JOC Article

Reactivity of Fullerene Epoxide: Preparation of Fullerene-Fused Thiirane, Tetrahydrothiazolidin-2-one, and 1,3-Dioxolane

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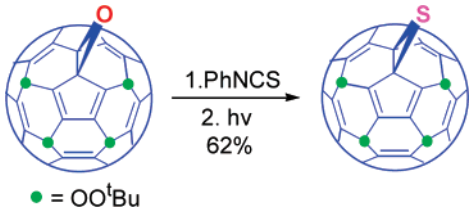

The epoxide moiety in the fullerene-mixed peroxide $C_{60}(O)(OO^tBu)_4$ **1** reacts readily with aryl isocyanates ArNCS (Ar = Ph, Naph) to form both the thiirane derivative $C_{60}(S)(OO^tBu)_4$ and fullerene-fused tetrahydrothiazolidin-2-one. The reaction of **1** with trimethylsilyl isothiocyanate TMSNCS yields the isothiocyanate derivative $C_{60}(NCS)(OH)(OO^tBu)_4$, the isothiocyanate and hydroxyl moieties of which could be converted to a fullerene-fused tetrahydrothiazolidin-2-one ring with alumina quantitatively. Treating **1** with $BF_3{\cdot}Et_2O$ yields the fullerene-fused [1,3,2]-dioxoborolane derivative $C_{60}(O_2BOH)(OO^tBu)_4$. In the presence of aldehyde or acetone, $BF_3{\cdot}Et_2O$ catalyzes the conversion of epoxide to fullerene-fused 1,3-dioxolane derivatives. The products are characterized by spectroscopic data. Two of the compounds are also characterized by single-crystal X-ray analysis.

Introduction

Fullerene epoxide is one of the first fullerene derivatives. A number of methods have been reported for their synthesis in the early days of fullerene chemistry.[1] Diederich et al. isolated $C_{70}O$ from a fullerene mixture generated by resistive heating of graphite.[1a] Photooxidation of C_{60} in oxygenated benzene solution afforded $C_{60}(O)$ as the sole isolable product.[1b] Dimethyldioxirane also reacts with C_{60} to form $C_{60}(O)$ together with 1,3-dioxolane derivatives.[1c,d] Other methods such as methyltrioxorhenium-hydrogen peroxide,[1e] ozonolysis,[1f] chemically generated singlet oxygen,[1g] and *m*-chloroperbenzoic acid[1h] have also been reported to oxidize fullerenes into fullerene epoxides. The last method is the most frequently used method because of its relative high yields. Various multiadducts $C_{60}(O)_n$ have been detected by mass spectra.[1] Isomerically pure bis- and tris-adducts have been characterized.[1d,h,i] Several groups have theoretically investigated the structure of fullerene epoxides.[2]

Compared to the extensive study on the preparation and structure of fullerene epoxides, little is known about their further

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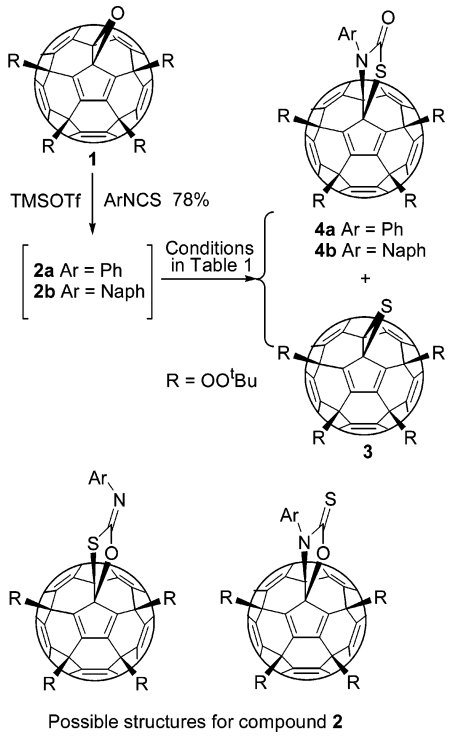
functionalization. A major problem hindering the chemistry of fullerene epoxide is the time-consuming HPLC separation of the mixture of epoxides $C_{60}(O)_n$ resulting from the nonselective epoxidation reactions. In addition, slow degradation of the fullerene epoxides adds more difficulty for their functionalization. Nevertheless, Tajima et al. succeeded in converting C_{60}-(O) into 1,3-dioxolane derivatives.[3] The same group also reported the Lewis acid-assisted nucleophilic substitution of C_{60}-(O) to form 1,4-bisadduct (para-addition).[4] Heating a mixture of $C_{60}O_{1-3}$ and C_{60} under various conditions produces both $C_{120}O$ and $C_{120}O_2$.[5]

We have reported the reaction between *tert*-butylperoxo radicals and C_{60} to give the epoxide-containing derivative **1**.[6] Presence of the *tert*-butylperoxo groups results in high solubility and easy purification by flash chromatography. Further study indicates that compound **1** also shows good chemoselectivity under mild conditions. The epoxide moiety could be converted to vicinal diol and halohydrins in good yields by Lewis acids.[7] The *tert*-butylperoxo groups remain unchanged in these reactions, and greatly facilitate product purification and characterization. Here we report the transformation of the epoxide moiety into thiirane and various five-membered heterocyclic derivatives.

Results and Discussion

Reactions of Aryl Isothiocyanates with 1. Sulfur-containing fullerene derivatives have attracted much attention due to their interesting photophysical properties.[8] Various sulfur-containing fullerene derivatives have been prepared.[9,10] The simplest sulfur-containing fullerene derivative is the thiirane derivative $C_{60}S$, analogous to the well-known fullerene epoxide $C_{60}O$. It has been the subject of theoretical calculations,[11] which suggested that a [6,6]-closed structure might be stable relative to dissociation to C_{60} and atomic sulfur or to $2C_{60}$ and S_2. Heymann et al. observed $C_{60}S^-$ and $C_{60}S^+$ ions in the gas phase by analyzing mixtures of C_{60} and elemental sulfur by LDI-TOF.[12] But attempted syntheses were not successful. In an effort to prepare the fullerene thiirane derivatives, we first tried the reaction between **1** and isothiocyanates.

SCHEME 1. Preparation of Thiirane 3 and Tetrahydrothiazolidin-2-one 4



Isothiocyanates are common sulfurating reagents in classical organic chemistry.[13] They react with epoxides to form sulfur heterocycles under various conditions. The epoxide moiety of **1** readily reacts with aryl isothiocyanate PhNCS in the presence of TMSOTf to give the epoxide-opened derivative **2** in good yields (Scheme 1). The reaction and all the purification procedure were carried out in the dark to avoid photoinduced decomposition. Other Lewis acids such as BF_3 were also tested but gave lower yields due to formation of other products.

Compound **2** is stable for several hours. The ^{13}C NMR spectra of both **2a** and **2b** were quite complex, indicating the presence of at least two compounds. Possible structures of **2** are shown in Scheme 1. Upon storage in the dark for several days at r.t.,

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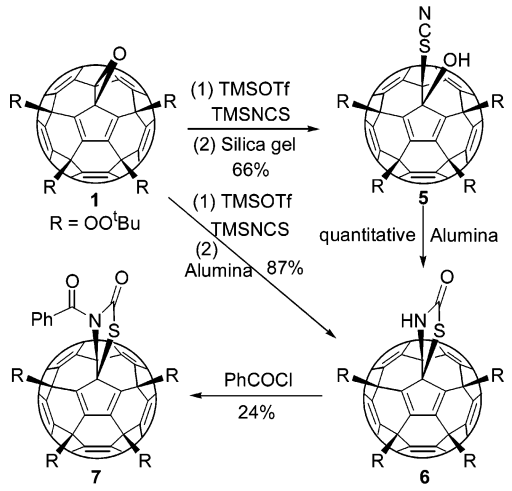
TABLE 1. Preparation of Compound 3 and 4 under Different Conditions[a]

entry	Ar	conditions	**3** (%)	**4** (%)
1	Ph	A	80	8
2	Ph	B	13	59
5	Ph	C	trace	79
3	Naph	A	74	15
4	Naph	B	23	53

[a] Notes: Reaction conditions: A, compound **2** in CH_2Cl_2, hν, r.t.; B, compound **2** stored as powder r.t. in the dark; C, The CH_2Cl_2/toluene solution of compound **2a** from chromatography without further evaporation was refluxed in the dark. For A and B, the yields were based on **2**; for C, the yield was based on **1**.

SCHEME 2. Preparation of Isothiocyanate 5 and Related Reactions

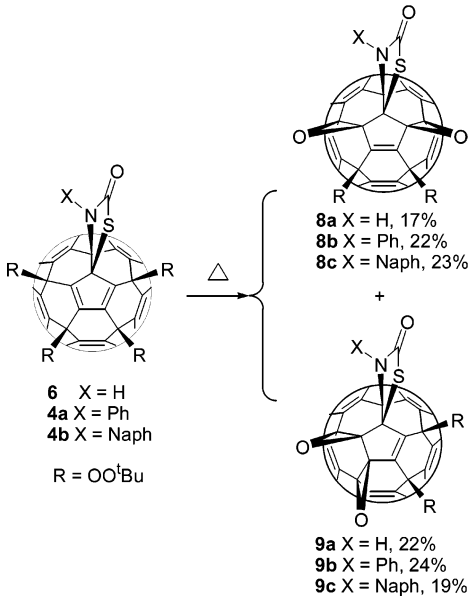


it gradually changed into compounds **3** and **4**. Exposure of the phenyl derivative **2** to visible light gave the thiirane derivative **3** as the major product, whereas refluxing its CH_2Cl_2/toluene solution in the dark gave **4a** as the major product (entries 1−3 in Table 1). Isolation of **2** is necessary to convert it to **3** or **4** efficiently. Heating or irradiating the reaction mixture of **1** and isothiocyanates led to a complicated mixture of products.

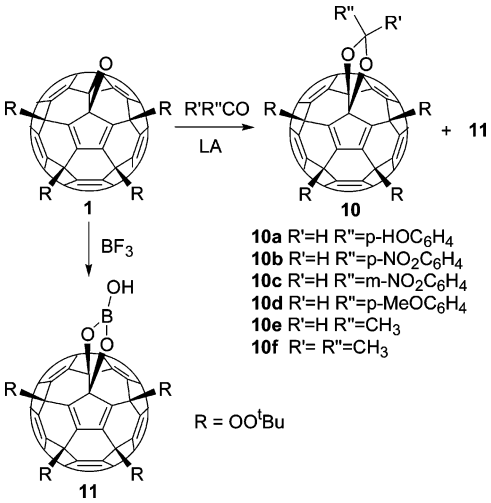
Reaction of Trimethylsilyl Isothiocyanate with 1. Under similar conditions to the above aryl isothiocyanate reactions, treatment of **1** with TMSNCS led to different results (Scheme 2). After TLC indicated that most of the starting material **1** was consumed, the resulting solution was transferred on to silica gel column. The solution quickly changed from red-orange to black upon contact with silica gel. The isothiocyanate adduct **5** was eventually eluted out as a red-orange band. In an effort to avoid the effect of silica gel, the reaction solution was treated with neutral alumina column. The thiozolidinone derivative **6** was obtained. Treating the thiocyanate **5** with neutral alumina gave compound **6** in quantitative yield. As expected, treating **6** with benzoyl chloride yielded acylated product **7**.

Thermolysis of the Thiazolidinone Derivatives. The thiazolidinone ring in compound **4** is very stable at r.t. There is hardly any decomposition after storing the solid for a few weeks. Upon heating at 110 °C in chlorobenzene, two O−O bonds in the *tert*-butylperoxo addends were cleaved to form the diepoxides **8** and **9** (Scheme 3). Yields of **8** and **9** were almost the same for both the phenyl and the naphthenyl derivatives. To avoid formation of uncharacterizable products, 2 equiv of C_{60} was added in the solution. The added C_{60} probably acted as a trap for active species resulting from the cleavage of the *tert*-butylperoxo groups.

SCHEME 3. Formation of Bis-epoxides



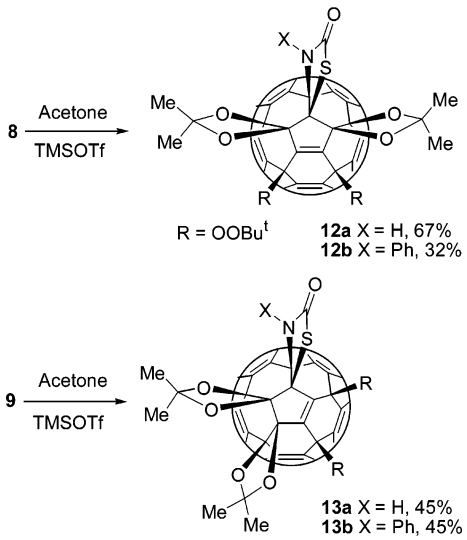
SCHEME 4. From Epoxide to Acetal and Borate



Acetalization of Epoxy Rings with Aldehydes and Acetone. The epoxy moiety in the present compounds can be readily converted to 1,3-dioxolane derivatives by treatment with aldehyde or acetone in the presence of Lewis acid. The reaction was faster in dichloromethane than that in benzene. Aromatic aldehydes with an electron-donating group gave a higher yield than those with an electron-withdrawing group. Yield of the aliphatic aldehyde CH_3CHO is similar to the aromatic aldehydes with an electron-donating group at around 51%. The [1,3,2]-dioxoborolane derivative **11** was formed as a byproduct due to presence of water. In the absence of aldehyde, excess BF_3 etherate reacted with **1** to give the derivative **11** as the major product (Scheme 4).

Under similar conditions, both the epoxy moieties in compounds **8** and **9** could be acetalized by acetone to form compound **12** and **13**, respectively (Scheme 5). The bisepoxide and the corresponding bis-1,3-dioxolane derivatives have similar R_f values on silica gel. To facilitate purification, the reaction was stopped after all the starting material was consumed. There

SCHEME 5. Formation of Bisacetals



was no monoacetalization intermediate detected under these conditions. We have previously reported the reaction of **1** with CF_3COOH to give ortho-ester type 1,3-dioxolane derivative.[6b] Treating **8a** with CF_3COOH gave a mixture of several isomers as indicated by ^1H NMR and ESI-MS.

Several methods have been reported in the literature for the preparation of fullerene-fused 1,3-dioxolane derivatives. The above reactions are analogous to the method by Tajima et al.[3] who reported mono- and bis-1,3-dioxolane fullerene derivatives by addition of aldehyde to $C_{60}(O)$ and regioisomerically pure fullerene diepoxide $C_{60}(O)_2$. Several other methods can also produce 1,3-dioxolane fullerene derivatives: the formal [2 + 3] cycloaddition of dimethyldioxirane to C_{60},[1c] the reaction of benzyl alcohol with C_{60} in the presence of air,[14] and the addition of CF_3COOI[15] or $(CF_3CO)_2OO$[16] to C_{60}.

Single-Crystal X-ray Structure of 4a and 10d. Various methods were tried to grow suitable crystals for X-ray diffraction analysis. Slow evaporation of compound **4a** in a mixture of CS_2 and ethanol yielded crystals as layered sheets, which contained some CS_2 molecules in the crystals, but the solvent molecules escaped from the crystals very quickly preventing X-ray diffraction data collection. To modify the crystallization process, the crystals were then redissolved in CS_2, and some acetonitrile, CH_2Cl_2, and ethanol were added. Slow evaporation gave rectangle crystals. The X-ray diffraction analysis showed the crystals were twinned and could not be solved. Recrystallization of the same sample in a mixture of CS_2, ethanol, acetonitrile, and hexafluorobenzene at 5 °C eventually gave suitable crystals for X-ray analysis. Crystals of **10d** were also obtained from a mixture of CS_2, hexane, ethanol, acetonitrile, CH_2Cl_2, and hexafluorobenzene at 5 °C.

Crystal structures of **4a** (Figure 1) show that the sulfur atom is attached to the central pentagon, while the nitrogen atom is located outside. The phenyl ring is perpendicular to the thiazolidinone ring with a dihedral angle at 85.4°, and the thiazolidinone ring is perpendicular to the central pentagon on the C_{60} with a dihedral angle at 87.5°. The longest bond on the fullerene cage is 1.562 Å at the thiazolidinone fullerene-fusion bond. The double bonds on the central pentagon are the shortest among all the fullerene double bonds on the cage at 1.326 and 1.343 Å. The single bond on the central pentagon is 1.460 Å, which is well within the range of other single bonds on the fullerene cage. This indicates that the conjugation effect of the 1,4-diene on the central pentagon is negligible.

The structure of **10d** shows the dioxolane ring as an envelope conformation, in which the two oxygen atoms and the two fullerene carbons are planar. The phenyl ring is at the equatorial position of the envelope and perpendicular to the envelope plane with a dihedral angle of 86.0°. The longest bond on the fullerene cage of **10d** is the dioxolane fullerene-fusion bond at 1.576 Å, which is close to the above thiazolidinone fusion bond in **4a**. Double bonds on the central pentagon are 1.325 and 1.351 Å.

Spectroscopic Data and Structure Assignment. In light of the above X-ray analysis result, structures of other compounds were derived from their spectroscopic data. ESI-MS spectra in the positive mode gave molecular ion signals M + NH_4^+ or M + H^+ as the base peak for all the compounds except **8** and **9**, the base peak of which appeared in the negative mode as M + CH_3O^-. A mixture of methanol and $CDCl_3$ or $CHCl_3$ was used in measuring the ESI-MS spectra. The epoxide moiety may be opened through addition of methanol under the negative-mode conditions.

Compounds **3**, **4a**, **5**, **6**, **7**, **8a**, **8b**, **10f**, **11**, and **12** are C_s symmetric. Their ^1H and ^{13}C NMR spectra showed the expected C_s pattern. In their ^{13}C NMR spectra there were 28 signals (a few of which were overlapped) in the region for sp^2 fullerene carbon atoms and four C (sp^3) fullerene signals. Chemical shifts of the thiirane derivative **3** are almost identical to those of the corresponding oxirane **1**. The two sp^3 fullerene carbons connecting the four *tert*-butyl groups appear at 84.0, 81.3 ppm and 84.8, 81.0 ppm, respectively, for compound **3** and the oxirane **1**. The only difference is at the three-membered ring. The thiirane fullerene carbons appear at 52.9, 57.0 ppm, whereas the oxirane fullerene carbons appear at 75.9, 71.4 ppm.

The relative location of the OH and SCN groups in compound **5** was confirmed by HMBC spectrum. The OH group showed correlation with the unique central pentagon carbon signal at 155.3 ppm. This is similar to the analogous C_s symmetric compound C_{60} (OH)Cl(OOtBu)$_4$, which was characterized by single-crystal X-ray analysis, and its HMBC spectrum also showed correlation to the unique central pentagon carbon signal at 157.3 ppm. But the NMR data could not differentiate between the two possible isomers for **5**, i.e. the thiocyanate with the sulfur atom attached to the C_{60} as depicted in Scheme 2 and the isothiocyanate with the nitrogen atom attached to C_{60}. The thiocyanate **5** was chosen because the IR spectrum did not show an intense stretching band in the range from 1500 to 2600 cm^{-1}, which is expected for the RNCS derivative.

Compound **6** and its benzyl derivative **7** showed NMR spectra similar to that of the analogous compound **4a**. Since the relative location of the nitrogen and the sulfur atoms in **4a** was characterized by single-crystal X-ray analysis as discussed above, it is reasonable to assume that compounds **6** and **7** have the same addition pattern.

Structure assignments for the C_1 symmetric compounds are less conclusive. The ESI-MS and NMR spectra clearly revealed what groups are attached on the C_{60} cage, but the data could not assign their relative locations unambiguously. Structures of

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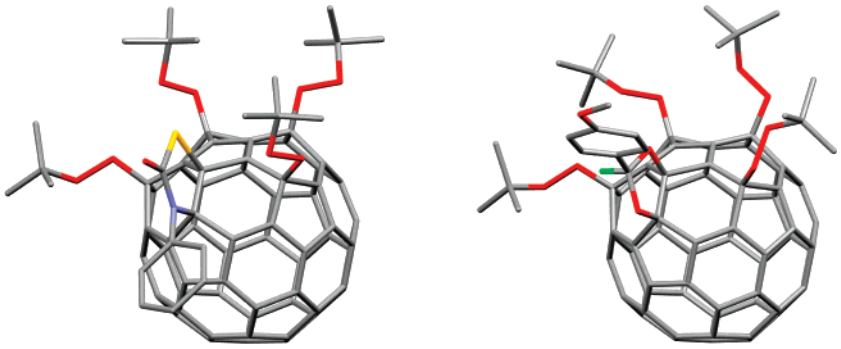
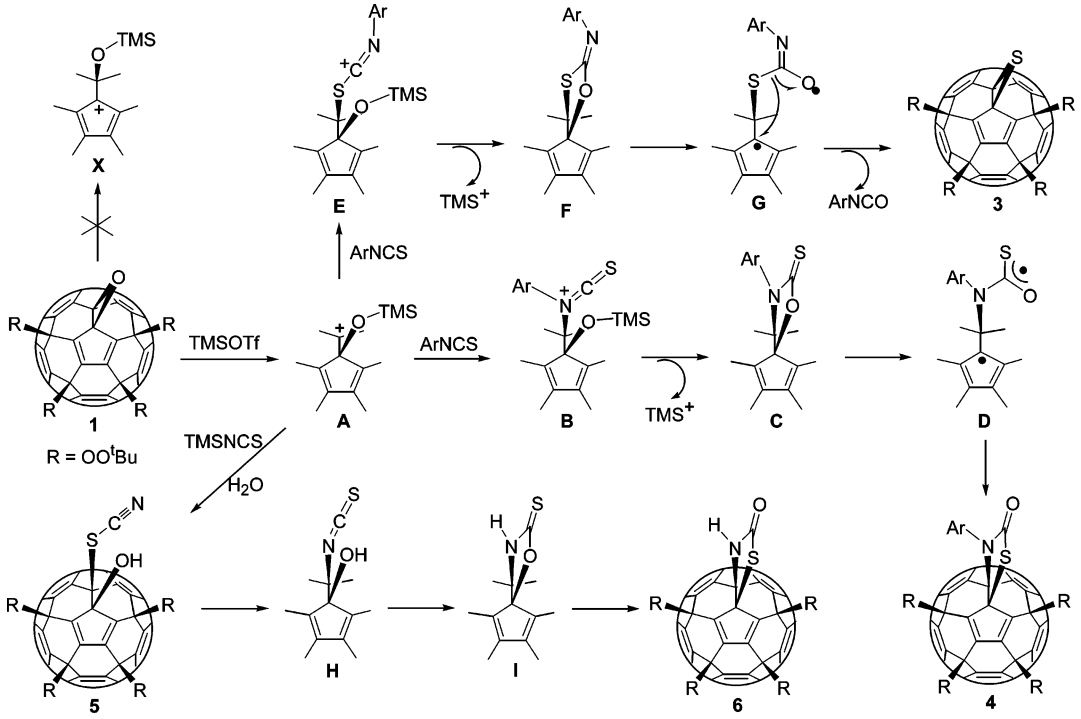


FIGURE 1. Single-crystal X-ray structures of compounds **4a** (left) and **10d** (right). For clarity, hydrogen atoms on the methyl and phenyl groups were not shown. Grey, carbon; red, oxygen; blue, nitrogen; green, hydrogen; yellow, sulfur.

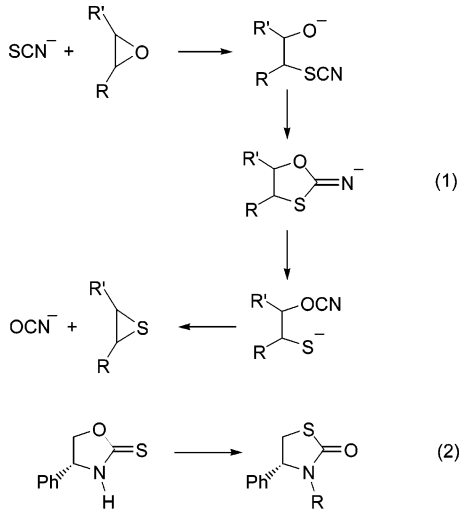
SCHEME 6. Proposed Pathway for the Formation of Compounds 3, 4, and 5



the naphthenyl derivatives **4b** and **8c** were derived by comparison to its phenyl C_s symmetric analogues **4a** and **8b**. The naphthenyl group is probably too bulky and cannot rotate freely, thus leading to the C_1 symmetric NMR spectra. The bisepoxide derivatives **9** are isomers of the corresponding bisepoxides **8**. Assuming that the locations of the thiazolidinone and the two *tert*-butylperoxo groups are the same as those in **4**, there is no other reasonable alternative structure for these bisepoxides. The characteristic C═O stretching bands for the carbonyl group in compounds **4**, **8**, and **9** range from 1960 to 1963 cm^{-1}, indicating there is no significant change in the locations of the addends. The 1,3-dioxolane derivatives **10a** to **10e** showed similar NMR patterns. Their structure should be the same as the X-ray structure of **10d**.

Mechanism Consideration. Scheme 6 shows possible pathways for the formation of the thiirane **3** and thiazolidinone **4**. The first step is the TMSOTf-mediated epoxide opening to give the fullerene carbocation intermediate **A**. The opening is regioselective because the other alternative **X** is antiaromatic with the cation on the central cyclopentadiene pentagon. Addition of ArNCS to cation **A** would form either intermediate **B** or intermediate **E**, depending on whether N or S attacks the cation. Loss of TMS group from **B** then forms the neutral product **C**. Homolysis of the fullerene C−O bond forms the relatively stable cyclopentadienyl radical intermediate **D**. This is different from the Lewis acid-induced heterolytic cleavage in the first step, where the same fullerene C−O heterolysis gave an antiaromatic intermediate **X**. Recoupling of the radicals in **D** with the sulfur atom finally results in the thiazolidinone **4**. The fullerene C−O bond in the intermediate **F** can also be cleaved homolytically to form **G** in a process similar to the formation of **D**. Loss of ArNCO from **G** forms the thiirane **3**. Table 1 shows that photolysis favored the formation of **3**, and thermal reaction in the dark favored the formation of **4**. The present mechanism cannot explain this phenomenon clearly. Perhaps photolysis is a more efficient method than thermolysis for the homolytic bond cleavage just like in many other organic reactions. Two homolysis steps (**F** to **G** and **G** to **3**) are involved for the formation of **3**, whereas only one homolysis step (**C** to **D**) is required for the formation of **4**. The phenomenon also implies that intermediates **F** and **C** are interconvertible under photolysis or thermolysis, the mechanism of which is probably

SCHEME 7. Related Conversions in Classical Organic Chemistry



analogous to the Dimroth rearrangement such as the second reaction in Scheme 7.

In the case of TMSNCS reaction with **1**, the thiocyanate derivative **5** was isolated because TMS is a better leaving group than the aryl group. The alumina-induced conversion of compound **5** to **6** probably goes through the isomerization of **5** to the isothiocyanate intermediate **H**, which then forms the oxazolidine-2-thione intermediate **I**. The process is similar to the formation of **4** from intermediate **B**.

Transformations, analogous to the above mechanisms, have been reported in classical organic chemistry.[17] For example, a similar intermediate was proposed in the widely accepted mechanism for the well-established conversion of epoxide to episulfide using ammonium thiocyanate (Scheme 7 (1)).[17] The conversion of oxazolidine-2-thione to thiazolidin-2-one is also known in classical organic chemistry (Scheme 7 (2)).[17] Such Dimroth rearrangements usually involve ionic intermediates. Radical intermediates **D** and **G** were proposed for the present fullerene reactions (Scheme 6) instead of ionic species. The cyclopentadienyl radical in the center of **D** and **G** should be more stable than the corresponding antiaromatic cation. The structure with a negative charge on the center pentagon of **D** and **G** is also unlikely since this would require a positive charge on the other group with more electronegative heteroatoms such as oxygen.

Conclusion

The present results show that fullerene epoxide opens into the fullerene cation intermediate easily in the presence of a Lewis acid such as $BF_3{\cdot}Et_2O$ and TMSOTf. Sulfur and oxygen nucleophiles add to the fullerene cation to form stable sulfur- and oxygen-bonded fullerene derivatives, respectively. Rearrangement processes of the fullerene-fused heterocycles exhibit similar mechanisms with those observed for analogous organic compounds. Fullerene epoxide has been converted into fullerene thiirane, which exists as the 6,6-closed structure in agreement with theoretically calculated results.[11] Under the conditions employed in this study, the four *tert*-butyl peroxo groups in the present compounds remain unchanged. Further work is in progress to investigate the chemistry of the fullerene-mixed peroxides in detail and to explore their applications in controlled cage-opening reactions.

Experimental Section

All the reagents were used as received. Benzene and dichloromethane used for reactions was distilled from potassium under nitrogen; other solvents were used as received. Reactions were carried out under lab light in air at r.t. except where indicated. Chromatographic purifications were carried out with 200−300 mesh silica gel. Compounds not shown below are included in the Supporting Information. The NMR spectra were recorded at 298 K. ESI-MS spectra were recorded with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as the solvent. (+) ESI-MS indicates positive mode and (−) ESI-MS indicates negative mode.

Caution: A large amount of peroxide is involved in some of the reactions; care must be taken to avoid possible explosion.

Preparation of Intermediates 2. To a stirred solution of the compound **1** (132 mg, 0.12 mmol) and PhNCS (0.283 mL, 2.40 mmol) in dichloromethane (20 mL) at 30 °C was added TMSOTf (26 μL, 0.12 mmol) in a single portion with the flask wrapped by aluminum foil. The resulting mixture was stirred for 1 h at 30 °C, and the reaction was quenched by adding 10 drops of 2 M HCl. The organic layer was separated, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was chromatographed on silica gel column eluting with toluene. The first band was trace amount unreacted **1**. The second band was **2a**. The eluted solution of **2a** was evaporated and dried under atmosphere at r.t. with the bottle wrapped with aluminum foil. Yield: 115 mg, 78%. Compound **2b** was prepared by the same procedure as **2a** except that PhNCS was replaced by 1-naphthyl isothiocyanate. Yield: 78%, 73 mg from 80 mg of compound **1**.

Note: These compounds were unstable under light. Light should be avoided throughout the experimental procedure. Its spectra should be measured immediately.

Preparation of Compounds 3 and 4. Method A: Compound **2a** (112 mg, 0.091 mmol) was dissolved in dichloromethane (12 mL). The solution was then transferred into a Dewar container, the inside-surface of which can reflect light just like a mirror. Two household luminescent light bulbs (12 W, commercial household light bulb) were placed above the container. The solution was illuminated for 90 min, the reaction was stopped and the resulting solution was evaporated in the dark. The residue was dissolved in 4 mL benzene and chromatographed on a silica gel column eluting with benzene. The first red band was the major product **3**. Yield: 78 mg, 80%. The second red band was trace amount of **2a**. After these two bands were eluted, the solvent was changed to CH_2Cl_2. The third band was compound **4a** (9 mg, 8%). When the substrate **2a** was changed to compound **2b**, **3** and **4b** were prepared by the same procedure. Yield: **3**, 74%, 40 mg from 62 mg of **2b**; **4b**, 15%, 9 mg from 62 mg of **2b**.

Method B: The solid sample of compound **2b** (85 mg, 0.067 mmol) was used just after the solution was evaporated and dried at room temperature. The flask was wrapped with aluminum foil and stored at r.t. for 4 days in the dark. Then the resulting solid sample was directly chromatographed on a silica gel column eluting with toluene. The first red band was the product **3**. Yield: 17 mg, 23%. The second red band was trace amount of unreacted **2b**. After these two bands were eluted, the solvent was changed to CH_2Cl_2. The third band was compound **4b** (47 mg, 53%). When the substrate **2b** was changed to compound **2a**, **3** and **4a** were prepared by the same procedure. Yield: **3**, 13%, 4 mg from 32 mg of **2a**; **4a**, 59%, 19 mg from 32 mg of **2a**.

Method C: To a stirred solution of the compound **1** (100 mg, 0.092 mmol) and PhNCS (0.218 mL, 1.84 mmol) in dichlo-

(17) (a) Sakai, S.; Niimi, H.; Kobayashi, Y.; Ishii, Y. *Bull. Chem. Soc. Jpn.*, **1977**, *50*, 3271. (b) Baba, A.; Shibata, I.; Kashiwagi, H.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 341. (c) Robiette, R.; Dekoker-Malengreau, A.; Marchand-Brynaert, J. *Heterocycles* **2003**, *60*, 523.

romethane (20 mL) at 30 °C was added TMSOTf (17 μL, 0.092 mmol) in a single portion with the flask wrapped by aluminum foil. The resulting mixture was stirred for 1 h at 30 °C, the reaction was quenched by adding 3 mL 2M HCl. The organic layer was separated, dried with Na_2SO_4, filtered, and directly chromatographed on a silica gel column eluting with toluene. The major band **2a** was collected in a flask wrapped with aluminum foil. The collected solution containing **2a** was refluxed for around 24 h (until **2a** disappeared as indicated by TLC). The resulting solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with benzene as eluent. The first band was trace amount of **3**, the following band was **4a** (88 mg, 79%). When the PhNCS was changed to NaphthNCS, the intermediate **2b** was obtained based on the TLC analysis. However similar procedure (refluxing for 4 days) did not give the desired product **4b**.

Characterization Data for Compound 3. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.46 (s, 18H); 1.39 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 150.82; 149.30 (4C); 149.26; 148.74; 148.01 (1C); 147.76; 147.65; 147.60; 147.35; 147.27 (4C); 147.10; 147.06; 146.89; 146.83; 146.36; 145.74; 145.60 (1C); 145.12; 144.60; 144.39; 143.94; 143.54; 143.21; 142.78; 142.76; 141.79; 84.02; 81.82 (2*C*-$(CH_3)_3$); 81.63 (2*C*-$(CH_3)_3$); 81.34; 57.03 (1C, C−S); 52.94 (1C, C−S); 26.79 ($6CH_3$); 26.76 ($6CH_3$). FT-IR (microscope): 2978; 2926; 2853; 1473; 1460; 1387; 1363; 1260; 1242; 1193; 1128; 1107; 1043; 1020; 873; 753. (+) ESI-MS : *m*/*z* (rel intens) 1127 (100) [M + NH_4]. HRMS $C_{76}H_{36}SO_8Na$ (M + Na) calcd 1131.2023, found 1131.2076.

Characterization Data for Compound 4a. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.34−7.30 (m, 3H); 7.24 (d, 2H); 1.462 (s, 18H); 1.458 (s, 18H). ^{13}C NMR (CS_2/$CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 167.69 (1C); 154.93; 150.29; 148.97; 148.92; 148.08; 148.04 (1C); 147.95; 147.91; 147.70; 147.47; 146.95; 146.92; 146.90 (1C); 146.51; 145.57 (4C); 145.09; 144.57; 144.35; 144.03; 143.86; 143.53; 143.25; 143.00; 142.96; 142.64; 141.47; 138.51; 136.38 (1C, N−C in Ph); 131.27 (2C, Ph); 129.23 (2C, Ph); 129.06 (1C); 82.31; 81.55 (4*C*-$(CH_3)_3$); 80.68; 72.39 (C−N); 65.15 (C−S); 26.65 ($6CH_3$); 26.62 ($6CH_3$). FT-IR (microscope): 2978; 2932; 1692(C═O); 1593; 1492; 1477; 1454; 1387; 1364; 1334; 1308; 1242; 1193; 1157; 1115; 1103; 1041; 1019; 938; 870; 818; 752; 696; 673. Assignment was obtained from DEPT135 spectrum. (+) ESI-MS : *m*/*z* (rel intens) 1228(100) [M + 1], calcd $C_{83}H_{41}NO_9S$ MW = 1227. HRMS $C_{83}H_{41}NO_9SNa$ (M + Na) calcd 1250.2394, found 1250.2400; $C_{83}H_{42}NO_9S$ (M + H) calcd 1228.2575, found 1228.2578.

Crystal system, space group: Monoclinic, *P*2(1)/*c*, unit cell dimensions: a = 23.477(5) Å, α = 90°, b = 13.864(3) Å, β = 111.31(3)°, c = 19.873(4) Å, γ = 90°, volume = 6026(2) Å.^{3} Final R indices [$I > 2\sigma(I)$], R_1 = 0.0575, wR_2 = 0.1077.

Preparation of Compounds 5 and 6. To a stirred solution of compound **1** (40 mg, 0.037 mmol) and TMSNCS (160 μL, 1.17 mmol) in dichloromethane (5 mL) at room temperature was added TMSOTf (16 μL, 0.074 mmol). The resulting mixture was directly chromatographed on silica gel column after 10 min, eluting with dichloromethane and ethyl acetate (4:1). Compound **5** was the only band collected. The eluted solution of the product was evaporated, washed by methanol several times to remove the TMSOH and other impurities, and dried under atmosphere at r.t. with the bottle wrapped with aluminum foil. Yield: 28 mg, 66%.

Compound **6** was obtained when the above the solution of reaction mixture was directly chromatographed on 200−300 mesh neutral Al_2O_3 gel column instead of silica gel, using the same eluent (dichloromethane and ethyl acetate in 4:1 ratio). Yield: 87%, 73 mg from 80 mg of compound **1**. The silica gel product **5** could nearly quantitatively be transferred to **6** by chromatography on neutral Al_2O_3 column eluting with CH_2Cl_2/ethyl acetate mixtures.

Characterization Data for Compound 5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.61 (s, 1H); 1.51 (s, 18H); 1.47 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 155.25; 149.24; 149.17; 148.85; 148.79; 148.47; 148.43 (1C); 148.36; 148.27; 147.79; 147.67; 147.50; 147.25; 147.13 (3C); 145.66; 144.91 (4C); 144.73; 144.70; 144.20; 144.12; 143.85; 143.57; 143.15; 142.64; 140.85; 137.50; 113.28 (1C); 83.46 (2*C*-$(CH_3)_3$); 82.21 (1C, C−OH); 82.10; 82.05 (2*C*-$(CH_3)_3$); 81.08; 65.66 (C−S); 26.85 ($6CH_3$), 26.74 ($6CH_3$), assignment was obtained from HMBC spectrum. FT-IR (microscope): 3462; 2979; 2930; 2150; 1473; 1456; 1387; 1364; 1261; 1244; 1192; 1154; 1101; 1043; 1023; 909; 868; 732. (+) ESI-MS : *m*/*z* (rel intens) 1169 (100) [M + NH_4], 1152(86) [M + 1]; (−) ESI-MS : *m*/*z* (rel intens) 1150-(100) [M − 1]; calculated for $C_{77}H_{37}O_9SN$ MW = 1151. HRMS $C_{77}H_{37}O_9SNNa$ (M + Na) calcd 1174.2081, found 1174.2060; HRMS $C_{77}H_{41}O_9SN_2$ (M + NH_4) calcd 1169.2527, found 1169.2511.

Characterization Data for Compound 6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.89 (s, 1H); 1.46 (s, 18H); 1.38 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 170.94 (1C, C═O); 154.43; 150.58; 149.21; 149.14; 148.37; 148.28; 148.26 (1C); 148.15; 147.82; 147.63; 147.21; 147.12; 147.06 (1C); 146.75; 146.45; 145.69; 145.50; 144.98; 144.58; 144.21; 144.19; 143.70; 143.47; 143.20; 143.13; 142.80; 141.47; 138.27; 82.57; 81.98 (2*C*-$(CH_3)_3$); 81.86 (2*C*-$(CH_3)_3$); 80.87; 68.07 (C−N); 67.05 (C−S); 26.76 ($6CH_3$), 26.66 ($6CH_3$). Assignment was obtained from HMBC spectrum. FT-IR (microscope): 3392; 3268; 2979; 2930; 2870; 1709 (NHCO); 1676 (NHCO); 1473; 1456; 1387; 1364; 1260; 1243; 1193; 1134; 1104; 1039; 1020; 908; 870; 733. (+) ESI-MS : *m*/*z* (rel intens) 1169 (100) [M + NH_4]. HRMS $C_{77}H_{41}O_9SN_2$ (M + NH_4) calcd 1169.2527, found 1169.2523.

Preparation of Compound 7. To a stirred solution of compound **6** (66 mg, 0.057 mmol) and benzoyl chloride (160 μL, 1.15 mmol) in dry dichloromethane (11 mL) at room temperature was added anhydrous Na_2CO_3 (12 mg, 0.114 mmol). The resulting suspension was refluxed for 4 h, and the reaction mixture solution was directly chromatographed on silica gel column, eluting with dichloromethane and petroleum ether (2:1). The first band was trace amount of unknown compounds and unreacted PhCOCl. The second red band was the main product **7** (17 mg, 24%). After the two bands were eluted, the solvent was changed to CH_2Cl_2 and ethyl acetate (4:1). The third band was the unreacted compound **6** (33 mg, 50%).

Characterization Data for Compound 7. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.26−8.24 (m, 2H); 7.59−7.55 (m, 3H); 1.485 (s, 18H); 1.344 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 170.97 (1C, C═O); 162.07 (1C, C═O); 154.21; 151.29; 149.21; 149.10; 148.35; 148.30 (1C); 148.26; 148.08; 147.88; 147.62; 147.32; 147.27; 146.94 (1C); 146.85; 146.10; 145.82; 145.55; 145.20; 144.52; 144.45; 143.71; 143.44; 143.41; 143.10; 142.56; 141.75; 138.11; 135.15 (1C, Ph); 131.44 (1C, Ph); 130.79 (1C, Ph); 129.95 (1C, Ph); 129.03 (1C, Ph); 126.69 (1C, Ph); 82.78; 81.95 (2C-$(CH_3)_3$); 81.68 (2C-$(CH_3)_3$); 80.95; 73.64 (C−N); 57.66 (C−S); 26.85 ($6CH_3$), 26.65 ($6CH_3$). FT-IR (microscope): 2979; 2930; 2869; 1774; 1748; 1698; 1624; 1600; 1473; 1452; 1387; 1364; 1258; 1242; 1194; 1144; 1104; 1092; 1040; 1019; 909; 870; 733; 705. (+) ESI-MS : *m*/*z* (rel intens) 1256 (100) [M + 1], calcd $C_{84}H_{41}O_{10}SN$ MW = 1255. HRMS $C_{84}H_{41}O_{10}SNNa$ (M + Na) calcd 1278.2343, found 1278.2332; $C_{84}H_{41}O_{10}SNK$ (M + K) calcd 1294.2083, found 1294.2067.

Preparation of Compounds 8 and 9. To a stirred solution of compound **4a** (72 mg, 0.059 mmol) in chlorobenzene (36 mL) at room temperature was added C_{60} (85 mg) under nitrogen atmosphere. The resulting solution was stirred and heated for 16 h in an oil bath at 110 °C. The resulting solution was chromatographed on a silica gel column, eluting with toluene. The first purple band was C_{60} and other unknown compounds. After the first band was eluted, the solvent was changed to CH_2Cl_2. The second red band was the unreacted **4a** (23 mg, 32%). The third band was compound **9b** (15 mg, 24%). The fourth band was **8b** (14 mg, 22%). Compounds **9a** and **8a** were prepared by the same procedure except the reaction temperature changed to 130 °C. Yield: **9a**, 22%, 18 mg from 96 mg of **6**; **8a**, 17%, 14 mg from 96 mg of **6**). Compounds **9c** and **8c** were also prepared by the same procedure at 130 °C.

TABLE 2. Yields and Conditions for the Preparation of Compounds 10 and 11

reactant	Lewis acid	solvent	time, h	product	yield (%)
p-HOC_6H_4CHO (5 equiv)	$BF_3{\cdot}Et_2O$ (5 equiv)	CH_2Cl_2	0.5	**10a**	52
				11	trace
p-HOC_6H_4CHO (5 equiv)	$BF_3{\cdot}Et_2O$ (5 equiv)	PhH	5	**10a**	30
				11	16
p-$NO_2C_6H_4CHO$ (5 equiv)	$BF_3{\cdot}Et_2O$ (5 equiv)	PhH	3	**10b**	38
				11	29
p-$NO_2C_6H_4CHO$ (5 equiv)	$BF_3{\cdot}Et_2O$ (5 equiv)	CH_2Cl_2	0.5	**10b**	20
				11	trace
m-$NO_2C_6H_4CHO$ (10 equiv)	$BF_3{\cdot}Et_2O$ (10 equiv)	PhH	2	**10c**	40
				11	25
p-$MeOC_6H_4CHO$ (5 equiv)	$BF_3{\cdot}Et_2O$ (5 equiv)	CH_2Cl_2	9	**10d**	51
				11	trace
acetaldehyde (5 equiv)	$BF_3{\cdot}Et_2O$ (5 equiv)	CH_2Cl_2	1	**10e**	51
acetone (40 equiv)	TMSOTf (1.5 equiv)	CH_2Cl_2	2	**10f**	59
	$BF_3{\cdot}Et_2O$ (5 equiv)	CH_2Cl_2	12	**10f**	48
trace H_2O in solvent	$BF_3{\cdot}Et_2O$ (5 equiv)	PhH	12	**11**	66

Yield: **9c**, 19%, 15 mg from 90 mg of **4b**; **8c**, 23%, 18 mg from 90 mg of **4b**.

Characterization Data for Compound 8a. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.06 (broad, 1H); 1.41 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 169.95 (1C, C═O); 149.74; 148.63; 148.53; 148.28; 148.19; 148.01 (1C); 147.97; 147.83; 147.37 (1C); 147.34; 146.93; 146.52; 146.33; 146.02; 145.73; 145.49; 145.23; 144.71; 144.64; 144.26; 144.07; 144.03; 143.65; 143.22; 142.77; 139.36; 136.77; 83.13; 82.28 (2*C*-$(CH_3)_3$); 76.50; 72.65 (C−N); 66.62; 61.36(C−S); 26.68 (6CH_3). FT-IR (microscope): 3392; 3184; 3073; 2979; 2930; 2870; 1709 (NHCO); 1680 (NHCO); 1463; 1420; 1387; 1363; 1262; 1243; 1191; 1160; 1142; 1124; 1080; 1045; 1014; 908; 899; 874; 819; 788; 759; 732. (+) ESI-MS : *m*/*z* (rel intens) 1028 (82) [M + Na]; (−) ESI-MS : *m*/*z* (rel intens) 1004 (100) [M − 1]. HRMS $C_{69}H_{19}NO_7SNa$ (M + Na) calcd 1028.0774, found 1028.0795.

Characterization Data for Compound 9a. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.72 (broad, 1H); 1.49 (s, 9H); 1.41 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 1C except noted. δ: 169.38 (1C, C═O); 149.88; 149.75; 148.75; 148.61; 148.55; 148.44; 148.35; 148.15; 148.03; 147.98; 147.79; 147.74 (2C); 147.56; 147.45; 147.38; 147.29; 146.88; 146.85; 146.74; 146.60; 146.57 (2C); 146.23; 145.84; 145.76; 145.51; 145.24; 145.02; 144.94; 144.76; 144.61; 144.54 (2C); 144.46; 144.19; 144.05 (2C); 143.99; 143.72 (3C); 143.04; 142.87; 142.61; 142.45; 141.98; 141.93; 141.87; 140.15; 138.58; 137.57; 82.71; 82.36 (1*C*-$(CH_3)_3$); 82.14 (1*C*-$(CH_3)_3$); 81.15; 70.92; 70.57; 69.75; 68.73 (C−N); 68.04; 62.43 (C−S); 26.72 (3CH_3); 26.65 (3CH_3). FT-IR (microscope): 3387; 3193; 3081; 2979; 2930; 1711 (NHCO); 1682 (NHCO); 1455; 1421; 1387; 1363; 1262; 1244; 1191; 1142; 1093; 1039; 1021; 907; 850; 796; 758; 732. (+) ESI-MS : *m*/*z* (rel intens) 1028 (82) [M + Na]; (−) ESI-MS : *m*/*z* (rel intens) 1004 (100) [M − 1]. HRMS $C_{69}H_{18}NO_7S$ (M − 1) calcd 1004.0810, found 1004.0819.

Preparation of Compounds 10 and 11. Compound **1** was dissolved in dry dichloromethane or benzene. The flask was wrapped with aluminum foil and stirred at 30 °C. Then aldehyde or acetone and $BF_3{\cdot}Et_2O$ were added. Progress of the reaction was monitored by TLC. When the **1** was nearly consumed, 2 mL of 2 M aqueous HCl was added to the mixture. The organic layer was separated, dried with Na_2SO_4, and filtered. The solvent was removed. The residue was chromatographed on a silica gel column with dichloromethane/petroleum ether (2/1) as eluent to afford the main product **10**. The reaction time and the yield for each individual nucleophile are listed in Table 2 (all the yields are the isolated yields). Yield: **10a**, 52%, 23 mg from 40 mg of **1**; trace **11**; Yield: **10a**, 30%, 20 mg from 60 mg of **1**; **11**, 16%, 10 mg from 60 mg of **1**; Yield: **10b**, 30%, 17 mg from 40 mg of **1**; **11**, 29%, 12 mg from 40 mg of **1**; Yield: **10b**, 20%, 9 mg from 40 mg of **1**; trace **11**; Yield: **10c**, 40%, 18 mg from 40 mg of **1**; **11**, 25%, 11 mg from 40 mg of **1**; Yield: **10d**, 51%, 23 mg from 40 mg of **1**; trace **11**; Yield: **10e**, 51%, 21 mg from 40 mg of **1**; Yield: **10f**, 59%, 25 mg from 40 mg of **1** (TMSOTf as catalyst); **10f, 48**%, 20 mg from 40 mg of **1** ($BF_3{\cdot}Et_2O$ as catalyst); Yield: **11**, 66%, 41 mg from 60 mg of **1**.

Characterization Data for Compound 10d. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.78 (d, 2H); 7.02 (d, 2H); 6.63 (s, 1H); 3.89 (s, 3H, Me); 1.45 (s, 27H); 1.41 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 1C except noted. δ: 161.23 (1C, Ph); 151.60; 150.66; 149.17; 149.13; 149.09; 149.05; 148.96; 148.69; 148.40; 148.36; 148.23; 148.19; 148.17 (2C); 148.14; 147.82; 147.72; 147.56; 147.48; 147.32; 147.28; 147.22 (2C); 147.17; 146.88; 146.78; 146.65; 146.35; 145.68; 145.61 (2C); 145.54; 145.52; 145.49; 145.39; 145.07; 144.85; 144.51; 144.42; 144.17; 144.15; 144.04; 143.64; 143.60; 143.40; 143.36; 143.26; 143.19; 142.90; 142.71; 141.36; 141.15; 139.41; 138.58; 129.21 (2C, Ph); 127.06 (1C, Ph); 113.84 (2C, Ph); 105.72; 90.14; 84.60; 83.29; 82.95; 81.87 (2*C*-$(CH_3)_3$); 81.56 (1*C*-$(CH_3)_3$); 81.47 (2C, 1C + 1*C*-$(CH_3)_3$); 80.71, 26.82 (3CH_3 in ^{t}Bu); 26.80 (3CH_3 in ^{t}Bu); 26.77 (3CH_3 in ^{t}Bu); 26.69 (3CH_3 in ^{t}Bu). FT-IR (microscope): 3434; 2979; 2929; 2870; 1617; 1601; 1522; 1454; 1388; 1364; 1267; 1243; 1193; 1167; 1120; 1099; 1047; 1021; 1001; 908; 871; 836; 755; 733. (+) ESI-MS : *m*/*z* (rel intens) 1246 (40, M + NH_4), 1251(96, M + Na), 1267 (100, M + K), (−) ESI-MS: 1259 (100, M + MeO), calculated for $C_{84}H_{44}O_{11}$ MW = 1228. HRMS $C_{84}H_{48}O_{11}N$ (M + NH_4) calcd 1246.3222, found 1246.3220; $C_{84}H_{44}O_{11}Na$ (M + Na) calcd 1251.2776, found 1251.2810; $C_{84}H_{44}O_{11}K$ (M + K) calcd 1267.2515, found 1267.2514.

Crystal system, space group: monoclinic, *P*2(1)/*c*, unit cell dimensions: a = 23.525(5) Å, α = 90°, b = 14.298(3) Å, β = 93.55(3)°, c = 18.395(4) Å, γ = 90°, volume = 6176(2) Å.^{3} Final R indices [$I > 2\sigma(I)$], R_1 = 0.0731, wR_2 = 0.1278.

CCDC-633218 and CCDC-638148 contain the crystallographic data for **4a** and **10d**, respectively. The crystallographic data can be obtained free of charge via www.ccdc.cam.ac.uk/consts/retrieving-.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK; fax: (+44)1223−366-033; or e-mail: deposit@ccdc.cam.ac.uk

Characterization Data for Compound 10e. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.91 (q, 1H); 1.79 (d,3H); 1.47 (s, 9H); 1.45 (s, 9H); 1.41 (s, 9H); 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 1C except noted. δ: 151.37; 150.88; 149.20; 149.17; 149.15; 149.12; 149.05; 148.97; 148.70; 148.43; 148.24 (2C); 148.22; 148.17 (2C); 147.75; 147.64; 147.61; 147.58; 147.35; 147.33; 147.25 (2C); 147.20; 146.88; 146.83; 146.44; 146.20; 145.74; 145.60; 145.57 (4C); 145.52; 145.07; 144.83; 144.53; 144.39; 144.33; 144.10; 144.02; 143.63 (2C); 143.47; 143.39; 143.35; 143.19; 142.98; 142.68; 141.49; 141.21; 139.67; 138.34; 103.45 (CH); 90.40; 84.77; 83.22; 82.94; 81.89 (C(CH_3)$_3$); 81.83 (C(CH_3)$_3$); 81.56 (C(CH_3)$_3$); 81.53 (C(CH_3)$_3$); 80.72; 80.70; 26.82 (3CH_3); 26.77 (9CH_3); 18.92. FT-IR (microscope): 2978; 2922;

2851; 1461; 1418; 1387; 1364; 1260; 1243; 1194; 1144; 1118; 1100; 1027; 1007; 905; 871; 755; 732. (+) ESI-MS : *m*/*z* (rel intens) 1154 (100) [M + NH_4]; calculated for $C_{78}H_{40}O_{10}$ MW = 1136. HRMS $C_{78}H_{44}O_{10}N$ (M + NH_4) calcd 1154.2960, found 1154.2940.

Characterization Data for Compound 10f. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.94 (s, 2CH_3); 1.46 (s, 18H); 1.37 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 151.43; 149.23; 149.12; 149.02; 148.59; 148.17(4C); 148.14; 147.60; 147.26 (5C); 147.21 (1C); 146.89; 146.31; 145.85; 145.58; 145.47; 145.16; 144.90; 144.42; 143.99; 143.55; 143.31; 143.28; 142.65; 141.28; 137.94; 116.02 (1C); 92.08; 86.03; 83.12; 81.89; 81.78 (2*C*(CH_3)$_3$); 81.36 (2*C*(CH_3)$_3$); 80.74; 27.84; 26.85 (6CH_3); 26.71 (6CH_3). FT-IR (microscope): 2979; 2926; 2853; 1463; 1385; 1363; 1243; 1217; 1194; 1175; 1098; 1061; 1021; 1009; 901; 873; 757 cm^{-1}, (+) ESI-MS : *m*/*z* (rel intens) 1168 (100, M + NH_4). HRMS $C_{79}H_{42}O_{10}Na$ (M + Na) calcd 1173.2670, found 1173.2675.

Characterization Data for Compound 11. ^{1}H NMR ($CDCl_3$, 400 MHz): 4.27 (s, 1H in OH); 1.47 (s, 18H); 1.42 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 151.16; 149.57; 149.13; 149.12; 148.62; 148.34 (3C); 148.16; 148.09; 147.56; 147.30 (3C); 147.26; 146.92; 145.88; 145.63; 145.19; 145.14; 145.04; 144.83; 144.46; 144.20; 143.81; 143.47; 143.23; 142.94; 141.15; 139.47; 89.87; 83.51; 82.37; 82.14 (2*C*-(CH_3)$_3$); 81.97 (2*C*-(CH_3)$_3$); 80.80; 26.72 (6CH_3); 26.70 (6CH_3). FT-IR (microscope): 3453; 2980; 2931; 2871; 1529; 1467; 1387; 1364; 1306; 1262; 1243; 1230; 1193; 1121; 1106; 1092; 1058; 1023; 1006; 979; 896; 871; 755; 728; 695. (−) ESI-MS : *m*/*z* (rel intens) 1181 (100) [M − OH + 2 OCH_3], (+) ESI-MS : *m*/*z* (rel intens) 1168 (100) [M − OH + OCH_3+ NH_4]. HRMS $C_{76}H_{37}O_{11}BNa$ (M + Na) calcd 1159.2326, found 1159.2354.

Preparation of Compounds 12 and 13. To a stirred solution of compound **8b** (28 mg, 0.026 mmol) and acetone (76 μL, 1.04 mmol) in dry dichloromethane (10 mL) at 30 °C was added TMSOTf (18 μL, 0.104 mmol). The flask was wrapped with aluminum foil and stirred. The color of the solution slowly changed from light red to dark red. After being stirred for 30 min, 2 mL of 2 M aqueous HCl was added to the mixture. The organic layer was separated, dried with Na_2SO_4, and filtered. The solvent was removed. The residue was chromatographed on a silica gel column with dichloromethane as eluent to afford the main product **12b** (10 mg, yield: 32%). Compounds **12a, 13a**, and **13b** were prepared by the same procedure. Yield: **12a**, 67%, 12 mg from 16 mg of **8a**; **13a**, 45%, 11 mg from 22 mg of **9a**; **13b,** 45%, 14 mg from 28 mg of **9b**.

Characterization Data for Compound 12a. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40 (broad, 1H); 1.99 (s, 6H); 1.98(s, 6H); 1.31 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 2C except noted. δ: 168.04 (1C, C═O); 148.97; 148.67 (1C); 148.64; 148.61; 148.44; 148.37; 148.09 (4C); 147.87; 147.84; 147.73; 147.71 (1C); 147.44; 145.83; 144.71; 144.67; 144.41; 143.71; 143.64; 143.59; 143.57; 142.78; 141.46; 141.06; 140.71; 139.82; 135.89; 117.25; 93.90; 85.42; 82.06 (1C, C−N); 81.55 (2*C*-(CH_3)$_3$); 81.41; 68.85-(C−S); 29.41 (2CH_3); 28.74 (2CH_3); 26.97 (6CH_3). FT-IR (microscope): 3389; 3145; 3064; 2978; 2934; 2868; 1700 (NHCO); 1677 (NHCO); 1455; 1384; 1366; 1262; 1241; 1221; 1191; 1175; 1150; 1120; 1077; 1061; 1034; 1007; 934; 908; 891; 821; 761; 733. (+) ESI-MS : *m*/*z* (rel intens) 1145 (100) [M + Na], 1122 (52) [M + 1]; (−) ESI-MS : *m*/*z* (rel intens) 1120 (100) [M − H], 1152 (26) [M + CH_3O]. HRMS $C_{72}H_{24}NO_8S$ (M − CH_3COCH_3 − 1) calcd 1062.1228, found 1062.1222; $C_{69}H_{18}NO_7S$ (M − 2 CH_3-$COCH_3$ − 1) calcd 1004.0810, found 1004.0815.

Characterization Data for Compound 13a. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.99 (broad, 1H); 1.86 (s, 3H); 1.83 (s,3H); 1.50 (s, 3H); 1.43 (s, 3H); 1.42 (s, 9H); 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 1C except noted. δ: 169.79 (1C, C═O); 150.34; 149.95; 149.76; 149.37; 148.66; 148.54 (3C); 148.41 (2C); 148.38; 148.35; 148.33; 148.25 (3C); 148.21; 148.02; 147.90; 147.81; 147.79; 147.72; 147.67 (2C); 147.65; 147.47; 147.06; 146.86; 146.06; 146.02; 145.76; 145.41; 145.33; 144.87; 144.84; 144.82 (2C); 144.77; 144.64; 144.51; 144.45; 144.41; 144.38; 144.09 (2C); 143.88; 143.79 (3C); 143.64; 143.60; 143.42; 143.33; 142.29; 116.16; 116.10; 89.08; 88.85; 82.11 (1*C*-(CH_3)$_3$); 81.89 (1*C*-(CH_3)$_3$); 81.17; 78.07; 67.76; 65.88; 28.26 (CH_3); 27.87 (CH_3); 26.85 (3CH_3); 26.76 (CH_3); 26.69 (4CH_3). FT-IR (microscope): 3388; 3182; 3070; 2979; 2929; 2868; 1709 (NHCO); 1677 (NHCO); 1454; 1421; 1385; 1365; 1243; 1219; 1192; 1141; 1112; 1080; 1021; 908; 882; 869; 850; 797; 758; 733. (+) ESI-MS : *m*/*z* (rel intens) 1086 (100) [M − CH_3COCH_3 + Na]; (−) ESI-MS: *m*/*z* (rel intens) 1062 (100) [M − CH_3COCH_3 − 1], 1004 (32) [M − 2 CH_3COCH_3 − 1]; calculated for $C_{75}H_{31}NO_9S$ MW = 1121. HRMS $C_{72}H_{26}$-NO_8S (M − CH_3COCH_3 + 1) calcd 1064.1374, found 1064.1359; $C_{72}H_{25}NO_8SNa$ (M −CH_3COCH_3 + Na) calcd 1086.1193, found 1086.1155.

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Supporting Information Available: Characterization data for compounds not listed in the experimental section, selected NMR, MS, IR spectra, and crystallographic data for **4a** and **10d**. The material is available free of charge via the Internet at http://pubs.acs.org.

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