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(8) Preliminary experiments indicate the Cu(II) salts are equally effective in promoting the methanolysis of the selenol esters.

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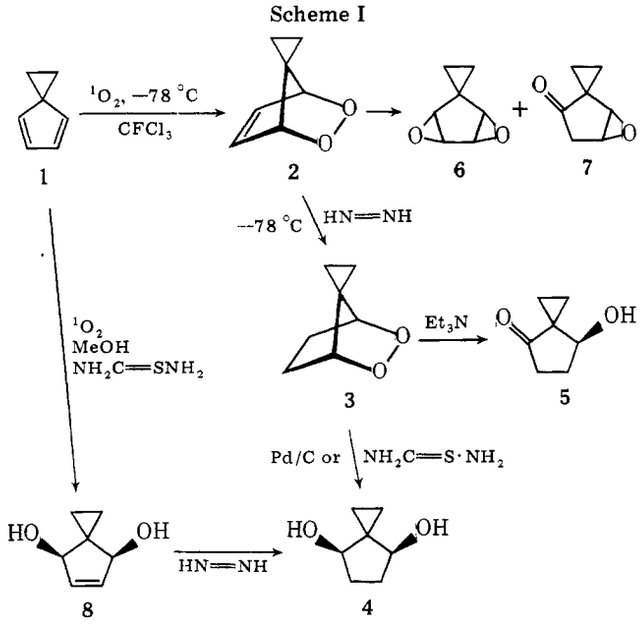
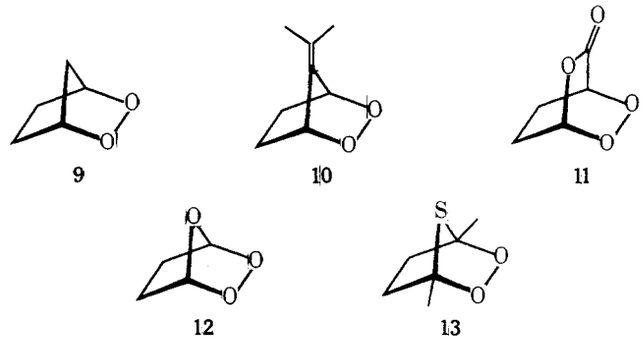
Synthesis and Characterization of 7-Spirocyclopropyl-2,3-dioxabicyclo[2.2.1]hept-5-ene[1]

Summary: The title compound, **3**, was prepared by diimide reduction of the unstable endoperoxide **2** which was obtained by photooxygenation of spiro[2.4]hepta-4,6-diene (**1**) and characterized by catalytic reduction to its diol **4** and base-catalyzed rearrangement to its ketol **5**.

Sir: Although the singlet oxygenation of spiro[2.4]hepta-4,6-diene (**1**) has been reported,[2] the intermediacy of the expected endoperoxide **2** could only be inferred from the formation of the diepoxide **6** and ketoepoxide **7** as the major rearrangement products (cf. Scheme I). Recently we have been successful in trapping the unstable singlet oxygen adducts derived from cyclopentadiene,[3] 6,6-dimethylfulvene, α-pyrone,[5] furan,[6] and 2,5-dimethylthiophene[7] by diimide reduction to their respective bicyclic peroxides **9–13.** In view of this convenient peroxide bond-preserving technique, we have reinvestigated the singlet oxygenation of the spirodiene **1** and established the intervention of its unstable endoperoxide **2** by direct NMR monitoring and reductive trapping in the form of the stable bicyclic peroxide **3.**

Scheme I





The photooxygenation of **1** in $CFCl_3$ at −78 °C with tetraphenylporphyrin (TPP) as sensitizer using a General Electric 400-W sodium lamp gave after warm-up to room temperature the reported[2] rearrangement products **6** and **7.** However, when the singlet oxygenation was monitored by subambient (−50 °C) NMR analysis, after 5 h of irradiation the characteristic spirodiene **1** resonances at δ 1.50 (singlet, cyclopropyl, 4 H) and δ 5.85 and 6.30 (multiplets, olefinic, 4 H) had been completely replaced by new resonances at δ 0.90 (broad singlet, cyclopropyl, 4 H), 4.58 (triplet, J = 2.0 Hz, bridgehead, 2 H), and 6.53 (triplet, J = 2.0 Hz, olefinic, 2 H), ascribed to the unsaturated endoperoxide **2** as the expected singlet oxygenation adduct of **1.** Not even traces of the diepoxide **6** and ketoepoxide **7** rearrangement products of **2** could be detected by NMR at −50 °C in $CFCl_3$. Warming of the reaction mixture to 0 °C promoted rapid replacement of the above signals assigned to **2** by those reported[2] for **6** and **7.** Furthermore, photooxygenation of the spirodiene **1** in MeOH with Rose Bengal as sensitizer in the presence of thiourea afforded the unsaturated diol **8** in 60% yield, liquid, n^{20}_D 1.4930 (after VPC collection on a 5 ft × ¼ in. aluminum column packed with 5% SE 30 on Chromosorb P and operated at a column temperature of 125 °C). Its characterization rests on satisfactory elemental analysis, ^1H NMR ($CDCl_3$, Me_4Si) resonances at δ 0.85 (s, cyclopropyl, 4 H), 2.60 (broad s, OH, exchanged with D_2O, 2 H), 3.98 (s, OCH, 2 H), and 6.05 (s, olefinic, 2 H), and IR ($CHCl_3$) bands at 3710–3125 (OH), 3070–3020 (cyclopropyl CH and olefinic CH), 2990–2900 (aliphatic CH), and 1710 cm^{-1} (C═C).

Treatment of the photooxygenate with excess diimide, generated in situ from potassium azodicarboxylate as described previously,[3] at −78 °C in $CFCl_3$ afforded the stable saturated endoperoxide **3** in 68% yield, pale yellow needles, mp 32 °C [after sublimation at 30 °C (0.15 mmHg)]. The bicyclic peroxide **3** gave a satisfactory elemental analysis and exhibited ^1H NMR (CCl_4) resonances at δ 0.85 (m, cyclopropyl, 4 H), 1.87 (broad s, methylenic, 4 H), and 3.80 (broad s bridgehead, 2 H) and IR (CCl_4) bands at 3080 (cyclopropyl CH), 2980–2940 (aliphatic CH), 1460 (CH_2 bending), and 1018 cm^{-1} (peroxide). The following chemical transformations confirm this structure assignment. Thus, catalytic hydrogenation of **3** over 10% Pd/C as well as thiourea reduction in MeOH gave the *cis*-diol **4** in 92% yield, n^{20}_D 1.4935 (after VPC collection under the conditions described for diol **8**). Diol **4** gave a satisfactory elemental analysis and exhibited ^1H NMR ($CDCl_3$) resonances at δ 0.30–1.00 (m, cyclopropyl, 4 H), 1.95 (broad s, CH_2, 4 H), 2.39 (broad s, –OH, exchanged with D_2O, 2 H), and 3.48 (m, OCH, 2 H) and IR ($CHCl_3$) bands at 3710–3200 (OH), 3065 (cyclopropyl CH), 2995–2860 (aliphatic CH), 1420 (CH_2 bending), and 1040 cm^{-1} (CO). Diol **4** could also be obtained by diimide reduction of the unsaturated diol **8** in MeOH at 0 °C, showing identical spectral data. Finally, treatment of the saturated endoperoxide **3** with triethylamine in CH_2Cl_2 at 0 °C gave the ketol **5** in 87% yield, n^{20}_D 1.4856 (after VPC collection under the conditions described for diol

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4). Ketol **5** exhibited a satisfactory elemental analysis and showed ^{1}H NMR ($CDCl_3$) resonances at δ 1.18 (broad s, cyclopropyl, 4 H), 1.72 (broad s, OH, exchanged with D_2O, 1 H), 1.90–2.70 (m, CH_2, 4 H), and 4.11 (m, OCH, 1 H) and IR ($CHCl_3$) bands at 3700–3240 (OH), 3060 (cyclopropyl CH), 2995–2940 (aliphatic CH), 1720 (C=O), 1446 and 1412 (CH_2 bending), and 1070 and 1050 (CO).

On the basis of the spectral data and chemical transformations (cf. Scheme I) the intervention of the strained unsaturated endoperoxide **2** in the photooxygenation of spirodiene **1** is confirmed. Its reductive trapping with diimide offers a convenient synthetic entry to the saturated bicyclic peroxide **3**, difficult to come by via alternatives routes. We are extending this synthetic methodology to prepare otherwise inaccessible bicyclic peroxides in order to explore their thermal and photochemical behavior.

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(8) NIH Career Development Awardee (1975–1980).

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