Efficient Acetalization of Epoxy Rings on a Fullerene Cage

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Fullerene epoxides react with benzaldehyde derivatives in the presence of a pyridinium hexafluoroantimonate to give corresponding 1,3-dioxolane derivatives of [60]fullerene in excellent yields. The activation energy for the reaction of fullerene monoepoxide with benzaldehyde was determined to be 112.7 kJ mol^{-1}. This result shows that fullerene epoxides undergo the stepwise S_N1-like acetalization reaction.

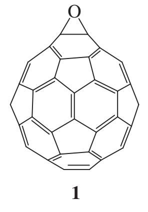
Fullerene epoxides, $C_{60}O_n$, have been used as a building block for the construction of nanostructures.[1] They have also received attention from the viewpoint of their possible application in the fields of electronic materials and biological sciences.[2,3] Chemical transformation of fullerene epoxides, however, has scarcely been studied, despite general recognition that the epoxides could serve as convenient starting materials for the synthesis of functionalized fullerene derivatives.[4] The chemical transformation of fullerene epoxides is expected to play an important role in the development of functionalization of a fullerene cage, because it can readily afford a variety of polyfunctionalized fullerene derivatives with conservation of the arrangement of epoxy rings on the fullerene surface starting from regioisomeric fullerene polyepoxides.

Recently, we succeeded in the isolation of some regioisomeric fullerene epoxides generated by the epoxidation of [60]fullerene (C_{60}) with *m*-chloroperbenzoic acid (*m*-CPBA) by means of high performance liquid chromatography (HPLC), and carried out their structural characterization by spectroscopic analysis.[5] Isolation of regioisomeric fullerene epoxides will make it possible to characterize their physical and chemical properties and also to explore their application in the field of materials science. Furthermore, a large quantity of fullerene epoxides will soon become available from Japanese suppliers.[6] The recent development of the large-scale production of fullerene epoxides thus prompted us to develop a new methodology for synthesis of polyfunctionalized fullerene derivatives by means of efficient chemical transformation of regioisomerically pure fullerene polyepoxides. In this communication, we report the first efficient synthesis of 1,3-dioxolane derivatives of C_{60} by addition of benzaldehydes to fullerene epoxides in the presence of a pyridinium salt.

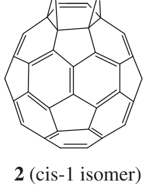
Reaction of a toluene solution of fullerene epoxide **1** with excess amount (200 equiv.) of benzaldehyde at 75 °C for 60 min in the presence of 0.29 equiv. of *N*-(1-phenethyl)-2-cyanopyridinium hexafluoroantimonate that had been prepared according to the reported method[7] led to the formation of 1,3-dioxolane **3a** in 92% yield together with a very small amount of pristine fullerene C_{60} based on the HPLC. The product **3a** was isolated by flash column chromatography on silica gel. The atmospheric pressure chemical ionization (APCI) mass spectrum of **3a** showed a molecular ion peak at m/z 842 corresponding to a 1:1 adduct of **1** and benzaldehyde. The 1,3-dioxolane structure for **3a** was unambiguously confirmed by direct comparison of its FT-IR, ^{1}H and ^{13}C NMR spectra with those previously reported.[8]

Reaction of **1** with 4-*n*-butoxybenzaldehyde under the same conditions as above also took place to produce 1,3-dioxolane **3b** in 95% yield, which was isolated by the same procedure as that for **3a**. The APCI mass spectrum of **3b**, which showed a molecular ion peak at m/z 914, agreed with the 1:1 adduct of **1** and 4-*n*-butoxybenzaldehyde. The 1,3-dioxolane structure for **3b** was assigned based on comparison of its NMR and IR spectra with those for **3a**. In the ^{13}C NMR spectrum, the signals for the sp^3 carbons of acetal and fullerene moiety were observed at δ 102.95 and 93.86, respectively. In the ^{1}H NMR spectrum, in addition to the four phenyl protons and nine butoxy protons, one singlet methine proton was observed at δ 7.22. These chemical shifts of sp^3 carbons and methine proton of the acetal were in good agreement with those of **3a**.

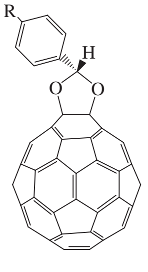
The acetalization reaction of **1** with benzaldehyde at 75 °C for one day did not proceed at all in the absence of the pyridinium salt and resulted in the complete recovery of **1**. This result suggests that the pyridinium salt induces a catalytic C–O bond cleavage of the epoxy ring to generate a carbocation on the carbon atom of fullerene moiety, followed by nucleophilic attack of benzaldehyde on the cation as shown in Scheme 1. Generally a Lewis acid catalyzed acetalization of oxiranes is considered to follow a concerted S_N2-like mechanism involving backside attack of the carbonyl oxygen on an epoxide carbon atom.[9] However, such a backside attack on the fullerene epoxide is unable to occur owing to occupation by the fullerene cage of the entire side opposite the epoxy ring. Consequently, with a fullerene epoxide, an energetically unfavorable S_N1-like attack of a carbonyl compound on the carbocation from the fullerene surface is forced to



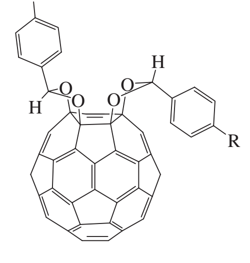
1



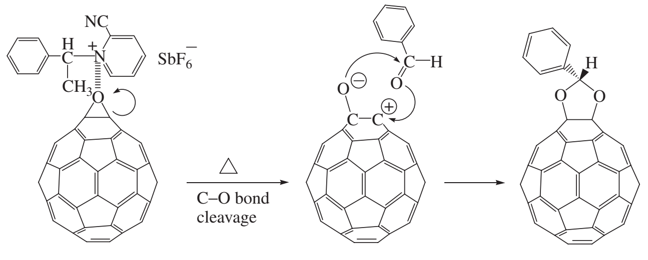
2 (cis-1 isomer)



3a (R=H)
3b (R=*n*-BuO)



4 (R=*n*-BuO)



1 **3a**

Scheme 1. Stepwise S_N1-like acetalization of fullerene epoxide **1** with benzaldehyde.

take place with requirement of relatively high activation energy for the C–O bond cleavage of the epoxy ring as shown in Scheme 1. The activation energy for the reaction of **1** with benzaldehyde was determined to be $112.7\,\mathrm{kJ\,mol^{-1}}$ from the Arrhenius plots of $\ln k$ vs $1/T$, where k is the pseudo-first order rate constant and T is the reaction temperature (four different temperatures from 328 to 353 K). Based on the activation energy, the rate constant at room temperature (293 K) can be calculated to be $9.5 \times 10^{-7}\,\mathrm{s^{-1}}$, which is more than 10^3 times smaller than that at 348 K ($k = 1.43 \times 10^{-3}\,\mathrm{s^{-1}}$ at 348 K). Therefore, it is not surprising that the pyridinium salt catalytic acetalization of **1** with benzaldehyde did not take place at room temperature, although a Lewis acid catalyzed acetalization of oxiranes such as but-2-ene epoxides or styrene oxide readily proceeds at room temperature and even at 0 °C to yield 1,3-dioxolanes.[10]

The application of the present acetalization reaction to the regioisomerically pure fullerene diepoxide **2** (*cis*-1 isomer) would lead to chemical transformation of the two epoxy rings with conservation of their arrangement on the fullerene cage. Under reaction conditions similar to those mentioned above, the fullerene diepoxide **2** was also subjected to acetalization with 4-*n*-butoxybenzaldehyde to yield bis-1,3-dioxolane **4** in 91% yield. The molecular ion peak at m/z 1108 observed by the APCI mass spectrum of **4** corresponded to that of 1:2 adduct of $C_{60}O_2$ and the aldehyde. The visible absorption spectrum of **4** showed a sharp band at 423 nm, which is characteristic of the *cis*-1 isomer **2**.[11] The appearance of the sharp peak at 423 nm of **4** suggests that the acetalization reaction of **2** occurs with conservation of the arrangement of the two epoxy rings on the fullerene cage. The ^{13}C NMR spectrum of **4** showed 53 signals for the fullerene carbons, indicating a lack of symmetry of the fullerene cage. The four signals at δ 90.68, 91.83, 92.21, and 93.5, respectively, originated from the four unequivalent sp^3 carbons, and the remaining 49 signals from δ 136 to 150 were assigned to the sp^2 carbons. Its ^{13}C NMR spectrum also exhibited two signals at δ 103.76 and 104.40 corresponding to the two unequivalent acetal carbons. In the ^{1}H NMR spectrum, two acetal protons were observed at δ 6.85 and 7.15 as two singlets with equal intensity. In addition, two sets of four phenyl protons and nine *n*-butoxy protons with a 1:1 integral ratio were observed. Thus, the NMR spectra clearly demonstrate that the two dioxolane rings are unsymmetrically disposed with respect to the fullerene moiety, so that they are in magnetically different environments, resulting in different chemical shifts for sp^3 carbons and methine protons. The above NMR analysis confirmed the structure of the bis-1,3-dioxolane to be the isomer depicted in **4**. To our best knowledge, this is the first chemical transformation of a regioisomerically pure fullerene diepoxide taking place under conservation of the arrangement of the two epoxy rings on the fullerene cage. It is anticipated that the application of this chemical transformation to other regioisomers of fullerene polyepoxides would provide a new approach to the synthesis of poly-1,3-dioxolane derivatives of C_{60} having a regioisomerically pure structure which are essential for studies in materials science such as investigation of promising candidates for the electron acceptor in plastic solar cells.

In conclusion, the present study has shown that the acetalization reaction of fullerene epoxides with benzaldehydes readily takes place in the presence of a pyridinium hexafluoroantimonate to afford corresponding 1,3-dioxolane derivatives of C_{60} in excellent yields. The present results lead to a fascinating synthetic approach for obtaining a variety of regioisomerically pure poly-1,3-dioxolane derivatives of C_{60} starting from a regioisomer of fullerene polyepoxides.

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