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SINGLET OXYGENATION OF CYCLOOCTA-1,3,5-TRIENE: FORMATION OF (4.2.2)- AND (2.2.2)- CYCLOADDUCTS.[1]

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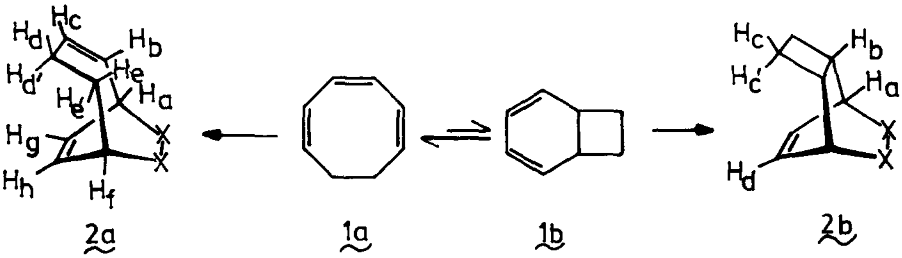
Abstract: Photosensitized singlet oxygenation of 1,3,5-cyclooctatriene affords the (4.2.2)- and (2.2.2)-type endoperoxides, which were reduced with diimide, thermally isomerized, and deoxygenated with triphenylphosphine.

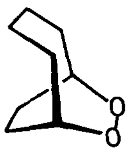
Cycloocta-1,3,5-triene (1) is a versatile substrate for cycloaddition in view of its diverse dienic reactivity.[3] Thus, in principle the (2+4)-cycloadducts 2a and 2b can be obtained, representing respectively the (4.2.2)- and (2.2.2)-products of the monocyclic (1a) and bicyclic (1b) valence isomers (eq. 1). For example, with N-phenyl-1,2,4-triazoline-3,5-dione we confirmed that the respective urazole derivatives 2a and 2b were formed in 80% and 20% yields.[5]



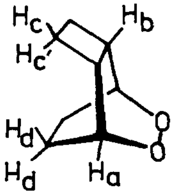
(eq.1)

Since singlet oxygen resembles N-phenyl-1,2,4-triazoline-3,5-dione in its dienophilic reactivity, we decided to explore the photosensitized oxygenation of cycloocta-1,3,5-triene (**1**) in the interest of providing a convenient and efficient entry into novel bicyclic peroxides of potential synthetic utility. Herewith we report our results on the synthesis, characterization, and chemical transformation of the (4.2.2)- and (2.2.2)-cycloadducts **2a** and **2b** (X = O), respectively.

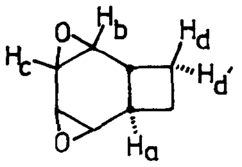
Tetraphenylporphyrin (TPP)-sensitized photooxygenation of cycloocta-1,3,5-triene (**1**) in CCl_4 at 30°C under irradiation with a General Electric 150 W sodium street lamp afforded the two cycloadducts **2a** and **2b** (X = O) in 82% and 18% yields, respectively. The (4.2.2)-cycloadduct **2a**, mp 42-44°C, and the (2.2.2)-cycloadduct **2b**, mp 83-84°C, both sublimed at 30°C and 0.1 torr, gave a satisfactory elemental analysis[6] for the $C_8H_{10}O_2$ summation formula. The ^1H-NMR spectra (CCl_4, TMS) show peaks for isomer **2a** at δ 1.59-2.60 ppm (4H; H_d,$H_{d'}$,H_e,$H_{e'}$; multiplet), δ 4.57 ppm (1H; H_f; multiplet), δ 4.86 ppm (1H; H_a; multiplet) and δ 5.39-6.54 (4H; H_b,H_c, H_g and H_h; multiplet), and for isomer **2b** at δ 1.32 ppm (2H, H_c; multiplet), δ 1.82 ppm (2H; $H_{c'}$; multiplet), δ 2.70 ppm (2H; H_b; multiplet), δ 4.15 ppm (2H; H_a; multiplet) and δ 6.37 ppm (2H; H_d; multiplet). The IR spectra (CCl_4, cm^{-1}) show characteristic bands for isomer **2a** at 3020 (olefinic C-H), 2910 (aliphatic C-H), 1635 (C=C) and for isomer **2b** at 3020 (olefinic C-H), 2940 (aliphatic C-H), and 1610 (C=C). Both endoperoxide isomers show parent peaks at m/e 138 in the MS (70 eV). Additional support for these structural assignments comes from chemical transformations including diimide reduction to the saturated endoperoxides **3a** and **3b**, thermal isomerization of **2b** to the bisepoxide **4b** and triphenylphosphine deoxygenation into **5a** and **5b**. These results are detailed below.



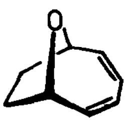
3a



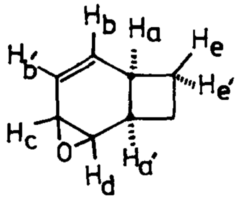
3b



4b



5a



5b

Reduction of the cycloadducts **2a** and **2b** (X = O) in situ with a 5-fold excess of diimide, generated from potassium azodicarboxylate, in MeOH at 0-20°C afforded the saturated endoperoxides **3a** and **3b** in 86% and 94% yields, respectively. The physical data are mp 95-96°C (lit.[7] mp 96-98°C) for **3a** and mp 98°C (sublimed at 40°C and 0.1 torr) for **3b**; the latter gave a satisfactory elemental analysis for the $C_8H_{12}O_2$ summation formula. The ^{1}H-NMR spectrum (CCl_4, TMS) of **3b** shows δ 0.83-1.33 ppm (2H; H_c; multiplet), δ 1.63-2.12 ppm (2H; $H_{c'}$; multiplet), δ 2.08 ppm (4H; H_d; multiplet), δ 2.86 ppm (2H; H_b; multiplet), and δ 3.75 ppm (2H; H_a; multiplet).

Thermal isomerization of **2b** in CCl_4 at 110°C afforded the bisepoxide **4b** in 96% yield, mp 69°C (sublimed at 40°C and 0.1 torr). The ^{1}H-NMR spectrum (CCl_4, TMS) shows δ 2.88 ppm (2H; H_c; multiplet), δ 1.30-2.10 ppm (4H; H_d; multiplet), and δ 2.10-2.55 ppm (4H; H_a and H_b; multiplet). The bisepoxide **4b** gave a satisfactory elemental analysis[6] for the $C_8H_{10}O_2$ summation formula.

On treatment with triphenylphosphine in CH_2Cl_2 at 30°C the products **5a** and **5b** were obtained in 62% and 74% yields, respectively. Both are clear liquids with bp 60°C at 10 torr and n_D^{20} 1.5254 for **5a**[7] and bp 30°C at 3 torr and n_D^{20} 1.5060 for **5b**, which gave a satisfactory elemental analysis[6] for the $C_8H_{10}O$ summation formula. The ^{1}H-NMR spectrum (CCl_4, TMS) of **5b** shows resonances at δ 1.94-2.64 ppm (6H; H_e,$H_{e'}$,H_a and $H_{a'}$; multiplet), δ 3.11 ppm (2H; H_c and H_d; multiplet), and δ 5.79 ppm (2H; H_b and $H_{b'}$; multiplet) and the IR spectrum (CCl_4, cm^{-1}) exhibits bands at 3020 (olefinic C-H), 2960 (aliphatic C-H), and 1640 (C=C), and the MS (70 eV) shows the molecular ion peak at m/e 122.

The experimental data presented here clearly establish the formation of the (2+4)-cycloadducts **2a** and **2b** of the respective monocyclic **1a** and bicyclic **1b** valence isomers with singlet oxygen. Thus, singlet oxygenation of cycloocta-1,3,5-triene (**1**) constitutes a convenient entry into the preparation of novel endoperoxides of versatile synthetic potential.

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REFERENCES

1) Paper No. 85 in the Cyclic Peroxide Series.

2) NIH Career Development Awardee (1975-80).

3) A.C. Cope and A.C. Haven, J. Am. Chem. Soc., **74**, 4867 (1952).

4) K. Alder, Chem. Ber., **87**, 1492 (1954).

5) W. Adam and I. Erden, unpublished results. The physical constants and spectral data are (cf structures **2a** and **2b** in eq. 1 for the proton labels): Urazole **2a**: mp 185-186°C (from EtOH); satisfactory elemental analysis[6] for the summation formula $C_{16}H_{15}N_3O_2$; ^{1}H-NMR ($CDCl_3$, TMS) shows peaks at δ 1.70-2.50 ppm (4H; H_d,$H_{d'}$,H_e,$H_{e'}$; multiplet), δ 4.75 ppm (1H; H_f; multiplet), δ 4.95 ppm (1H; H_a; multiplet), δ 5.75 ppm (2H; H_b and H_c; multiplet), δ 6.43 ppm (2H; H_g and H_h; multiplet), and δ 7.15 ppm (5H; Ph; br. singlet); IR ($CHCl_3$, cm^{-1}) shows bands at 3040 (olefinic and aromatic C-H), 2920 (aliphatic C-H), and 1755 and 1698 (urazole C=O).

   Urazole **2b**: mp 201-201.5°C (from EtOH); satisfactory elemental analysis[6] for the summation formula $C_{16}H_{15}N_3O_2$; ^{1}H-NMR ($CDCl_3$; TMS) shows peaks at δ 1.43 ppm (2H; H_c; multiplet), δ 1.95 ppm (2H; $H_{c'}$; multiplet), δ 2.90 ppm (2H; H_b; multiplet), δ 4.73 ppm (2H; H_a; multiplet), δ 6.42 ppm (2H; H_d; multiplet), and δ 7.15 ppm (5H; Ph; br. singlet); IR ($CHCl_3$, cm^{-1}) shows bands at 3040 (olefinic and aromatic C-H), and 1763 and 1705 (urazole C=O).

6) Atlantic Analytical Laboratories, Atlanta, Georgia.

7) H. Heap, G.E. Green, and G.H. Whitham, J. Chem. Soc.(C), 160 (1969); the ^{1}H-NMR and IR spectral data of **5a** matched those reported for the authentic substance.

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