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Synthesis of Fullerene Oxides Containing Both 6,6-Closed Epoxide and 5,6-Open Ether Moieties through Thermolysis of Fullerene Peroxides

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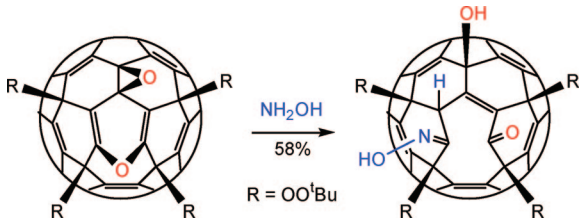

Thermolysis of the fullerene hexaadduct $C_{60}(OO^tBu)_6$ results in cleavage of two O−O bonds and elimination of two *tert*-butoxy groups to form two isomeric products with the formula $C_{60}(O)_2(OO^tBu)_4$ in comparable yields. The two oxygen atoms exist as two epoxy groups in one isomer **3**, and as an epoxy and an ether group in the other isomer **2**. Addition of hydroxylamine to **2** opens both the epoxy and the ether moieties to give a cage-opened keto-ketoxime derivative.

Fullerene oxides are among the most intensively studied fullerene derivatives.[1] A number of methods have been reported to convert fullerenes into various fullerene oxides.[2] In most cases the 6,6-closed epoxides were produced. The first epoxide $C_{70}O$ was isolated directly from fullerene soot by Diederich et al.[3] Photooxidation of C_{60} generated the first C_{60} oxide $C_{60}O$ as the only isolable product.[4] Both of these two oxides were determined to be the epoxide isomer instead of the ether (oxahomofullerene). Although theoretical calculations predicted the ether isomer to be of comparable stability with the epoxide,[5] it remained unknown until 2001 when Weisman and co-workers uncovered that photolysis and thermolysis of the ozonide $C_{60}(O_3)$ yields the ether and epoxide isomer, respectively.[6] A closely related oxahomofullerene derivative $C_{60}F_{18}O$ was reported by Taylor et al. in which the oxygen atom is inserted into a fluorinated 5,6-junction.[7] Contrary to pristine C_{60}, the 6,6-junction in multiple fullerene adducts can also be inserted with an oxygen to form the ether structure.[8]

Fullerene multioxides $C_{60}O_n$ can be readily produced through classical oxidants such as *m*-chloroperoxybenzoic acid.[2f,h] These multioxides are usually complex mixtures. Isolation and structural assignment are quite challenging. Electronic and ^{13}C NMR spectra were obtained for several triepoxides.[9] The data suggest that these epoxy groups are most likely located at adjacent positions. Diannulene and epoxyannulene structures were proposed as possible isomers for fullerene dioxide $C_{60}O_2$, but their low yield and instability prevented full characterization.[10] So far just one isomer of the dioxide $C_{60}O_2$ has been characterized by single-crystal X-ray analysis, which showed two epoxy groups on the same hexagon.[2f] Here we report the preparation and single-crystal X-ray structure of a fullerene derivative containing an epoxy group at the 6,6-junction and an ether moiety at the 5,6-junction.

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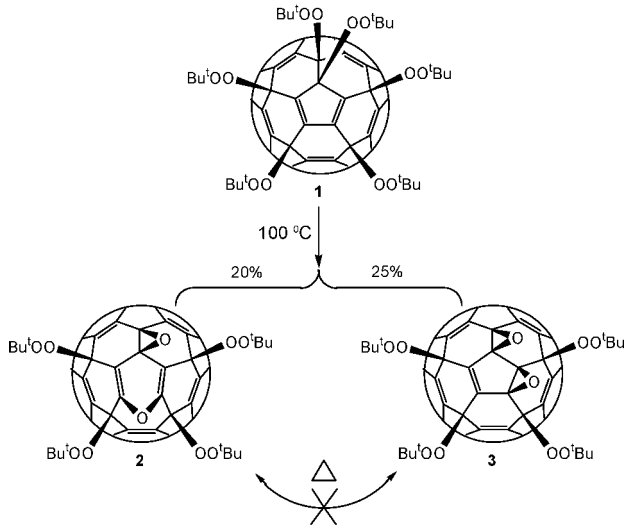
SCHEME 1. Thermolysis of Fullerene-Mixed Peroxide

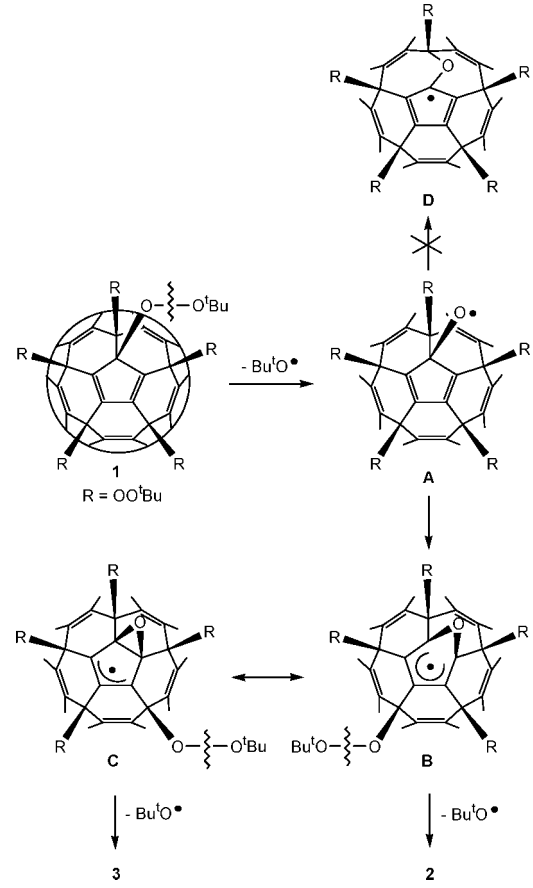


In search of fullerene skeleton modification methods, we have been investigating the chemistry of fullerene-mixed peroxides[11] such as the hexa-adduct **1**,[11c] which can be easily prepared from *tert*-butylhydrogen peroxide and C_{60}. To test its thermal stability, we heated **1** in chlorobenzene. Two isomeric products were isolated, namely epoxy ether **2** and the diepoxide **3** (Scheme 1). Addition of some C_{60} improves the selectivity of the thermolysis, probably by trapping reactive decomposition species. Heating isolated pure **2** or **3** could not lead to their interconversion, instead giving a complicated mixture of decomposition products. The diepoxide **3** is a known compound that was synthesized by epoxidation of the monoepoxide derivative $C_{60}(O)(OO^tBu)_4$ with *m*-CPBA in our previous report.[12]

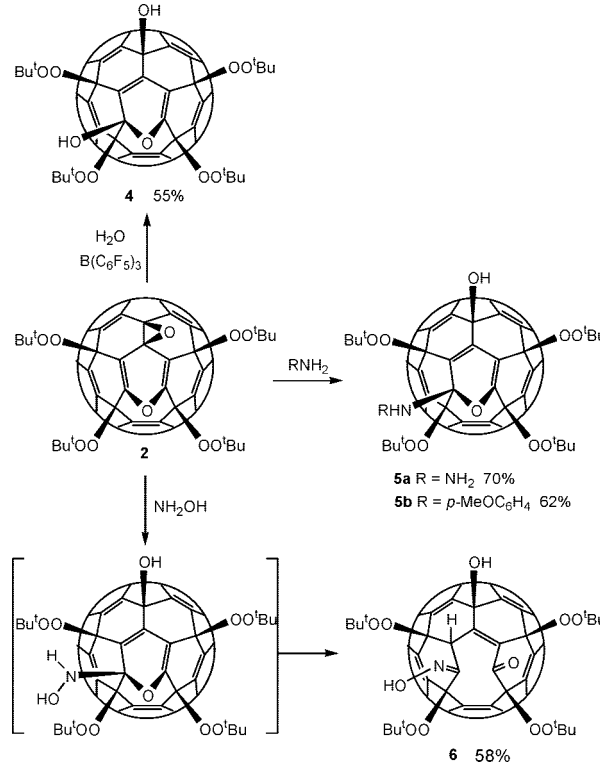
Scheme 2 shows a possible pathway for the thermolysis of compound **1**. Heating results in homolysis of the O−O bond on the central pentagon, which is the most reactive site among the six peroxo groups due to steric reasons. In our previous study, we have shown that cleavage of the O−^{t}Bu bond on the central pentagon is dominant under irradiation,[11c] which eventually leads to cage-opened compounds. In the second step, the oxygen radical in **A** either inserts into an adjacent 5,6-junction to form the pentadienyl radical **B** or adds to the diene moiety to form the allyl radical **C**. Further cleavage of another O−O bond from intermediates **B** and **C** produces compounds **2** and **3**, respectively. The comparable yields of compounds **2** and **3** indicate that the two radical intermediates **B** and **C** have similar stability. There is no product observed corresponding to intermediate **D**. Insertion at the 6,6-junction of radical **A** is not favorable because the steric strain would lift the oxygen-bound carbon above the central pentagon, thus destabilizing the cyclopentadienyl radical in **D**.

The presence of the ether moiety in compound **2** greatly affects the reactivity of the epoxide group. Tris(pentafluorophenyl)boron catalyzed the addition of water to **2** to form the acetal **4** (Scheme 3). Amino nucleophiles hydrazine and *p*-anisidine added directly to form analogous aminoacetals **5a** and **5b**, respectively. Addition of hydroxylamine resulted in the cage-opened derivative **6**, in which both the epoxide and ether moieties were cleaved. Hydroxylamine probably attacks the same ether carbon as in the formation of **4** and **5**, but the hydroxylaminoacetal is apparently not stable and rearranges into the keto-ketoxime **6**.

SCHEME 2. Possible Mechanism of the Thermolysis



SCHEME 3. Reactions of Compound 2



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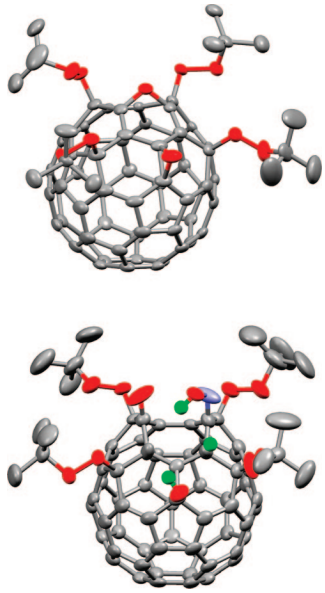

FIGURE 1. Structure of compounds **2** (above) and **6** (below). For clarity hydrogen atoms on the *tert*-butyl groups were omitted. The structure of **6** has a position exchange disorder involving the carbonyl and the ketooxime group. Color scheme: gray C, red O, blue N, and green H.

Spectroscopic data are in agreement with the structures depicted in Schemes 1 and 3. The epoxy ether **2** has C_s symmetry. Its pyran sp^2 carbons appeared at 167.0 and 124.6 ppm, which are quite different from other sp^2 carbons on the cage ranging from 138.9 to 149.5 ppm. The two sp^3 epoxy carbons appear at 67.7 and 67.6 ppm. The presence of the acetal moiety was deduced from the unique signal at 105.8, 103.1, and 97.4 ppm for compounds **4**, **5a**, and **5b**, respectively. This acetal carbon showed relatively higher intensity due to the NOE of OH or NH proton, a common phenomenon observed before for other fullerene acetal moieties.[8] The keto-ketoxime **6** showed a carbonyl peak at 190.4 ppm. The hydrogen in **6** appeared at 6.26 ppm as a sharp signal on the ^{1}H NMR spectrum, and its corresponding carbon appeared at 39.7 ppm on the ^{13}C NMR spectrum. But the location of the hydrogen in **6** could not be identified from these NMR data. The hydrogen could be adjacent to the ketoxime group as shown in Scheme 3 or adjacent to the carbonyl group. A disorder in the X-ray structure of **6** prevented us from distinguishing the two possible structures (see below).

Single-crystal X-ray structures were determined for compounds **2** and **6** as shown in Figure 1. The pyran moiety in **2** adopts a distorted boat conformation. The ether oxygen at the 5,6-junction is tilted toward the 6-membered ring. The distance between the two carbons bonded to the ether oxygen is 2.228 Å. The epoxide C−C bond length is 1.524 Å. Double bonds on the pyran ring are the shortest on the cage (1.324 and 1.333 Å). The structure of **6** is disordered in the cage-opened region. The presence of the ketooxime and carbonyl groups is clearly observed, but the two groups are disordered in the two positions. Therefore it is impossible to determine which one is adjacent to the H-bound sp^3 carbon. The structure shown in Figure 1 represents one of the possible structures. The distance between the carbonyl and ketooxime carbons is 2.768 Å.

In summary, thermolysis of fullerene peroxide was found to induce homolysis of the O−O bond. The resulting fullerene-bound oxygen radical forms either an epoxy or an ether moiety at the same 5,6-junction, which could serve as a precursor for cage-opened fullerenes. Further work is in progress to prepare cage-opened fullerene and heterofullerene derivatives by using fullerene peroxides.

Experimental Section

All the reagents were used as received. Dichloromethane was distilled over phosphorus pentaoxide. Other solvents were used as received. Compound **1** was prepared according to the improved procedure in ref 11c. **Caution**: Peroxides are potentially explosive compounds, care must be taken to avoid possible explosion.

Compound 2. C_{60} (83 mg, 0.12 mmol) was added to a stirred solution of compound **1** (290 mg, 0.23 mmol) in chlorobenzene (97 mL) in the dark at 100 °C. After the mixture was stirred for 65 min, the solution was evaporated. The residue was chromatographed on a silica gel column (30 mm × 50 mm) eluting with CH_2Cl_2/CS_2 (4:1). The first band was unreacted C_{60}. The second band was collected and evaporated to give compound **2** (52 mg, 0.047 mmol, 20%), and the third band was collected and evaporated to give compound **3** (65 mg, 0.059 mmol, 25%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (18H), 1.41 (18H); ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 2C except as noted, δ 168.99, 149.48, 148.70, 148.56, 148.40, 148.36, 148.06, 147.97 (1C), 147.70, 147.49, 147.44, 147.17, 146.72, 146.36, 146.24, 145.49 (1C), 145.12, 144.96, 144.25, 144.15, 142.97 (4C), 142.33, 142.21 (4C), 139.95, 138.93, 124.63, 90.51, 84.30, 82.37, 81.73, 67.66 (1C), 67.56 (1C), 26.57, 26.23; IR (microscope) 2798, 2923, 2850, 1363, 1193, 1015 cm^{-1}; ESI-MS *m*/*z* (rel intensity) 1131 (100, M + Na$^+$); ESI-HRMS 1131.2237 calcd for $C_{76}H_{36}NaO_{10}$ 1131.2201.

Crystals of **2**·CS_2 suitable for X-ray diffraction were obtained from slow evaporation in a mixture of CS_2 and ethanol. Crystal data: monoclinic, space group $P2_1/c$, a = 18.9125(3) Å, b = 14.3843(2) Å, c = 20.3313(4) Å, β = 108.279(1)°, volume = 5251.9(2) Å^3; final R indices [$I > 2\sigma(I)$] R_1 = 0.0586, wR_2 = 0.1429. One of the four *tert*-butylperoxo groups is disordered into two orientations (crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-652052).

Compound 4. Tris(pentafluorophenyl)borane (3 mg, 0.0059 mmol) was added to a stirred solution of compound **2** (27 mg, 0.024 mmol) in CH_2Cl_2 (10 mL) at 30 °C. After 10 min, the solution was directly transferred onto a silica gel column (20 mm × 30 mm) and eluted with toluene/petroleum ether/AcOEt (10:10:1). The first band was a trace amount of unreacted **2**. The second band was collected and evaporated to give compound **4** (15 mg, 0.013 mmol, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (s, 1H), 3.62 (s, 1H), 1.45 (s, 18H), 1.41 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 1C except as noted, δ 155.03, 149.73, 149.06, 148.99, 148.87, 148.60 (2C), 148.50, 148.45, 148.30, 148.24, 148.20, 147.91 (2C), 147.87 (2C), 147.83, 147.68, 147.61 (2C), 147.46, 147.06 (2C), 146.93, 143.86, 146.38, 146.26, 146.20, 145.71, 145.61, 145.43, 145.15, 145.01, 144.80, 144.69, 144.65, 144.51, 144.41, 144.10, 144.02, 143.71, 143.25, 143.17, 143.15, 142.91, 142.39, 140.46, 140.44, 139.39, 138.88, 137.93, 133.26, 125.61, 122.88, 105.83, 94.19, 92.62, 84.02, 82.76, 82.10, 82.06, 82.03, 80.62, 72.60, 26.87, 26.81, 26.67, 26.64; FT-IR (microscope) 3397 (broad), 2977, 2926, 2854, 1364, 1241, 1191, 1102, 1087, 1060 cm^{-1}; ESI-MS *m*/*z* (rel intensity) 1149 (100, M + Na$^+$); ESI-HRMS 1149.2338, calcd for $C_{76}H_{38}NaO_{11}$ 1149.2306.

Compound 5a. N_2H_4·H_2O (85%) (1 μL) was added to a stirred solution of compound **2** (25 mg, 0.023mmol) in CH_2Cl_2 (6 mL). After 1 min, the solution was directly transferred to a silica gel column (20 mm × 30 mm) and eluted with toluene/petroleum ether/AcOEt (10:10:1). The first band was a trace amount of unreacted **2**. The elutent was then changed to toluene/petroleum ether/AcOEt (5:5:1). The second band was collected and evaporated to give compound **5a** (18 mg, 0.016 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (s, 1H), 3.66 (s, 1H), 1.47 (s, 9H), 1.45 (s, 9H), 1.43 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 1C except as noted, δ 155.54, 149.81, 149.05, 148.96, 148.84, 148.62, 148.51, 148.50, 148.35 (2C), 148.28, 148.25 (2C), 148.17, 147.95, 147.87, 147.81, 147.78, 147.68, 147.46, 147.14, 147.08, 147.06, 146.87, 146.44, 146.42, 146.28 (2C), 145.80, 145.76, 145.52, 145.35, 145.26, 145.15, 144.79, 144. 69 (2C), 144.37, 144.03, 143.96, 143.80, 143.29, 143.16, 143.07, 142.52, 142.22, 142.20, 140.55, 140.19, 139.45, 138.09, 132.47, 124.49, 121.96, 103.10, 94.50, 93.14, 84.05, 82.99, 82.14, 82.05, 81.96, 80.84, 72.54, 26.97, 26.83, 26.69, 26.66; FT-IR (microscope) 3534, 3375, 2978, 2977, 1365, 1258, 1241, 1191, 1089, 1056, 1021, 805 cm^{-1}; ESI-MS *m*/*z* (rel intensity) 1141 (97, M + H$^+$); ESI-HRMS did not show molecular ion signal.

Compound 5b. *p*-anisidine (300 mg, 2.42 mmol) was added to a stirred solution of compound **2** (42 mg, 0.038 mmol) in toluene (5 mL) at 50 °C. After 50 min, the solution was directly transferred onto a silica gel column (20 mm × 30 mm) and eluted with toluene/petroleum ether/AcOEt (10:10:1). The first band was a trace amount of unreacted **2**. The second band was collected and evaporated to give compound **5b** (29 mg, 0.024 mmol, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.47 (d, 2H), 6.99−6.97 (d, 2H), 6.04 (s, 1H), 3.88 (s, 3H), 3.66 (s, 1H), 1.48 (s, 9H), 1.37 (s, 9H), 1.33 (s, 9H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 1C except as noted, δ 155.94, 154.18, 149.75, 149.03, 148.98, 148.80, 148.62, 148.48, 148.47, 148.35, 148.28, 148.23 (3C), 148.18 (3C), 147.87, 147.82, 147.81, 147.60, 147.45, 147.39, 147.08, 147.05 (2C), 146.47, 146.31, 145.78 (2C), 145.65, 145.53, 145.47, 145.26, 145.19, 144.77, 144.50 (2C), 144.34, 144.17, 143.97, 143.95, 143.31, 143.26, 143.17, 142.98, 142.14, 141.29, 140.23, 140.15, 139.34, 138.19, 137.19, 132.77, 124.64, 122.03, 121.59, 114.12, 114.04, 97.38, 96.20, 93.36, 84.38, 82.08, 82.06, 81.90, 81.55, 80.58, 72.56, 55.77, 26.90, 26.66, 26.55, 26.40; FT-IR (microscope) 3535, 2978, 2931, 1512, 1365, 1244, 1191, 1086, 1054, 1022, 872 cm^{-1}; ESI-MS *m*/*z* (rel intensity) 1232 (100, M + H$^+$); ESI-HRMS did not show molecular ion signal.

Compound 6. To a stirred solution of compound **2** (10 mg, 0.0090 mmol) in CH_2Cl_2 (3 mL) was added a solution of $NH_2OH\cdot HCl$ (3.48 mg, 0.05 mmol) and K_2CO_3 (3.45 mg, 0.025 mmol) dissolved in 50 μL of water at room temperature. After 12 min, the solution was directly transferred onto a silica gel column (20 mm × 30 mm) and eluted with toluene/petroleum ether/AcOEt (10:10:1). The first band was a trace amount of unreacted **2**. The elutent was then changed to toluene/petroleum ether/AcOEt (5:5:1). The second band was collected and evaporated to give compound **6** (6 mg, 0.0053 mmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1H), 3.9 (broad, 1H), 1.43 (s, 9H), 1.37 (s, 9H), 1.34 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 1C except as noted, δ 190.21, 150.42, 149.54, 149.33, 149.20, 149.13, 149.03, 148.93, 148.88, 148.81, 148.72, 148.69, 148.61 (2C), 148.60, 148.48, 148.41, 148.37, 148.21, 148.09, 148.08, 147.97, 147.70, 147.55, 147.14, 146.47, 145.84, 144.96, 144.82, 144.77, 144.75, 144.73, 144.68, 144.65, 144.38, 144.29, 144.25, 144.04, 143.84, 143.58, 143.09, 142.56 (2C), 142.05, 141.50, 141.19, 140.66, 140.56, 140.08, 139.70, 137.08, 134.65, 134.62, 91.15, 88.42, 87.15, 85.68, 82.74, 81.97, 81.68, 81.48, 73.67, 39.63, 26.95 (3C), 26.72 (9C); FT-IR (microscope) 3525, 3320, 2978, 2928, 1730, 1456, 1388, 1365, 1191, 1065, 1010, 733 cm^{-1}; ESI-MS *m*/*z* (rel intensity) 1164 (100, M + Na$^+$); ESI-HRMS 1142.2616, calcd for $C_{76}H_{40}NO_{11}$ 1142.2596.

Crystals of $\mathbf{6}\cdot 5H_2O\cdot 3CDCl_3$ suitable for X-ray diffraction were obtained from slow evaporation in $CDCl_3$ in the NMR tube. Crystal data: monoclinic, space group $P\ 2_1/c$, a = 13.9150(2) Å, b = 25.7935(4) Å, c = 22.4441(4) Å, β = 117.0560(10)°, volume = 7174.0(2) Å^3; final R indices [$I > 2\sigma(I)$] $R_1 = 0.1066$, $wR_2 = 0.3136$ (crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-716211).

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Supporting Information Available: Selected spectroscopic data for all the new compounds and crystallographic data for **2** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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