

Supporting Information for:

Less Sensitive Oxygen-Rich Organic Peroxides Containing Geminal Hydroperoxide Groups

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1. Experimental Procedures

General Considerations

Syntheses of all organic peroxides were carried at room temperature under ambient atmosphere. Chemicals were purchased from Sigma-Aldrich, Acros Organics, EMD, or Alfa Aesar and were used without further purification. ACS grade solvents were obtained from EMD and Fisher Scientific. Geminal hydroperoxides **1**, and **3–5** were synthesized using a modified published general procedure for geminal hydroperoxides.¹ Compound **2** was obtained with sufficient purity using concentrated HCl as the catalyst and no column purification was required.

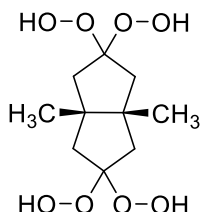
Silica gel 60, 230–400 mesh (EMD Chemicals) was used to perform silica gel column chromatography.² ASTM TLC plates precoated with silica gel 60 F₂₅₄ (250 µm layer thickness) were used for thin-layer chromatography (TLC). TLC spots were observed using a UV lamp and/or a potassium permanganate solution as a stain (3 g KMnO₄, 20 g K₂CO₃, 5 mL 5% w/v aqueous NaOH, 300 mL H₂O). The spots on the stained TLC plates were visualized after heating with a heat gun.

¹H and ¹³C{¹H} NMR spectra were obtained at 400 MHz and 101 MHz, respectively, in CD₃OD as indicated and were referenced to the residual proton and carbon resonances of the solvent (¹H δ 3.31, ¹³C 49.00 ppm). Mass spectra were obtained on an electrospray time-of-flight high-resolution Waters Micromass LCT Premier XE mass spectrometer. Infrared spectra were obtained from a Shimadzu MIRacle 10 IRAffinity-1 equipped with a single reflection ATR accessory (**1** and **3–5**) and a Perkin-Elmer One FT-IR Spectrum BXII instrument with a Smith ATR Dura Sample IRII accessory (**2**). Melting points were determined on an Electrothermal IA 9300 melting point apparatus and are uncorrected. Thermogravimetric (TGA/DTA) measurements to determine the decomposition temperatures of **1–5** were performed at a heating rate of 5 °C min⁻¹ with an OZM Research DTA 552-Ex instrument.

Caution: The H₂O₂ solutions are strong oxidizers that may cause explosions. All organic peroxides are potentially explosive and require handling with extreme care. Reactions and manipulations should be run in fume hoods behind blast shields. Personal safety gear should include a face shield, leather gloves, a leather apron, and hearing protection. Peroxide compounds should not come into contact with strong acids, metal salts, or easily oxidized species. All reactions should be run at or below room temperature and performed on small scales. Specifically, **3** exploded upon concentrating a solution containing ca. 30 mg of crystals on the walls of the flask, and shattered the flask and damaged the stir bar.

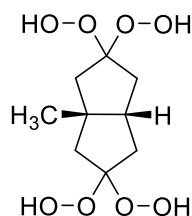
Qualitative Energetic Properties: Qualitative sensitivities to heat, impact, and electrostatic discharge were determined to assess initial safety issues. Tests included burning about 3-5 mg of the compound in the Bunsen burner flame, striking 3-5 mg of the compound on a metal plate with a hammer, and passing an electrostatic discharge through 3-5 mg of the compound on a metal plate using an Electro Technic BD 10 Tesla coil (120 V, 0.35 A).

2,2,5,5-tetrahydroperoxy-*cis*-3,6-dimethyloctahydropentalene (1).



A 50-ml round bottomed flask was charged with a magnetic stir bar, I₂ (0.050 g, 0.2 mmol) in CH₃CN (3 mL), and then a 50 wt.% aqueous solution of H₂O₂ (0.5 mL, 9 mmol) was added. To this solution *cis*-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (0.166 g, 1.00 mmol) was added and the reaction was stirred at room temperature (23 °C) for 5 h. At this point, the reaction mixture was concentrated under reduced pressure, dissolved in 1 mL of DCM: CH₃OH (20:1) and the product was purified by silica gel column chromatography with CH₂Cl₂: CH₃OH = 20:1 to obtain **1** (0.061 g, 21%) as a white solid: mp not taken due to explosion hazard; IR (ν, cm⁻¹) 3365 (broad, m), 2965 (m), 2874 (m), 2808 (w), 1688 (w), 1452 (m), 1431 (m), 1380 (m), 1319 (m), 1274 (s), 1225 (m), 1189 (m), 1156 (m), 1125 (m), 1083 (m), 1045 (s), 1001, 993 (m), 982 (m), 945 (m), 901 (m), 866 (m), 826 (s), 798 (m), 732 (w); ¹H NMR (400 MHz, CD₃OD, 23 °C, δ) OOH resonances not observed due to exchange with CD₃OD, 2.18 (d, 4H, *J* = 14.8 Hz), 1.88 (d, 2H, *J* = 14.8 Hz), 1.01 (s, 6H, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃OD, 23 °C, ppm) 120.14 (peroxy C), 50.55 (C), 46.49 (CH₂), 22.27 (CH₃); Anal. Calcd for C₁₀H₁₈O₈: C, 45.11; H, 6.81. Found: C, 44.90; H, 6.90. Colorless, planar, hexagonal crystals of **1**•ether were obtained by slow evaporation from diethyl ether.

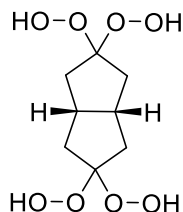
2,2,5,5-tetrahydroperoxy-3-methyloctahydropentalene (2).



A 100-ml round bottomed flask was charged with a magnetic stir bar and CH₃CN (20 mL). Then, *cis*-1-methylbicyclo[3.3.0]octane-3,7-dione (0.280 g, 1.84 mmol) was added and the mixture was stirred at room temperature (23 °C) until the solid was completely dissolved. Afterwards, 30 wt.% aqueous solution of H₂O₂ (2.00 mL, 19.7 mmol) and concentrated HCl (4 drops/0.100 g, 1.01 mmol) were added and the resulting solution was stirred at room temperature (23 °C) for 24 h. The solvent was removed under reduced pressure to obtain **2** (0.46 g, 93 %) as a white solid: mp not taken due to explosion hazard; IR (ν, cm⁻¹) 3371 (broad, m), 2954 (m), 2872

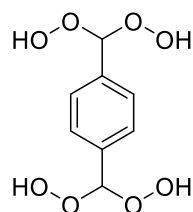
(m), 2349 (w), 2280 (w), 1722 (m), 1712 (m), 1631 (w), 1433 (m), 1379 (s), 1311 (s), 1262 (m), 1227 (m), 1162 (m), 1136 (m), 1048 (m), 994 (m), 953 (m), 935 (w), 832 (m), 802 (w), 752 (w); ^1H NMR (400 MHz, CD_3OD , 25 °C, δ) OOH resonances not observed due to exchange with CD_3OD , 2.42-2.31 (m, 1H, CH), 2.13 (d, 4H, $J = 28$ Hz, CH_2), 1.85 (d, 4H, $J = 32$ Hz, CH_2), 1.17 (s; 3H; CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3OD , 25 °C, ppm) 123.6 (peroxy C), 48.7 (C), 48.4 (CH) 46.8 (CH_2), 38.9 (CH_2), 28.1 (CH_3); Anal. Calcd for $\text{C}_9\text{H}_{16}\text{O}_8$: C, 42.84; H, 6.40. Found: C, 42.92; H, 6.17.

2,2,5,5-tetrahydroperoxyoctahydro-pentalene (3).



In a fashion similar to the preparation of **1**, treatment of I_2 (0.010 g, 0.040 mmol) in CH_3CN (1 mL) and a 50 wt.% aqueous solution of H_2O_2 (0.10 mL, 1.7 mmol) with *cis*-1,5-dimethylbicyclo[3.3.0]octane-3,7-dione (0.028 g, 0.20 mmol) afforded **3** (0.031 g, 64%) as a crude white solid. The product was purified by silica gel column chromatography with 4:1 CH_2Cl_2 :EtOAc, but an explosion occurred upon solvent removal under reduced pressure. The flask shattered and even the stir bar was damaged: mp not taken due to explosion hazard; ^1H NMR (400 MHz, CD_3OD , 23 °C, δ) OOH resonances not observed due to exchange with CD_3OD , 2.72-2.56 (m, 2H, CH), 2.18 (d of d, 4H, $J = 14.4, 8.8$ Hz), 1.86 (d of d, 4H, $J = 14.4, 5.6$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3OD , 23 °C, ppm) 122.10 (peroxy C), 40.54 (CH), 39.03 (CH_2); Anal. Calcd for $\text{C}_8\text{H}_{14}\text{O}_8$: C, 40.34; H, 5.92. Found: C, 39.98; H, 5.77.

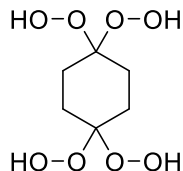
1,4-bis(dihydroperoxymethyl)benzene (4).



In a fashion similar to the preparation of **1**, by treatment of I_2 (0.200 g, 0.800 mmol) in CH_3CN (10 mL) and a 50 wt.% aqueous solution of H_2O_2 (1.84 mL, 32.0 mmol) with terephthalaldehyde (0.536 g, 4.00 mmol) a product mixture was obtained that was concentrated under reduced pressure. It was re-dissolved in dichloromethane (10 mL) and the solution was dried over anhydrous Na_2SO_4 . The decanted dichloromethane solution was again concentrated and the product was purified by silica gel column chromatography with 4:1 CH_2Cl_2 :EtOAc to obtain **1** (0.328 g, 35%) as a white solid: mp. 108–110 °C; IR (v, cm^{-1}) 3236 (broad, m), 2944 (w), 2816 (w), 2797 (w), 2762 (w), 2738 (w), 1699 (w), 1683 (w), 1413 (m), 1314 (m), 1201 (w), 1128 (w), 1033 (s), 982 (s), 930 (w), 869 (m), 825 (w), 781 (s), 693 (s); ^1H NMR (400 MHz, CD_3OD , 23

$^{\circ}\text{C}$, δ) OOH resonance not observed due to exchange with CD_3OD , 7.45 (s, 4H, CH), 6.10 (s, 2H, CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3OD , 23 $^{\circ}\text{C}$, ppm) 136.78 (aryl C), 128.02 (aryl CH), 110.73 (peroxy CH); Low resolution mass spectrum calculated for $[\text{C}_8\text{H}_{10}\text{O}_8\text{H}]^+$ 235.0; mass obtained 235.4; Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}_8$: C, 41.04; H, 4.30. Found: C, 41.02; H, 4.50. Colorless, diamond-shaped single crystals of **4** (0.218 g, 23%) were obtained by layering a solution of compound **4** in 1:1 THF:diethyl ether with hexane

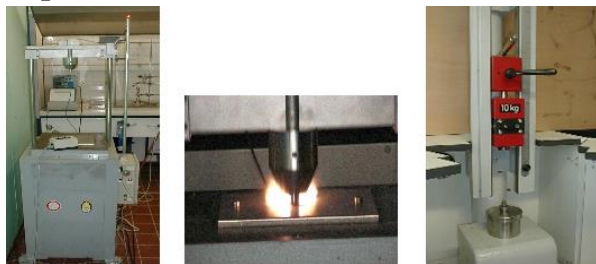
1,1,4,4-tetrahydroperoxycyclohexane (**5**).



1,4-Cyclohexadione (0.210 g, 2.62 mmol) was treated with a 30 wt.% aqueous solution of H_2O_2 (2.50 mL, 0.83 g, 24.4 mmol). After 1,4-cyclohexadione was dissolved completely, 3 drops of concentrated HCl were added and the reaction vessel was shaken cautiously. After four days a white solid precipitate was obtained. It was filtered off and washed with diethyl ether to obtain **5** (0.261 g, 47%) as a white solid. IR (ν , cm^{-1}) 3510 (m), 3264 (s), 3180 (s), 2958 (m), 2844 (m), 2340 (w), 1715 (w), 1584 (m), 1459 (m), 1437 (m), 1393 (m), 1371 (m), 1333 (m), 1287 (m), 1265 (s), 1159 (m), 1071 (s), 1002 (m), 973 (w), 955 (s), 913 (s), 876 (m), 858 (s), 772 (w), 630 (s); ^1H NMR (400 MHz, CD_3OD , 23 $^{\circ}\text{C}$, δ) OOH resonances not observed due to exchange with CD_3OD , 1.86 (s, 8H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3OD , 23 $^{\circ}\text{C}$, ppm) 109.83 (peroxy C), 26.73 (CH_2); Anal. Calcd. For $\text{C}_6\text{H}_{12}\text{O}_8$: C, 33.97; H, 5.70. Found: C, 33.61; H, 6.03. An X-ray quality single crystal was isolated from the white solid precipitate obtained from the reaction mixture.

2. Energetic Materials Testing Procedures

Impact Tests



Impact sensitivity tests were carried out according to STANAG 4489³ modified instructions⁴ using a BAM (Bundesanstalt für Materialforschung) drop hammer.⁵ Approximately 0.4 mL volume of a compound was placed in the sample holder (between two steel cylindrical blocks that are contained in a hollow steel cylinder) and a series of increasing weights was dropped from a fixed height or a fixed weight was dropped from varying heights. A test was considered positive when a sound (160 dB) was heard. Sensitivity was obtained when one out of six tests was positive.

Friction Tests



Friction sensitivity tests were carried out according to STANAG 4487⁶ modified instruction⁷ using the BAM friction tester. A line of approximately 5 mg of a compound was laid on a ceramic plate and a ceramic peg was kept on it. The ceramic plate was then moved from side-to-side so that the ceramic peg was exerting force on the sample. The force exerted on the sample was regulated by the weight and distance of the weight. A test was considered positive when a detonation was observed. Sensitivity was obtained when one out of six tests was positive.

Electrostatic Discharge Tests



Compounds were tested for the sensitivity towards electrical discharge using an OZM Electric Spark Tester ESD 2010 EN according to STANAG 4515 instructions.⁸ Approximately 0.1 mL volume of a compound was incorporated in a plastic tube and a charge is exerted through a steel electrode. The test is positive when a small hole was observed after the electricity interacted with the compound.

1. (a) K. Žmitek, M. Zupan, S. Stavber and J. Iskra, *Org. Lett.*, 2006, **8**, 2491-2494. (b) K. Žmitek, M. Zupan, S. Stavber and J. Iskra, *J. Org. Chem.*, 2007, **72**, 6534-6540.
2. C. W. Still, M. Kahn, A. Mitra, *J. Org. Chem.* 1978, **43**, 2923-2925.
3. NATO standardization agreement (STANAG) on explosives, *Impact Sensitivity Tests*, no. 4489, 1st ed., Sept. 17, **1999**.
4. WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, **2002**.
5. <http://www.bam.de>.
6. NATO Standardization Agreement (STANAG) on Explosives, *Friction Sensitivity Tests*, no. 4487, 1st ed., Aug. 22, **2002**.

7. WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, **2002**.
8. a) <http://www.ozm.cz> (accessed January 29, **2013**). b) NATO Standardization Agreement 4515, August 23, **2002**.