Preparation of [5,6]- and [6,6]-Oxahomofullerene Derivatives and Their Interconversion by Lewis Acid Assisted Reactions of Fullerene Mixed Peroxides

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Abstract: [60]Fullerene mixed peroxides $C_{60}(O)(OOtBu)_4$ exhibit chemo- and regioselective reactions under mild conditions. The epoxy moiety is opened by ferric chloride to form vicinal hydroxy chloride $C_{60}Cl(OH)(OOtBu)_4$. BF_3 is also effective in opening the epoxy moiety. The O–O bond of the fullerene mixed peroxide is cleaved by aluminum chloride to form both [5,6]- and [6,6]-fullerene hemiketals (oxohomo[60]fullerenes). A Hock-type rearrangement is proposed for the formation of the hemiketals, in which a fullerene C–C bond is cleaved. Lewis acids and/or visible light can initiate isomerization of the hemiketal isomers. Single-crystal X-ray analysis and theoretical calculations confirmed the results.

Keywords: epoxides · fullerenes · hemiketals · isomerization · peroxides

Introduction

Homofullerenes (fulleroids)[1] are systems in which the number of π electrons on the cage remains the same after chemical functionalization. In principle, two kinds of homofullerenes are possible: [5,6] open and [6,6] open. Derivatives of [5,6] open methanofullerene are readily prepared by carbene addition to C_{60}.[2] [5,6] open $C_{60}O$ (oxahomo[60]fullerene),[3] iminofullerenes[4], C_{60} dimer,[5] and C_{70} carbene adducts[6] have also been synthesized. However, additions at the [6,6] junction of fullerenes mostly result in [6,6] closed adducts;[7] [6,6] open homofullerenes are stable only in special cases.[8–10] Hirsch et al.[8] synthesized bis[6,6] homo[60]fullerenes with a 1,2,3,4 addition pattern and found that the energy difference between the closed and open bis[6,6] isomers are rather small.[9] Taylor et al.[10] reported a [6,6] open fluorooxahomofullerene derivative with oxygen bonded to fluorinated carbon atoms. Hemiketal moieties were suggested to be present in fullerenols at the [6,6] junction, but full identification was not possible because the products studied had different numbers of hydroxyl groups and were complex mixtures of isomers.[11] Recently, fullerenols were characterized as stable radical anions by Wilson et al.[12]

We have synthesized fullerene mixed peroxides with cyclopentadienyl moieties such as **1**[13] and found that further reactions of such mixed peroxide adducts gave open-cage

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Selected NMR, ESI-MS, and IR spectra; Cartesian coordinates of the optimized structures of isomers **3**, **4**, and **8**.

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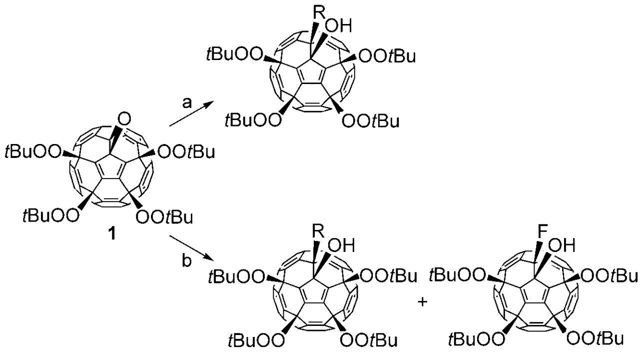
fullerene and hydroxylated fullerene derivatives with well-defined structures.[14] In light of the well-established and rich chemistry of classical peroxides, fullerene mixed peroxides appear to be excellent precursors for compounds with potential applications. Here we report the Lewis acid induced formation and single-crystal X-ray diffraction analysis of [5,6]- and [6,6]-oxahomo[60]fullerene derivatives (fullerene hemiketals).

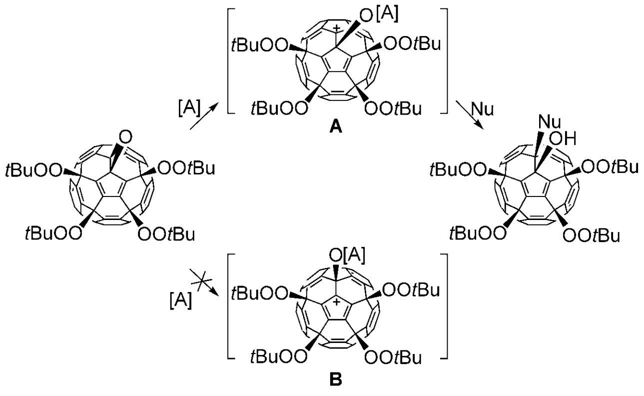
Results and Discussion

Lewis acids are known to catalyze the opening of epoxides and the heterolysis of the O–O bond of peroxides. Treating **1** with ferric chloride opened the epoxy moiety and yielded vicinal hydroxyl chloride **2a** (Scheme 1). Boron trifluoride is a more versatile Lewis acid for epoxide opening. In the presence of BF_3, addition of methanol, *tert*-butyl hydroperoxide, and hydrogen peroxide yielded **2b**, **2c**, and **2d**, respectively. Fullerenyl hydrogen peroxide **2d** was surprisingly stable and survived purification by column chromatography. In all BF_3-catalyzed reactions, a small amount of fluoro derivative **2e** was observed. That BF_3 was the fluorine source was confirmed by treating **1** with BF_3 alone in a control experiment. Product yields with BF_3 are lower than those with the ferric chloride. $BF_3 \cdot OEt_2$ was recently used as a fluorine source in the ring-opening hydrofluorination of epoxides.[15]



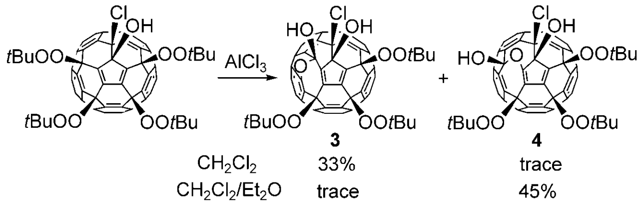
Scheme 1. Epoxy opening reactions. **2a** (R = Cl): route a) $FeCl_3$, 85%; **2b** (R = OMe): route b) BF_3, MeOH, 61%; **2c** (R = OO*t*Bu): route b) BF_3, *t*BuOOH, 23%; **2d** (R = OOH): route b) BF_3, H_2O_2, 16%; **2e** (R = F): route b) BF_3, 27%.

The relative location of the hydroxy group and the R substituent in compounds **2** cannot be determined by spectroscopic data. Mechanistic considerations favor structures as in Scheme 1. The Lewis acid Fe^{III} or BF_3 attacks the epoxy oxygen atom to form fullerene cation intermediate **A** (Scheme 2). The alternative **B** would not be stable because of its antiaromatic cyclopentadienyl cation character. Addition of a nucleophile to intermediate **A** results in a hydroxyl group on the central pentagon. The relative location of Cl and OH in **2a** agrees with the crystal structure of **4** (see below). Taylor et al. observed the conversion of antiaromatic C_5-symmetric cation $[C_{60}Ar_5]^+$, formed by treating $C_{60}Ar_5Cl$ (Ar = Ph or 4-FC_6H_4) with $AlCl_3$, to the more stable C_s isomer (analogous to **A**).[16]



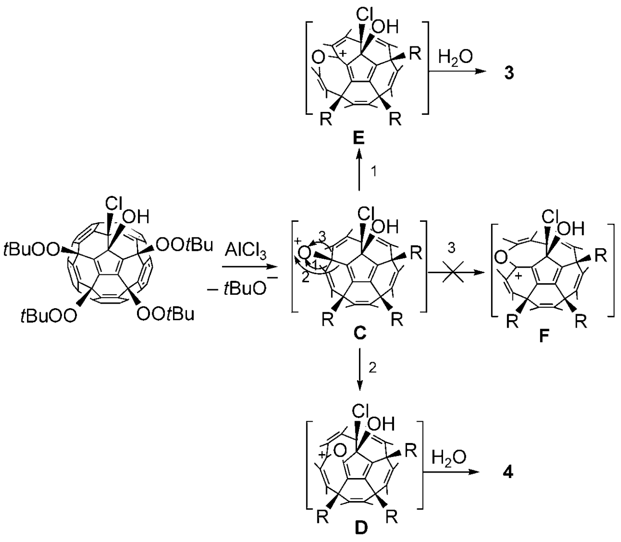
Scheme 2. Proposed mechanism for epoxy opening reactions.

Addition of $AlCl_3$ to **2a** led to heterolysis of the peroxo O–O bond and formation of hemiketal fullerene derivatives. The reaction gave two regioisomers **3** and **4** (Scheme 3). The hemiketal moiety is located at [5,6] and [6,6] junctions for **3** and **4**, respectively. The regioselectivity can be controlled effectively by varying the solvent. In pure dichloromethane, [5,6] hemiketal **3** is the major product with a trace of [6,6] hemiketal **4**. Addition of diethyl ether as cosolvent completely reverses the product ratio and affords **4** as the major product. Cosolvents such as CH_3CN and Me_2S also afford **4** as the major product, but in lower overall yields than with diethyl ether.



Scheme 3. Cleavage of fullerene C–C bond and formation of hemiketals **3** and **4**

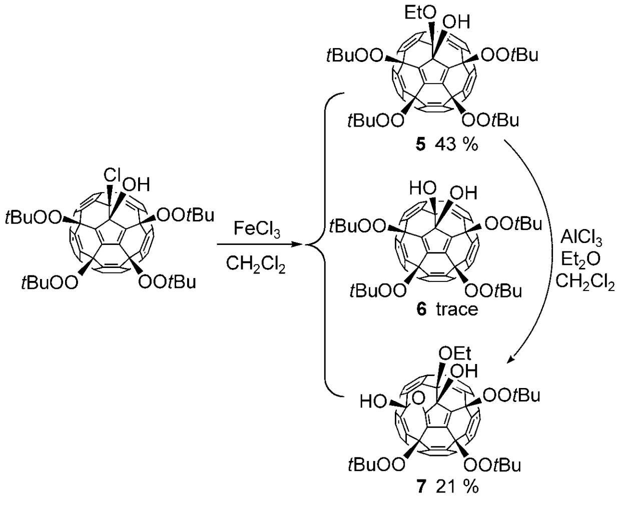
A possible mechanism for the formation of **3** and **4** is shown in Scheme 4. The key steps are similar to the well-known Hock rearrangement.[17] $AlCl_3$ initiates heterolysis of the peroxo bond to form oxonium cation **C** in the first step, which then rearranges to carbocation **D** or **E**. In the process a [6,6] or [5,6] junction is cleaved, respectively. In the absence of diethyl ether **E** is the favored species. The adjacent hydroxyl group probably stabilizes the carbocation of **E**. When diethyl ether is added **D** is the favored species since the carbocation position in **D** is located further from the crowded central pentagon as compared to that of **E**. Thus, diethyl ether may stabilize the cation in **D** more effectively for steric reasons. Cleavage of the other [5,6] junction would



Scheme 4. Proposed mechanism for the formation of **3** and **4**.

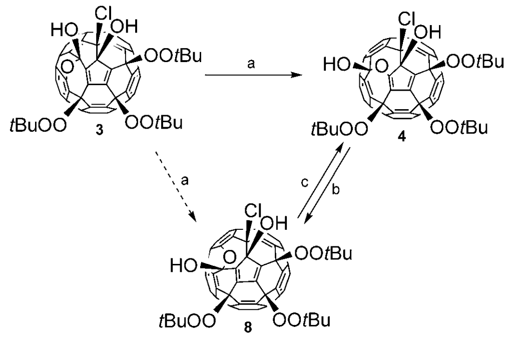
form carbocation **F**, but no hemiketal corresponding to this intermediate was detected under these conditions.

Ferric chloride reacts differently with compound **2**; three products were isolated (Scheme 5) in CH_2Cl_2. Compounds **5** and **6** are due to the replacement of the chlorine atom by ethoxy and hydroxy groups, respectively. The ethoxy group in **5** came from the ethanol used as a stabilizing agent in CH_2Cl_2. When CH_2Cl_2 was distilled from P_2O_5 and used as the solvent, only dihydroxy derivative **6** was obtained in low yield. Hemiketal **7** is probably due to further reaction of **5** with $FeCl_3$. Like the formation of **4**, compound **7** could be prepared by treating pure **5** with $AlCl_3$ in CH_2Cl_2/Et_2O. The mechanism of the reaction with ferric chloride may be cleavage of the C–Cl bond in the first step, followed by addition of EtOH or H_2O as nucleophile. Ferric chloride abstracts the chlorine atom preferably instead of initiating peroxo O–O bond heterolysis as occurs with $AlCl_3$.



Scheme 5. Cleavage of C–Cl bond with $FeCl_3$.

Hemiketals **3**, **4**, and **8** isomerize on addition of Lewis acids and/or irradiation with visible light (Scheme 6). Compound **3** isomerizes partially to **4** and to a new hemiketal **8** when treated with $La(NO_3)_3$ or $B(C_6F_5)_3$ under laboratory light. It is not clear whether **8** formed directly from **3** or by further isomerization of **4**, since **4** also gave **8** under the same conditions. Isomer **4** could also be converted to **8** by irradiation with an ordinary luminescent lamp in the absence of a Lewis acid. In total darkness isomerization of **3** or **4** was hardly detectable at room temperature.

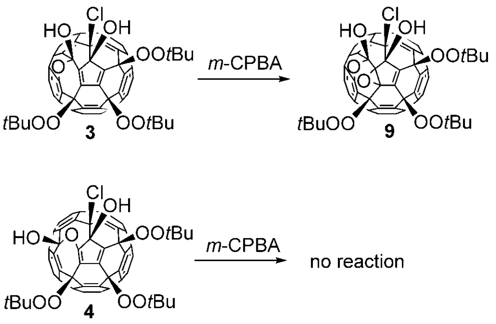


Scheme 6. Isomerization among hemiketals **3**, **4**, and **8**. a) $La(NO_3)_3{\cdot}x\,H_2O$ and laboratory light, or $B(C_6F_5)_3$ and laboratory light; b) $La(NO_3)_3{\cdot}x\,H_2O$ and laboratory light, or $B(C_6F_5)_3$ and laboratory light, or luminescent lamp (14 W); c) $CDCl_3$ in the dark. All at room temperature.

New hemiketal **8** was not stable and converted slowly to **4** in $CDCl_3$. The process was followed readily by ^1H NMR spectroscopy. A pure sample of **8** gave a mixture of **4** and **8** in 2.5:1 ratio after standing at room temperature in the dark for 110 h. Irradiation of **8** with a luminescent light bulb resulted in decomposition.

Various other experiments (see Experimental Section) indicate that photolysis by visible light is more efficient for the **3**→**4**→**8** conversion. Spontaneous conversion of **8** to **4** in total darkness is consistent with our computations, which indicate that **4** is more stable than **8**. The isomerization of **3**, which was computed to have the lowest energy, only took place photochemically in the presence of a Lewis acid. The isomerization processes observed here are reminiscent of the photoisomerization of [5,6] open to [6,6] closed $C_{70}(O)$ isomers reported by Weisman et al.[18]

Single crystals were obtained for hemiketal **4** by slow evaporation of a CS_2/*n*-pentane solution at 5 °C. Various attempts to grow suitable crystals of the [5,6] isomer **3** failed. Treating **3** with *m*-chloroperbenzoic acid (*m*CPBA) results in mono-epoxidation of the central pentagon and formation of **9** (Scheme 7). The introduction of the new epoxy moiety improves the crystallizability, and single crystals of **9** were obtained by slow evaporation of a benzene/n-hexane solution at 5 °C. Under the same conditions *m*CPBA does not react with hemiketal **4**.



Scheme 7. Epoxidation of fullerene hemiketals.

A strong internal hydrogen bond between the hydroxy group on the central pentagon and the adjacent peroxo oxygen atom is apparent in the crystal structure of **4** (Figure 1 a). The hemiketal hydroxy group forms a hydrogen bond with the peroxo group of a neighboring molecule. The bonding pattern of the ether oxygen atom is almost exactly the same in [6,6] hemiketal **4** and [5,6] hemiketal **9** (Figure 1 b). In both cases, the ether oxygen atom is more strongly bonded to the vinyl carbon atom than to the hemiketal carbon atom (1.367(4) versus 1.416(4) Å in **4** and 1.367(16) versus 1.409(12) Å in **9**). The two double bonds on the central pentagon of **4** are the shortest among all the double bonds on the surface. The crystal structures establish the fullerene hemiketal moieties at both the [6,6] and [6,5] junctions.

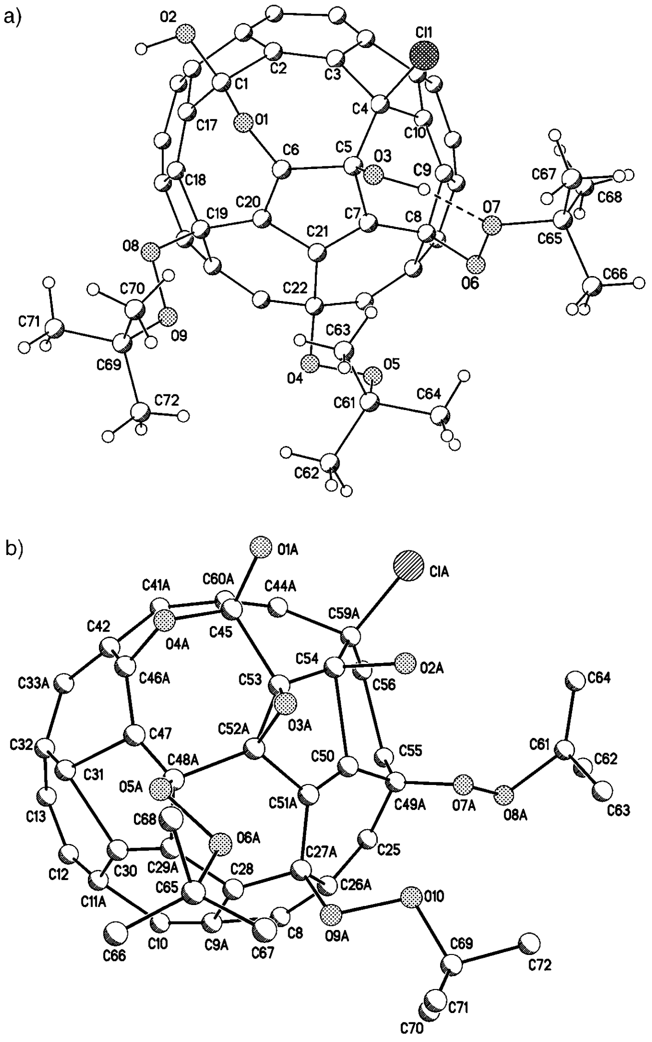


Figure 1. Single-crystal molecular structure of a) **4** and b) **9**; for clarity, H atoms (for **9**) and some atoms of the C_{60} cage are omitted.

The structures of **2** and **5** were verified by their NMR spectra, which indicate C_s symmetry with the expected number of ^1H and ^{13}C signals. The presence of a hemiketal moiety in **3**, **4**, **7**, **8**, and **9** was suggested by hemiketal carbon signals ranging from $\delta = 97.9$ to 108.0 ppm, but the structures of these unsymmetric hemiketals could not be established by the NMR spectra. The structures of **3** and **7** can be deduced from those of **4** and **9**, which were characterized by X-ray analysis (Figure 1): **3** is the precursor of **9**, and **7** exhibits a ^{13}C NMR pattern similar to that of **4**.

To determine the structures, especially for compound **8**, the ^{13}C NMR chemical shifts of **3**, **4**, and **8** were computed[19] by DFT at the B3LYP[20]/6-31G* level by employing the gauge-independent atomic orbital (GIAO) method,[21] and the geometries optimized at the same level. The computed structure of **4** agrees well with the crystal data. The ^{13}C chemical shifts were calculated relative to C_{60} and converted to the TMS scale by using the experimental value for C_{60} ($\delta = 143.2$ ppm).[22] This DFT-based approach provides reasonably accurate fullerene ^{13}C chemical shifts, as shown by earlier studies[23] and by the agreement between the computed and experimentally measured NMR data of **3** and **4** (Figure 2), the structures of which were confirmed (**4**) or deduced (**3**) from single-crystal X-ray analysis. The agreement between the observed and computed ^{13}C NMR spectrum for **8** (Figure 2) indicates that it has the structure as depicted in Scheme 6. Moreover, at the B3LYP/6-311+G* level with B3LYP/6-31G* geometries, **3** is the most stable of these species (total energy −3898.58731 a.u.), while **4** and **8** are higher in energy by 1.4 and 5.8 kcal mol^{-1}, respectively.

Conclusion

Selective cleavage of C–C, C–O, C–Cl, and O–O bonds can be achieved for fullerene mixed peroxides under mild conditions. Various Lewis acids catalyze the opening of the fullerene epoxy group. Aluminum chloride cleaves the fullerene peroxo bond to form both [6,6]- and [6,5]-fullerene hemiketals after rearrangement. Lewis acids and visible light easily initiate isomerization of these hemiketals. X-ray data clearly show hemiketal moieties at both the [5,6] and [6,6] junctions. Fullerene mixed peroxides are potential precursors for hole-opening reactions on the fullerene surface.[24] Further work is in progress to generate multihemiketal functionality and to open a large hole on the fullerene surface.

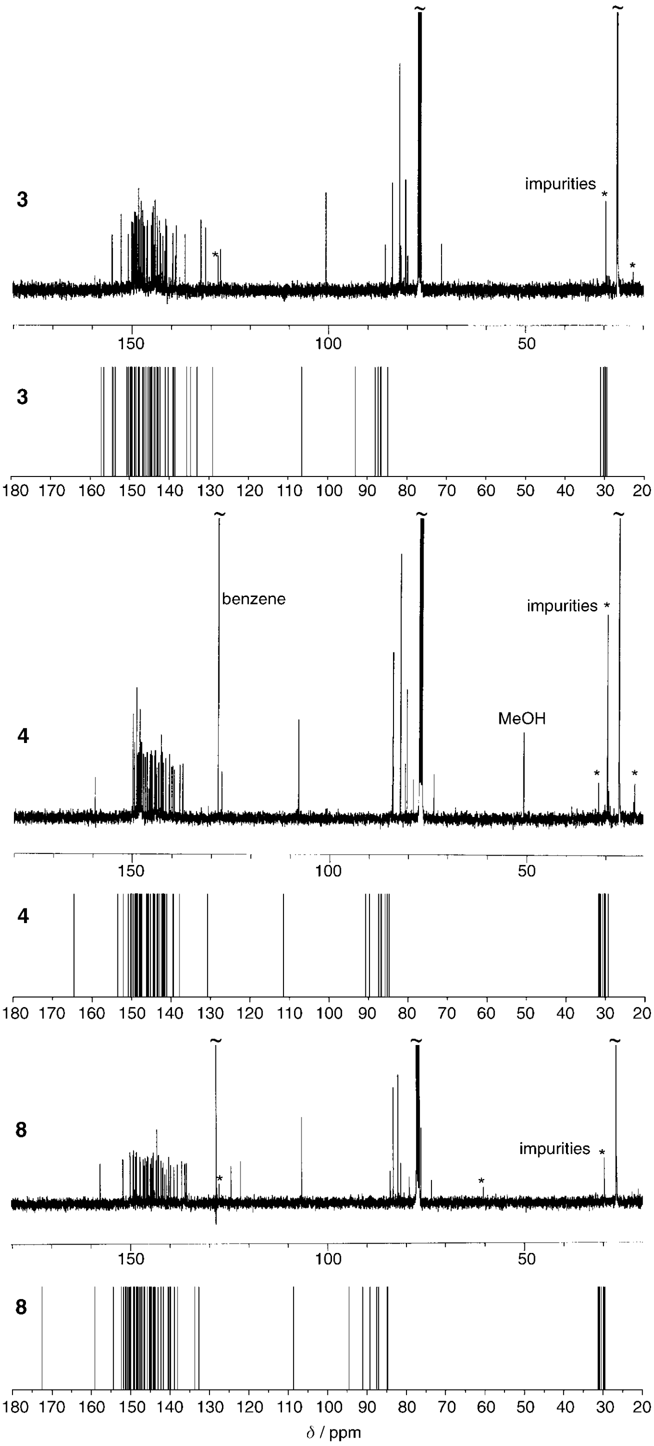


Figure 2. Observed (above) and computed (below) ^{13}C NMR spectra for **3**, **4**, and **8**.

Experimental Section

General: NMR spectra were recorded on a Bruker ARX 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer at 298 K, chemical shifts (δ) are given in ppm relative to TMS. ESI-MS spectra were recorded on a LCQ Decaxp Plus Spectrometer with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as solvent. FTIR spectra were recorded on Nicolet Magna-IR 750 in microscope mode. All reagents and solvents were used as received unless stated otherwise. Reactions were carried out under laboratory light in air at room temperature except where indicated. Chromatographic purifications were carried out with 200–300 mesh silica gel.

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

1,2-Epoxy-4,11,15,30-tetra-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (1): C_{60} (99 % pure, 200 mg, 0.28 mmol) was dissolved in *o*-dichlorobenzene (ODCB, 20 mL). Pyridine (100 μL) and *tert*-butyl hydroperoxide (TBHP, 70 %, 2 mL) were added. After the mixture was stirred for 10 min, a solution of $FeCl_3$ in H_2O (100 mg mL^{-1}, 100 μL) was added. The resulting solution was stirred at room temperature in the dark. Progress of the reaction was monitored by TLC. The reaction was stopped when the desired product **1** reached its maximum yield (ca. 18 h). Excess saturated aqueous solution of $Na_2S_2O_3$ or Na_2SO_3 was added to the reaction mixture to reduce unconsumed TBHP. The organic layer was mixed with petroleum ether (60–90 °C; 20 mL). The mixture was purified by column chromatography on silica gel (5 × 40 cm) with benzene/petroleum ether (1/1) as eluent. The eluted solution of **1** was evaporated and dried under atmosphere at room temperature in a bottle wrapped with aluminum foil. Yield: 140 mg, 46 %.

The spectra of **1** were identical to literature data.[13] The above procedure is an improved method.

1-Chloro-2-hydroxy-4,11,15,30-tetra-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (2a): Anhydrous $FeCl_3$ (15 mg, 0.09 mmol) was added to a solution of **1** (100 mg, 0.09 mmol) in benzene (10 mL). The mixture was stirred at room temperature. Progress of the reaction was monitored by TLC. The reaction was stopped when the desired product **2a** reached its maximum yield (ca. 0.5 h). The reaction mixture was purified by column chromatography on silica gel with toluene as eluent to afford **2a**. Yield: 88 mg, 85 %.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.94$ (s, 1 H); 1.483 (s, 18 H); 1.480 ppm (s, 18 H); ^{13}C NMR (C_6D_6/CS_2, 400 MHz, all signals represent 2 C except where noted): $\delta = 157.37$, 150.86, 150.37, 150.02, 150.00, 149.95, 149.61, 149.42 (3C), 149.31, 148.58, 148.41 (1 C), 148.39, 148.25, 147.94, 146.75, 146.13, 146.00, 145.45, 145.40, 144.99, 144.95, 144.36, 144.26, 143.68, 143.64, 142.25, 138.18, 83.30 ($C(CH_3)_3$), 82.99, 82.70 (1 C, COH), 82.36 ($C(CH_3)_3$), 82.02, 71.24 (1 C, CCl), 27.66 (6 CH_3), 27.57 ppm (6 CH_3); FTIR (microscope): $\tilde{\nu} = 3519$, 2978, 2925, 2852, 1456, 1387, 1363, 1260, 1243, 1193, 1148, 1101, 1051, 1021, 870, 845 cm^{-1}; ESI-MS: *m/z* (%): 1145 (100) [*M*+OH], 1174 (25); calcd for $C_{76}H_{37}ClO_9$: $M = 1128.5$.

1-Methoxy-2-hydroxy-4,11,15,30-tetra-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (2b): CH_3OH (1.8 mL, 1 M in CH_2Cl_2) was added to a solution of **1** (100 mg, 0.092 mmol) in CH_2Cl_2 (10 mL). After the mixture had been stirred for several minutes, $BF_3 \cdot Et_2O$ (180 μL, 1 M in CH_2Cl_2) was added. The mixture was stirred at room temperature for about 24 h. Progress of the reaction was monitored by TLC. The reaction was quenched by adding 10 drops of 2 M aqueous HCl when the desired product **2b** reached its maximum yield. The organic layer was separated, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as eluent. The first band was recovered **1** (35 mg, 35 %), the second was **2e** (trace), and the third was product **2b** (40 mg, 39 %).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 5.35$ (s, 1 H), 3.97 (s, 3 H), 1.48 (s, 18 H), 1.43 ppm (s, 18 H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2 C except where noted): $\delta = 155.46$, 150.01, 149.10, 148.98, 148.62, 148.56, 148.41 (1 C), 148.36, 148.32, 147.93, 147.64, 147.49 (1 C), 147.43, 147.31, 146.93, 145.83, 145.35, 144.91, 144.80, 144.36 (4 C), 143.95, 143.83, 143.31, 142.98, 142.72, 141.27, 138.79, 82.65 (1 C), 82.39, 82.09 ($C(CH_3)_3$), 81.82 ($C(CH_3)_3$), 81.22 (1 C), 80.89, 57.60 (1 C, OMe), 26.73 (6 CH_3), 26.68 ppm (6 CH_3); FTIR (microscope): $\tilde{\nu} = 3523$, 2977, 2929, 2870, 1457, 1363, 1260, 1243, 1193, 1149, 1092, 1050, 1020, 984, 873, 754 cm^{-1}; ESI-MS: *m/z* (%): 1142 (100) [*M*+OH+H]; calcd for $C_{77}H_{40}O_{10}$: $M = 1124$.

2-Hydroxy-1,4,11,15,30-penta-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (2c) was prepared by using a procedure similar to that for **2b** except that CH_3OH was replaced by anhydrous TBHP (1 M in CH_2Cl_2). Yield: 41 % (based on consumed **1**; conversion was 56 %).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=4.95$ (s, 1H), 1.49 (s, 18H), 1.44 (s, 18H), 1.39 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2C except noted): $\delta=154.66$, 150.81, 149.09, 149.00, 148.56, 148.45, 148.39(1C), 148.35, 148.32, 147.75, 147.51 (1C), 147.49, 147.35, 147.03, 146.89, 145.86, 145.75, 145.09, 145.00, 144.36, 144.26, 144.18, 143.77, 143.31, 143.14, 142.70, 141.42, 138.99, 85.39 (1C), 83.40, 82.69 ($C(CH_3)_3$), 82.62, 81.83 ($C(CH_3)_3$), 81.75 ($C(CH_3)_3$), 80.83 (1C, COH), 26.80 (6CH_3), 26.73 ppm (9CH_3); FTIR (microscope): $\tilde{\nu}=3522$, 2978, 2928, 2853, 1474, 1464, 1387, 1364, 1260, 1243, 1193, 1100, 1047, 1022, 1006, 873, 755 cm^{-1}; ESI-MS: *m/z* (%): 1200 (100) [M+OH+H]; calcd for $C_{80}H_{46}O_{11}$: $M=1182$.

1-Hydroperoxy-2-hydroxy-4,11,15,30-tetra-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (2d) was prepared by a procedure similar to that for **2b** except that CH_3OH was replaced by anhydrous H_2O_2. Yield: 25% (based on consumed **1**; conversion was 63%).

Preparation of anhydrous H_2O_2: 10 mL of 30% H_2O_2 was extracted with Et_2O (3×10 mL). The organic layer was dried with Na_2SO_4 and filtered. The solvent was evaporated. The anhydrous H_2O_2 should be used immediately, and excess H_2O_2 should be reduced with saturated Na_2SO_3 solution before disposal.

***Caution*:** all operations should be done behind a shield.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=11.06$ (s, 1H), 5.54 (s, 1H), 1.49 (s, 18H), 1.46 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2C except where noted): $\delta=155.20$, 149.26, 149.12, 149.07, 148.60, 148.48 (1C), 148.46, 148.43, 148.39, 147.73, 147.45, 147.41(1C), 147.27, 146.95, 146.51, 145.70(4C), 145.19, 144.70, 144.62, 144.44, 144.12, 144.02, 143.28, 143.09, 142.69, 141.01, 139.52, 85.91 (1C, COOH), 82.91 ($C(CH_3)_3$), 82.32, 82.27, 81.95 ($C(CH_3)_3$), 80.92 (1C, COH), 26.70 (6CH_3), 26.67 ppm (6CH_3); FTIR (microscope): $\tilde{\nu}=3482$, 3401, 2978, 2924, 2851, 1463, 1387, 1364, 1260, 1243, 1193, 1121, 1102, 1044, 1023, 1007, 868, 753 cm^{-1}. ESI-MS: *m/z* (%): 1144 (100) [M+OH+H]; 888(30); calcd for $C_{76}H_{38}O_{11}$: $M=1126$.

1-Fluoro-2-hydroxy-4,11,15,30-tetra-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (2e): $BF_3\cdot Et_2O$ (20 μL, 1 M in CH_2Cl_2) was added to a solution of **1** (75 mg, 0.069 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature. Progress of the reaction was monitored by TLC. The reaction was quenched by adding five drops of 2 M aqueous HCl when the desired product **2e** reached its maximum yield. The organic layer was separated, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with toluene as eluent. Yield: 21 mg, 27%.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=4.46$ (d, $J=4.4$ Hz, 1H), 1.49 (s, 18H), 1.45 ppm (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2C except where noted): δ: 155.39, 149.17, 149.13, 149.06, 148.91, 148.73, 148.43, 148.37, 147.77, 147.46, 147.27, 146.88, 145.80, 145.17 (1C), 145.09, 144.93 (1C), 144.90, 144.72 (br), 144.47, 144.41, 144.24, 144.00, 143.35(br), 143.31, 142.95, 141.10, 139.86, 139.83, 82.62 ($C(CH_3)_3$), 82.17, 81.99 (($C(CH_3)_3$), 81.83, 81.74, 81.31, 81.09, 80.93 (due to F coupling), 26.74 (6CH_3), 26.70 ppm (6CH_3); FTIR (microscope): $\tilde{\nu}=3537$, 2978, 2930, 2872, 1474, 1456, 1387, 1364, 1260, 1243, 1193, 1122, 1102, 1091, 1070, 1049, 1023, 1007, 872 cm^{-1}; ESI-MS: *m/z* (%): 1129 (100) [M+OH]; calcd for $C_{76}H_{37}FO_9$: $M=1112$.

1-Chloro-2,4-dihydroxy-11,15,30-tri-*tert*-butylperoxy-oxa^{4,17}-1,2,4,11,15,30-hexahydro[60]fulleroid (3): $AlCl_3$ (21.5 mg, 0.16 mmol) was added to a solution of **2a** (47 mg, 0.042 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred for 2.5 min at 0 °C. Then the reaction was quenched by adding 10 drops of 2 M aqueous HCl. The organic layer was separated. The water phase was extracted with $CHCl_3$ (3×5 mL). The organic phases were combined, dried with Na_2SO_4, and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with benzene/petroleum ether/ethyl acetate (10/10/1) as eluent. Unconverted **2a** (15 mg) was eluted as the first band, followed by product **3** (10 mg). Yield: 33% (based on consumed **2a**).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=5.12$ (s, 1H), 5.00 (s, 1H), 1.500 (s, 9H), 1.496 (s, 9H), 1.46 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 1C except where noted): $\delta=155.04$, 152.76, 150.92, 150.10, 149.81, 149.74, 149.58, 149.38, 149.26, 149.24, 149.12, 148.94, 148.79, 148.47, 148.33(2C), 148.17, 147.79, 147.72, 147.37, 147.34, 147.29, 147.26, 147.11, 146.80, 146.25, 146.11, 146.09, 145.14, 144.82, 144.74, 144.62, 144.44, 144.18, 144.16, 144.09, 144.01(2C), 143.61, 143.54, 143.05, 142.85, 142.26, 141.83, 141.51, 141.24, 139.75, 139.01, 138.83, 136.56, 132.54, 132.50, 131.36, 127.58, 100.68, 85.63, 83.85 ($C(CH_3)_3$), 82.02, 81.98 ($C(CH_3)_3$), 81.69, 80.41 ($C(CH_3)_3$), 79.91, 71.33, 26.73 (3CH_3), 26.60 ppm (6CH_3); FTIR (microscope): $\tilde{\nu}=3508$, 2978, 2928, 2853, 1458, 1387, 1364, 1245, 1191, 1163, 1130, 1107, 1086, 1041, 1017, 868 cm^{-1}; ESI-MS: *m/z* (%): 1090 (100) [M+OH+H]; 1086 (20) [M−Cl+CH_3O+OH+H]; calcd for $C_{72}H_{29}O_9Cl$: $M=1072.5$.

1-Chloro-2,4-dihydroxy-11,15,30-tri-*tert*-butylperoxy-oxa^{3,4}-1,2,4,11,15,30-hexahydro[60]fulleroid (4): Dry Et_2O (0.5 mL) was added to a solution of **2a** (166 mg, 0.15 mmol) in CH_2Cl_2 (10 mL). After the mixture had been stirred for 5 min, $AlCl_3$ (35 mg, 0.26 mmol) was added. The mixture was stirred at room temperature. Progress of the reaction was monitored by TLC. When the product **4** reached its maximum yield (about 10 h), the reaction was quenched by adding 1 mL of 2 M aqueous HCl. The organic layer was separated. The water phase was extracted with $CHCl_3$ (3×5 mL). The organic phases were combined, dried with Na_2SO_4, and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with benzene/petroleum ether/ethyl acetate (10/10/1) as eluent. Unconsumed **2a** (84 mg) was eluted as the first band, followed by product **4** (45 mg). Yield: 58% (based on consumed **2a**).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=5.62$ (s, 1H), 5.57 (s, 1H), 1.49 (s, 9H), 1.47 (s, 9H), 1.42 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 1C except where noted): $\delta=159.49$, 149.85 (2C), 149.45, 149.43, 148.98 (2C), 148.87, 148.80, 148.52, 148.44, 148.28, 148.22, 148.17 (2C), 148.05, 148.03, 147.98, 147.88, 147.78, 147.74, 147.73, 147.68, 147.37, 146.82, 146.35, 145.85, 145.57, 145.29, 145.01, 144.43, 144.25, 144.22, 144.17, 143.88, 143.50, 143.27, 142.88, 142.82, 142.72 (2C), 142.47, 142.45, 142.13, 141.60, 140.70, 140.63, 140.20, 140.16, 139.76, 139.33, 138.01, 137.23, 127.33, 108.00, 84.19, 83.93 ($C(CH_3)_3$), 82.08 ($C(CH_3)_3$), 82.04, 80.92, 80.47 ($C(CH_3)_3$), 78.83, 73.55, 26.73 (3CH_3), 26.62 ppm (6CH_3); FTIR (microscope): $\tilde{\nu}=3496$, 2978, 2926, 2851, 1456, 1388, 1364, 1261, 1244, 1190, 1147, 1109, 1051, 1027, 1005, 870, 839, 804 cm^{-1}; ESI-MS: *m/z* (%): 1090 (70) [M+OH+H]; 1086(100) [M−Cl+CH_3O+OH+H]; 1037(60); calcd for $C_{72}H_{29}O_9Cl$: $M=1072.5$.

1-Ethoxy-2-hydroxy-4,11,15,30-tetra-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (5): A solution of **2a** (80 mg, 0.07 mmol) in CH_2Cl_2 (25 mL) was cooled to 0 °C, and anhydrous $FeCl_3$ (23 mg, 0.14 mmol) was added. The mixture was stirred for about 10 h at 0 °C. Progress of the reaction was monitored by TLC. The reaction was quenched by adding 10 drops of 2 M aq. HCl. The organic layer was separated. The water phase was extracted with $CHCl_3$ (3×5 mL). The organic phases were combined, dried with Na_2SO_4, and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with benzene/petroleum ether/ethyl acetate (10/10/1) as eluent. Unconverted **2a** (15 mg, 19%) was eluted as the first band, product **5** (29 mg, 36%) as the second band, followed by product **6** (trace). Finally, product **7** was eluted (12 mg, 16%).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=4.74$ (s, 1H), 4.27 (q, $J=6.8$ Hz, 2H), 1.48 (s, 18H), 1.44 (s, 18H), 1.40 ppm (t, $J=6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 2C except noted): $\delta=155.59$, 150.07, 149.13, 149.00, 148.61, 148.59 (4C), 148.43 (1C), 148.40, 148.35, 147.66, 147.50 (1C), 147.47, 147.36, 146.99, 145.88, 145.39, 145.03, 144.87, 144.41 (4C), 143.97, 143.87, 143.36, 142.99, 142.70, 141.34, 138.57, 82.55, 82.42 (1C, COH), 82.12 ($C(CH_3)_3$), 81.99 (1C), 81.84 ($C(CH_3)_3$), 80.93, 66.04 (OCH_2), 26.76 (6CH_3), 26.73 (6CH_3), 15.68 ppm (CH_3); FTIR (microscope): $\tilde{\nu}=3522$, 2978, 2930, 1474, 1387, 1363, 1260, 1243, 1193, 1121, 1099, 1069, 1049, 1021, 1007, 908, 871, 733 cm^{-1}; ESI-MS: *m/z* (%): 1156 (100) [M+OH+H]; 1184 (50); calcd for $C_{78}H_{42}O_{10}$: $M=1138$.

1,2-Dihydroxy-4,11,15,30-tetra-*tert*-butylperoxy-1,2,4,11,15,30-hexahydro[60]fullerene (6): The preparation of **6** was as for **5**. The ^{1}H NMR spectrum of **6** was identical to that reported previously.[14]

1-Ethoxy-2,4-dihydroxy-11,15,30-tri-*tert*-butylperoxy-oxa^{3,4}-1,2,4,11,15,30-hexahydro[60]fulleroid (7): The preparation of **7** was as for **5**.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.91$ (br, 2H), 4.4–4.5 (m, 1H), 3.9–4.0 (m, 1H), 1.46–1.52 (m, 3H), 1.43 (s, 9H), 1.42 (s, 9H), 1.38 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 1C except noted): $\delta =$ 159.60, 149.82, 149.46, 149.44, 149.21, 148.97, 148.94, 148.84, 148.63 (2C), 148.51, 148.33, 148.25, 148.21 (2C), 148.13, 148.06, 148.02 (2C), 147.91, 147.86, 147.82, 147.73, 147.49, 146.67, 146.45, 146.14, 145.83, 145.73, 145.44, 145.26, 144.86, 144.37, 144.08, 144.02, 143.81, 143.61, 143.28, 142.78, 142.74 (2C), 142.71, 142.46, 142.22, 141.47, 140.61, 140.41, 140.38 (2C), 139.66, 139.51, 139.10, 138.73, 127.25, 107.60, 85.72, 84.22, 82.72 ($C(CH_3)_3$), 82.40 (COH), 81.77 ($C(CH_3)_3$), 81.74 ($C(CH_3)_3$), 81.33, 78.73, 66.51 (OCH_2), 26.74 ($3CH_3$), 26.72 ($3CH_3$), 26.70 ($3CH_3$), 15.62 ppm (CH_3); FTIR (microscope): $\tilde{\nu} = 3510$, 2977, 2926, 2853, 1456, 1387, 1364, 1259, 1244, 1191, 1152, 1108, 1071, 1051, 1023, 1002, 872, 757 cm^{-1}; ESI-MS: m/z (%): 1100 (100) [M+OH+H]; calcd for $C_{74}H_{34}O_{10}$: $M = 1082$.

1-Chloro-2,4-dihydroxy-11,15,30-tri-*tert*-butylperoxy-oxa^{4,5}-1,2,4,11,15,30-hexahydro[60]fulleroid (8): $La(NO_3)_3{\cdot}xH_2O$ (3 mg) was added to a solution of **4** (11 mg, 0.010 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature Progress of the reaction was monitored by TLC. When the desired product **8** reached its maximum yield (ca. 5 h), the reaction was quenched with 1 mL of water. The organic layer was separated. The water phase was extracted with $CHCl_3$ (3×5 mL). The organic phases were combined, dried with Na_2SO_4, and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with benzene/petroleum ether/ethyl acetate (10/10/1) to give a trace of unconverted **4**, followed by the desired product **8**. Yield: 5 mg, 45%.

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 5.23$ (s, OH), 4.74 (s, OH), 1.441 (s, 9H), 1.437 (s, 9H), 1.41 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 1C except where noted): $\delta =$ 157.66, 151.97, 150.14, 150.13, 150.04, 149.36, 149.25, 149.20 (2C), 149.17, 148.83, 148.63, 148.59, 148.55, 148.52, 148.38, 147.63, 147.53, 146.82, 146.70, 146.38, 146.36, 145.98, 145.77, 145.73, 145.57, 145.03, 145.00, 144.68, 144.46, 144.33, 144.16, 143.51, 143.39, 143.31(2C), 142.98, 142.94, 142.26, 142.24, 141.89, 141.79, 141.32, 140.84, 140.33, 140.26, 139.85, 139.06, 138.17, 136.99, 136.21, 135.85, 124.61, 122.14, 106.65, 84.06, 83.30 ($C(CH_3)_3$), 82.12 ($C(CH_3)_3$), 82.09 ($C(CH_3)_3$), 81.40, 79.23, 76.21, 73.56, 26.72 ($3CH_3$), 26.68 ($3CH_3$), 26.59 ppm ($3CH_3$); ESI-MS: m/z (%): 1090 (75) [M+OH+H]; 1037 (100) [M−Cl]; calcd for $C_{72}H_{29}O_9Cl$: $M = 1072.5$.

1-Chloro-3,14-epoxy-2,4-dihydroxy-11,15,30-tri-*tert*-butylperoxy-oxa^{3,4}-1,2,3,4,11,14,15,30-octahydro[60]fulleroid (9): mCPBA (25 mg, 70%, 0.1 mmol) was added to a solution of **3** (30 mg, 0.028 mmol) in benzene (5 mL). The mixture was stirred at room temperature Progress of the reaction was monitored by TLC. The reaction was stopped when the product **9** reached its maximum yield (ca. 1 h). The reaction mixture was purified by column chromatography on silica gel with benzene/petroleum ether/ethyl acetate (10/10/1) as eluent. Unconverted **3** (5 mg) was eluted as the first band, followed by product **9**. Yield: 15 mg, 59% (based on consumed **3**).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 5.05$ (s, 1H), 4.82 (s, 1H), 1.52 (s, 9H), 1.45 (s, 9H), 1.41 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, all signals represent 1C except where noted): $\delta = 152.84$, 150.35, 150.30, 150.29, 149.58, 149.49, 149.35, 149.25, 149.06, 148.92, 148.66, 148.50, 148.42, 148.35, 148.31, 148.12, 148.08, 147.97, 147.82, 147.51, 147.44, 147.42, 146.70, 146.32, 146.18, 146.11, 145.96, 145.64, 145.13, 145.05, 144.79, 144.72, 144.48, 144.31, 144.05, 143.99, 143.91, 143.80, 143.47, 143.38, 143.16, 141.90, 141.86, 141.28, 140.33, 139.32, 138.60, 138.59, 138.24, 131.24, 130.35, 129.25, 97.92, 86.52, 83.73 ($C(CH_3)_3$), 82.42 ($C(CH_3)_3$), 82.37 ($C(CH_3)_3$), 80.75, 80.61, 80.35, 76.16, 74.76, 70.36, 26.78 ($3CH_3$), 26.76 ppm ($6CH_3$); FTIR (microscope): $\tilde{\nu} = 3491$, 2978, 2923, 2850, 1462, 1387, 1364, 1245, 1192, 1152, 1109, 1051, 1020, 1011, 870, 831, 737 cm^{-1}; ESI-MS, m/z (%): 1106 (100) [M+OH+H], calcd for $C_{72}H_{29}O_{10}Cl$: $M =$ 1088.5.

X-ray structure analysis of 4 and 9: Single crystals of **4** and **9** were obtained by slow evaporation of solutions in CS_2/n-pentane and benzene/n-hexane, respectively, at 5 °C.

Crystal data for **4**: $C_{73}H_{29}ClO_9S_2$, $M_r = 1149.53$, monoclinic, $P2(1)/c$, $a =$ 23.405(5), $b = 10.614(2)$, $c = 19.767(4)$ Å, $\beta = 91.00(3)^\circ$, $V = 4909.6(17)$ Å^3, $T = 123(2)$ K, $Z = 4$, $\rho_{calcd} = 1.555$ Mg m^{-3}, graphite-monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, crystal size $0.40 \times 0.25 \times 0.15$ mm. Data were collected on a Rigaku RAXIS RAPID IP diffractometer, 8642 unique reflections ($R_{int} = 0.0471$). Refinement on F^2, final residuals $R1 =$ 0.0585 for 3708 reflections with $I > 2\sigma I$), $wR2 = 0.1136$ for all data.

Crystal data for **9**: $C_{81}H_{40}ClO_{11}$, $M_r = 1224.58$, triclinic, $P\bar{1}$, $a = 14.269(3)$, $b = 14.341(3)$, $c = 15.587(3)$ Å , $\alpha = 80.59(3)$, $\beta = 78.36(3)$, $\gamma = 62.50(3)^\circ$, $V = 2762.1(10)$ Å^3, $T = 123(2)$ K, $Z = 2$, $\rho_{calcd} = 1.472$ Mg m^{-3}, graphite-monochromatized $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, crystal size $0.60 \times 0.36 \times$ 0.28 mm^3. Data were collected on a Rigaku RAXIS RAPID IP diffractometer; 9540 unique reflections ($R_{int} = 0.0389$). Refinement on F^2, final residuals $R1 = 0.0798$ for 4581 reflections with $I > 2\sigma I$), $wR2 = 0.2469$ for all data. The crystal was disordered. Two molecules occupied the same position with slightly different orientations. To confirm the results, two sets of data were collected with two crystals grown separately from two samples. The two sets of diffraction data are exactly the same.

CCDC-252474 (**4**) and CCDC-252475 (**9**) contain 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.

Isomerization experiments on 3, 4, and 8

Isomerization starting from pure 3: Under laboratory light, **3** partially isomerized to **4** and a new hemiketal **8** when treated with $La(NO_3)_3$ or $B(C_6F_5)_3$ for 6 h; ratio of the products could not be determined accurately due to closely overlapping signals in the ^{1}H NMR spectrum, but it was evident that most (>50%) of **3** remained and there was more **4** than **8**. Irradiating **3** alone with a household lamp without a Lewis acid resulted in slow decomposition to unknown compounds.

In total darkness, standing in CH_2Cl_2 solution at room temperature for three days, standing in CH_2Cl_2 solution with Lewis acid $B(C_6F_5)_3$, or heating at 60 °C for 7 h in $CDCl_3$ did not result in detectable isomerization of **3** to **4** or **8**.

Isomerization starting from pure 4: Under laboratory light and with $La(NO_3)_3$ or $B(C_6F_5)_3$ as Lewis acid, 70% of isomer **4** (estimated by TLC) changed into **8** (yield 45%) and decomposition products over several hours. Irradiating **4** alone with a household lamp caused isomerization to the same extent in 1 h along with formation of decomposition products. Longer irradiation did not give more **8**, since **8** decomposed slowly under such conditions.

In total darkness, heating **4** at 60 °C in $CDCl_3$ solution for 7 h gave partial isomerization (the **4**/**8** ratio was about 3/1). Heating **4** to 60 °C in $CDCl_3$ in the presence of $B(C_6F_5)_3$ gave mainly decomposition products (some **8** could be detected and the **4**/**8** ratio was ca. 3.5/1).

Isomerization starting from pure 8: Irradiating isolated pure **8** with a household lamp decomposed it to some unknown highly polar compounds.

In total darkness **8** partially isomerized to **4** in $CDCl_3$ on standing at room temperature (the **4**/**8** ratio was 2.5/1 after 110 h). A solution of **8** in CH_2Cl_2 also partially (observable by TLC) and slowly (several days) isomerized to **4**.

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