear, indicating that the reaction was not carried out in a completely clean stepwise manner, and part

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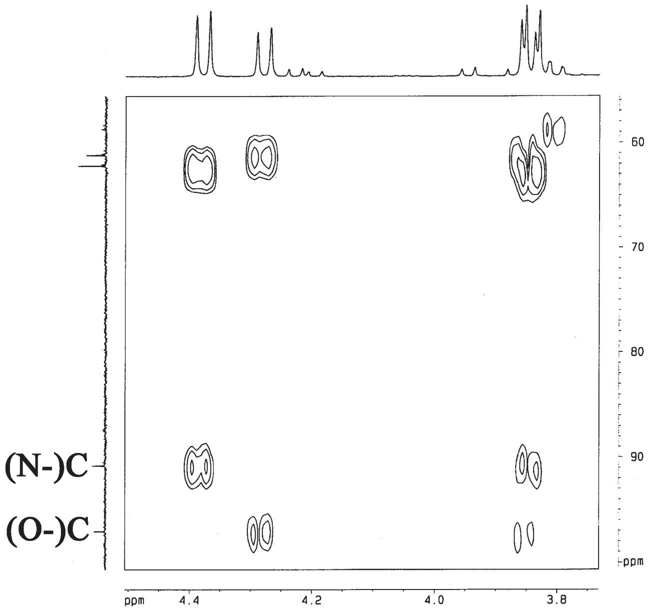

FIGURE 2. Expanded HMBC NMR spectrum of product **2A** in CS_2 with DMSO-d_6 as the external lock.

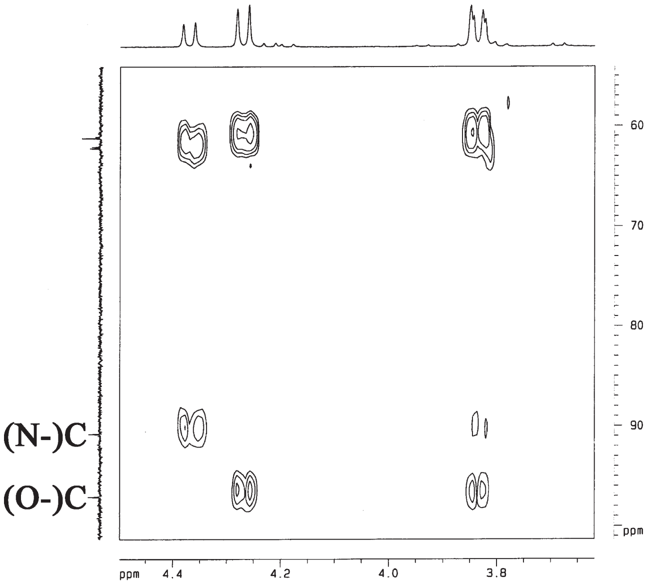

FIGURE 3. Expanded HMBC NMR spectrum of product **2B** in CS_2 with DMSO-d_6 as the external lock.

of the first-step added benzyls may contain $PhCD_2-$, while the benzyls added in the second-step may also contain $PhCH_2-$. As a result, **2A** is actually an isotopic mixture, and the integration area ratio in the ^1H NMR is therefore deviated from the theoretical value. Fortunately, the observed 25% peak reduction is significant enough to discern the benzyls with specific addition step. In the ^{13}C NMR of **2A**, the attention is paid to the sp^3 C_{60} region, since this is the region that can be used to distinguish the structure of the compound with HMBC NMR via the $^3J_{CH}$ couplings between the methylene protons and the carbon atoms bonded to heteroatoms.[11] It shows two resonances at 97.1 and 90.8 ppm, corresponding to the sp^3 C_{60} carbon atoms bonded to the oxygen and the nitrogen, respectively.[3,7,11,12] Resonances due to the C_{60} sp^3 carbon atoms bonded to the benzyls appear at 61.2 and 62.2 ppm, consistent with previous results.[3]

Figure 2 shows the expanded HMBC NMR for **2A**. The spectrum shows that the AB quartet corresponding to the methylene protons of the benzyls involved in the first-step addition (higher intensity) is correlated with the C_{60} sp^3 carbon atoms at 62.2 and 90.8 ppm, while the AB quartet corresponding to the methylene protons of the benzyls involved in the second-step addition (lower intensity) is correlated with the C_{60} sp^3 carbon atoms at 61.2 and 97.1 ppm. The result indicates that in compound **2A** the first-added benzyl group is selectively located adjacent to the C$-$N bond, while the second-added benzyl is selectively positioned next to the C$-$O bond. The benzyl assignment by HMBC is consistent with previous calculations,[10] which predict that the N atom has a greater C$-$H$\cdots$X bonding interaction with the adjacent methylene protons than the O atom, and would therefore result in the neighboring methylene protons resonating in the lower field compared with those located besides the C$-$O bond.

A control experiment was carried out following route B as outlined in Scheme 2, to confirm the assignment of the benzyls. The ^1H and ^{13}C NMR spectra of **2B** are essentially the same as those of **2A**, except the intensity of the two AB quartets are reversed, which is in good agreement with the reversed order of the addition. The results verify that the AB quartet in the lower field is due to the methylene protons of benzyls added during the first step, while the AB quartet in the upper field corresponds to the methylene protons of benzyls added during the second step. Figure 3 shows the HMBC NMR of product **2B**, which exhibits the same H$-$C couplings as those for **2A**, confirming that the addition of benzyls to dianionic **1** is a regioselective and step-dependent process.

Reaction Mechanism. Since the addend in dianionic **1** is singly bonded to the C_{60} core, the addition site for the first benzyl is only available at either the *o*- (a [6,6]-bond) or *p*-position with respect to the existing bond[4a] in considering that the appendage is not very bulky.[13] If the addition of the first benzyl took place at the *p*-position, it would lead to the cleavage of the remaining $C_{60}-Y$ bond for the subsequent addition of the second benzyl in order to form product **2**, which would result in the complete removal of the heterocycle. The experiment starting from anionic 1,4-$(PhCH_2)_2C_{60}$ has shown that the obtained oxazoline product has a different structure from that of **2** (see the ^1H NMR in the Supporting Information), indicating that compound **2** will not be formed via the retroaddition pathway. It is therefore only possible that the first benzyl will be added to C_{60} at the *o*-position with respect to the existing C$-$Y bond. In this case, the heteroatom correlated with the first-added benzyl in HMBC is the one that remains bonded to the C_{60} sphere in dianionic **1**. Accordingly, the N atom is the one that is bonded to the C_{60} sphere during the reaction, while the

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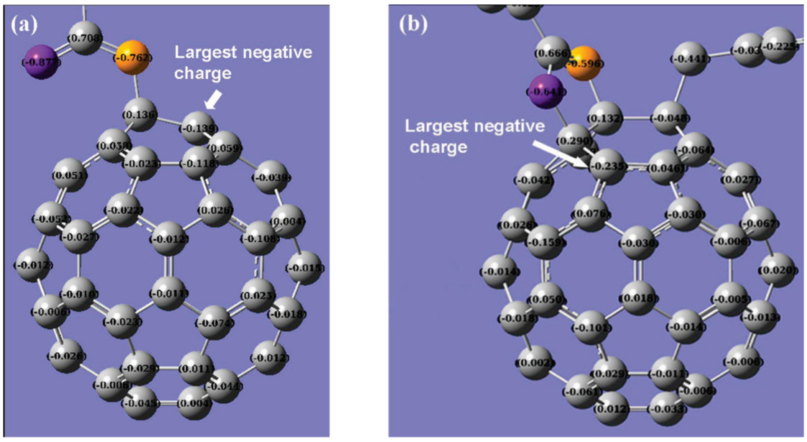
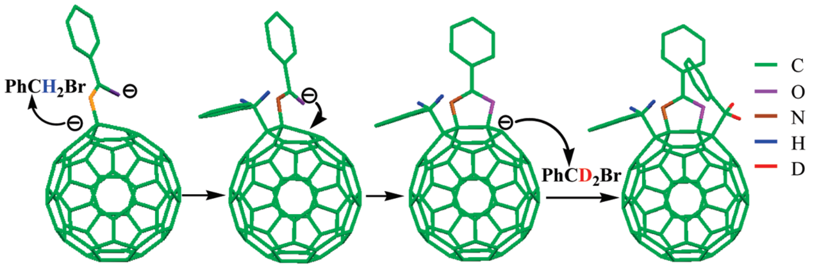


FIGURE 4. Calculated NBO charge distributions of (a) dianionic **1**, and (b) reaction intermediate with one benzyl bonded to C_{60} next to the C$-$N bond. See the Supporting Information for the charge distributions on the other side of the C_{60} sphere. The orange ball stands for the nitrogen atom, and the purple ball stands for the oxygen atom.

SCHEME 3. **Proposed Mechanism of the Rearrangement Reaction of Oxazoline Ring on C_{60} Surface**



$C_{60}$$-$O bond is cleaved heterolytically with the oxygen atom bearing a negative charge. The result is quite reasonable in considering that the oxygen anion is more stable than the nitrogen counterpart since the oxygen atom is more electronegative.

To obtain a better understanding of the reaction, a computational calculation at the HF/6-31G theoretical level with the Gaussian 03 program was carried out. Previous work has shown that the reaction of charged C_{60} species is usually a charge-directed process, where the addition takes place at the carbon atom with the largest charge density.[4a,11,14]

Figure 4a shows the natural bond orbital (NBO) charge distributions of the optimized dianionic **1**, where the oxygen atom is positioned away from the C_{60} [6,6]-junction and stays over a pentagon in order to leave the reaction site open for the coming benzyl. The result shows that the carbon atom of C_{60} at the *o*-position of the C$-$N bond indeed has a much greater negative charge (-0.139) than other C_{60} carbon atoms. In addition, the oxygen atom cleaved from the C_{60} sphere bears a significant amount of negative charge, in agreement with the experimental observations. It is noteworthy that, even though the oxygen anion carries a greater amount of negative charge as predicted by the calculations, no evidence has been found experimentally to show that the oxygen anion is involved in the S_N2 reaction with the benzyl bromide, which can be rationalized by the greater stability of the oxygen anion due to the strong electronegativity of the oxygen atom.

After the addition of the first benzyl, the number of negative charges on the intermediate is reduced to one. Since the C_{60} cage is more electron affinitive than the singly bonded hetero appendage as shown in the cyclic voltammogram (Figure 1d, $E_p^{ox} = -0.38$ V when an electron is removed from the C_{60} core for monoanionic **1**; $E_p^{ox} = -0.53$ V when an electron is removed from the singly bonded hetero appendage), the remaining one unit charge in the intermediate will then be surrendered from the hetero appendage to the C_{60} core via a ring-closure pathway. Consequently, the $C_{60}$$-$O bond is reconstructed but at the [5,6]-junction, since the carbon atom for the [6,6]-bond has been occupied by the first added benzyl. Figure 4b shows the NBO charge distributions of this reaction intermediate with one benzyl bonded to C_{60} next to the C$-$N bond. It shows that the carbon atom, which is at the *p*-position to the added benzyl and is next to the C$-$O bond, has the greatest negative charge (-0.235), predicting that this is the reaction site for the benzyl addition in the second step, in agreement with experimental results. It is noteworthy that the observed ring-opening and ring-closure processes for C_{60} oxazoline compound undergo the same pathway for the ring-opening of 2-oxazolines.[15] The proposed transformation mechanism for the oxazoline cycle on C_{60} surface is illustrated in Scheme 3.

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Conclusions

The rearrangement reaction of oxazoline ring from [6,6]- to [5,6]-junction on C_{60} surface upon 1,4-addition of benzyl bromide has been explored by using cyclic voltammetry and stepwise addition $PhCH_2Br$ and $PhCD_2Br$, where the benzyls with specific addition step are discerned by ^{1}H NMR. The results show that the C−O bond is heterolytically cleaved in dianionic **1**, and there is an exclusive selectivity of the C−O bond for the ring-opening and ring-closure during the isomerization process of the heterocycle, which is consistent with the pathway for the ring-opening of 2-oxazolines. The results have extended the scope of cyclic isomerization reactions of organofullerenes and are helpful to gain a better understanding on the chemistry of fullerenes.

Experimental Section

Synthesis of 2A (Route A). Typically, 50 mg (69.4 μmol) of **1**, which was obtained via the method reported previously,[3] was electroreduced at −1.10 V vs SCE in 50 mL of freshly distilled PhCN solution containing 0.1 M TBAP under a nitrogen atmosphere. The potentiostat was switched off when the theoretical number of coulombs required for a full conversion of **1** to $\mathbf{1}^{2-}$ was reached. Then 5 equiv of $PhCH_2Br$ (35.4 μL) was added into the solution, and the reaction was allowed to proceed for 3 min, followed by adding 5 equiv of $PhCD_2Br$ (35.4 μL). The reaction was allowed to proceed for about 2 h with stirring. The solvent was removed with a rotary evaporator under reduced pressure after the reaction was finished, and the residue was washed with methanol to remove TBAP before further purification. The slurry was separated by filtration, and the residue was put into toluene and sonicated. The soluble part was further purified by HPLC eluted with toluene over a Buckyprep column. Compound **2A** was obtained with an isolated yield of ~50%.

Spectral characterization of 2A: positive ESI FT-ICR MS: $C_{81}H_{17}D_2NO$, *m*/*z* for $[M + H]^+$ calcd 1024.1665, found 1024.1651; ^{1}H NMR (600 MHz, in CS_2, DMSO-d_6 was used as the external lock solvent) δ 8.13 (d), 7.40 (t), 7.36 (t), 7.10 (d), and from 6.95 to 6.80 (m), 4.11 (ABq, $\Delta\nu_{AB} = 324$ Hz, $J_{AB} = 13.2$ Hz), 4.06 (ABq, $\Delta\nu_{AB} = 258$ Hz, $J_{AB} = 13.2$ Hz); ^{13}C NMR (150 MHz, CS_2/DMSO-d_6) δ 161.6 (1C, C=N), 152.6 (1C), 152.4 (1C), 148.7 (1C), 148.5 (1C), 148.4 (1C), 148.2 (1C), 147.5 (1C), 146.6 (1C), 146.5 (1C), 146.5 (2C), 146.3 (1C), 146.0 (1C), 145.6 (1C), 145.5 (2C), 144.9 (2C), 144.8 (1C), 144.7 (2C), 144.6 (1C), 144.2 (1C), 144.1 (1C), 144.0 (1C), 144.0 (2C), 143.8 (1C), 143.78 (1C), 143.7 (2C), 143.6 (1C), 143.4 (2C), 143.3 (1C), 143.0 (1C), 142.9 (1C), 142.8 (1C), 142.6 (1C), 142.4 (1C), 142.3 (1C), 142.2 (1C), 142.0 (1C), 141.6 (1C), 141.55 (1C), 141.3 (1C), 141.2 (2C), 141.0 (1C), 139.3 (1C), 139.0 (1C), 137.6 (1C), 136.8 (1C), 136.4 (1C), 135.9 (1C), 135.8 (1C), 134.5 (1C, Ph), 134.2 (1C, Ph), 133.7 (1C, Ph), 131.5 (1C, Ph), 131.5 (2C, Ph), 131.3 (1C, Ph), 131.3 (1C, Ph), 131.3 (1C, Ph), 128.3 (2C, Ph), 128.2 (2C, Ph), 127.5 (2C, Ph), 127.4 (2C, Ph), 126.6 (1C, Ph), 126.3 (1C, Ph), 97.1 (1C, sp^3, C−O), 90.8 (1C, sp^3, C−N), 62.2 (1C, sp^3, C−CH_2Ph), 61.2 (1C, sp^3, C−CH_2Ph), 46.2 (1C, CH_2), 45.3 (1C, CH_2).

Synthesis of 2B (Route B). The procedures for the synthesis are similar to those of route A, except that 5 equiv of $PhCD_2Br$ (35.4 μL) was added into the system first, and the reaction was allowed to proceed for 3 min, followed by adding 5 equiv of $PhCH_2Br$ (35.4 μL). Compound **2B** was purified by HPLC eluted with toluene over a Buckyprep column with an isolated yield of ~50%.

Spectral characterization of 2B: positive ESI FT-ICR MS: $C_{81}H_{17}D_2NO$, *m*/*z* $[M + H]^+$ calcd 1024.1665, found 1024.1646; ^{1}H NMR (600 MHz, in CS_2, DMSO-d_6 was used as the external lock solvent) δ 8.13 (d), 7.40 (t), 7.35 (t), 7.10 (d), and from 6.95 to 6.80 (m), 4.10 (ABq, $\Delta\nu_{AB} = 324$ Hz, $J_{AB} = 13.2$ Hz), 4.06 (ABq, $\Delta\nu_{AB} = 258$ Hz, $J_{AB} = 13.2$ Hz); ^{13}C NMR (150 MHz, CS_2/ DMSO-d_6) δ 161.6 (1C, C=N), 152.6 (1C), 152.4 (1C), 148.7 (1C), 148.5 (1C), 148.4 (1C), 148.2 (1C), 147.5 (1C), 146.6 (1C), 146.6 (1C), 146.5 (2C), 146.3 (1C), 145.9 (1C), 145.6 (1C), 145.5 (2C), 144.9 (2C), 144.8 (1C), 144.7 (2C), 144.6 (1C), 144.2 (1C), 144.1 (1C), 144.0 (1C), 144.0 (2C), 143.8 (1C), 143.8 (1C), 143.7 (2C), 143.6 (1C), 143.4 (2C), 143.3 (1C), 143.0 (1C), 142.9 (1C), 142.8 (1C), 142.6 (1C), 142.4 (1C), 142.3 (1C), 142.2 (1C), 142.0 (1C), 141.6 (1C), 141.6 (1C), 141.3 (1C), 141.2 (2C), 141.0 (1C), 139.3 (1C), 139.0 (1C), 137.6 (1C), 136.8 (1C), 136.4 (1C), 135.9 (1C), 135.8 (1C), 134.5 (1C, Ph), 134.2 (1C, Ph), 133.7 (1C, Ph), 131.5 (1C, Ph), 131.5 (1C, Ph), 131.4 (1C, Ph), 131.3 (1C, Ph), 131.3 (1C, Ph), 128.3 (2C, Ph), 128.2 (2C, Ph), 127.5 (2C, Ph), 127.4 (2C, Ph), 126.6 (1C, Ph), 126.3 (1C, Ph), 97.1 (1C, sp^3, C−O), 90.8 (1C, sp^3, C−N), 62.2 (1C, sp^3, C−CH_2Ph), 61.2 (1C, sp^3, C−CH_2Ph), 46.2 (1C, CH_2), 45.3 (1C, CH_2).

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Supporting Information Available: General methods, characterizations of **2A** and **2B**, ^{1}H NMR of the oxazoline product obtained from the reaction of anionic 1,4-$(PhCH_2)_2C_{60}$, and calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.