

Reaction of Tungstic Acid–Hydrogen Peroxide with *endo*-Dicyclopentadiene: An Unusual Observation†

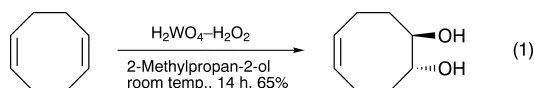
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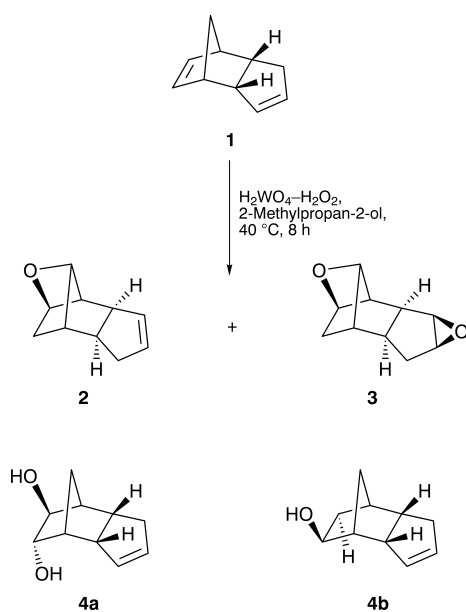
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The reaction of *endo*-dicyclopentadiene **1** with tungstic acid–hydrogen peroxide in 2-methylpropan-2-ol to form the polycyclic compounds **2** and **3** is reported, and a plausible mechanism for the formation of these products is discussed.

Either racemic or enantiomerically pure 1,2-diols are important structural units or synthetic building blocks for various biologically active and synthetic compounds in organic chemistry.^{1,2} It is not surprising therefore that a number of methods have been developed for their preparations.^{3–7}

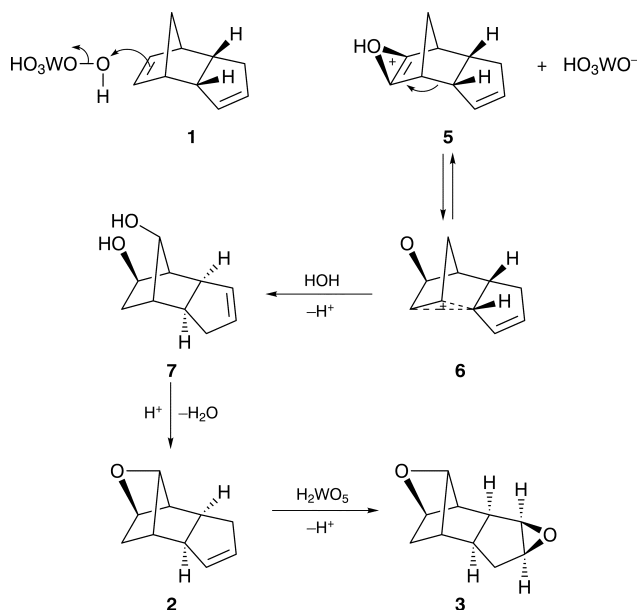


The electrophilic nature of the tungstic acid-catalysed *trans*-additions of hydrogen peroxide to olefins has long been known⁸ but it has not been exploited much. We have previously demonstrated the use of tungstic acid–hydrogen peroxide in 2-methylpropan-2-ol for the vicinal hydroxylation of *Z,Z*-cycloocta-1,5-diene to obtain the corresponding *trans*-diol in 65% yield, eqn. (1).⁹ It should be noted that *Z,Z*-cycloocta-1,5-diene poses considerable problems in hydroxylation with other hydroxylating agents,⁹ owing to its propensity towards transannular cyclization.¹⁰ In this connection, we now report that treatment of tungstic acid–hydrogen peroxide with *endo*-dicyclopentadiene **1** (the dimer of cyclopenta-1,3-diene, IUPAC name *endo*-tricyclo[5.2.1.0^{5,9}]deca-2,6-diene) in 2-methylpropan-2-ol at



40 °C for 8 h resulted in the formation of the two polycyclic compounds **2** and **3**, and no product corresponding to the expected diols **4a,b** was isolated (Scheme 1).

A plausible mechanism for the formation of these products is outlined in Scheme 2. The more strained double bond of the two in compound **1** is attacked first¹¹ to form the protonated epoxide **5** which in turn suffers a further attack through σ participation to generate initially the diol **7** via **6**.¹² This diol then undergoes protonation followed by dehydration due to the close proximity of the two hydroxyl functions to furnish the oxetane **2**. The oxetane **2** on further treatment with pertungstic acid undergoes epoxidation at the remaining double bond position to form **3**.



Experimental

IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer, NMR spectra on a JEOL GX 270 spectrometer and mass spectra using a VG 70-250 S double focusing magnetic sector mass spectrometer at a nominal resolution of 5000. Microanalyses were performed on a Coleman instrument. Column chromatography was carried out using Acme's silica gel (60–120 mesh) and spots were visualized in iodine vapor.

Reaction of Endo-dicyclopentadiene **1 with Tungstic acid–Hydrogen peroxide.**—A mixture of tungstic acid (0.2 g) and hydrogen peroxide (30%, 10.0 ml, 3.0 g, 0.09 mol) was added to a solution of *endo*-dicyclopentadiene **1** (5.0 ml, 4.9 g, 0.037 mol) in 2-methylpropan-2-ol (912 ml) at 40 °C under stirring. The reaction mixture was stirred for 3 h and further tungstic acid (0.1 g) was added. The reaction mixture was again stirred for 5 h and then filtered through a Celite pad to remove the suspended catalyst followed by removal of the solvent under reduced pressure (Negative peroxide test). The residue

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was then diluted with water (25 ml) and extracted with ethyl acetate (4 × 25 ml). The combined organic extracts were washed with water (20 ml) and dried over anhydrous sodium sulfate. Removal of the solvent followed by column chromatography of the residue over silica gel and elution (light petroleum–ethyl acetate, 95:5) gave **2** as a crystalline solid having a mentholic odor (1.1 g, 20.4%), mp 62–63 °C (Found: C, 80.56, H, 8.2. C₁₀H₁₂O requires C, 81.0; H, 8.1%); λ_{max} (MeOH) 210 nm; ν_{max} (neat) 2900, 1340, 1250, 1020, 900 cm⁻¹; δ_H (270 MHz, CDCl₃) 6.0 (m, 2 H, olefinic protons), 3.05, 3.10 (two m, 1 H each, H–O–CH), 2.80 (m, 1 H, allylic ring-junction proton), 2.70 (m, 2 H, allylic CH₃), 2.42 (br m, 1 H, ring-junction proton), 1.77 (br m, 1 H, bridgehead proton), 1.40 (m, 1 H, bridgehead proton), 1.22 (br m, 2 H, CH₂). δ_C (75 MHz, CDCl₃) 134.77, 134.56 (sp² carbons), 61.56, 60.46 (C–O–C), 51.87, 50.90, 46.33, 33.54, 43.86 and 30.99 (CH₂ and CH=). *m/z* 148.0886 (M⁺). Further elution (light petroleum–ethyl acetate, 90:10) gave the epoxide **3** as a colorless solid (2.0 g, 34%), mp 169–170 °C (Found: C, 73.60; H, 7.77. C₁₀H₁₂O₂ requires C, 73.17, H, 7.32%); ν_{max} (neat) 2963, 1457, 1390, 1022, 970, 832 cm⁻¹ δ_H (270 MHz, CDCl₃) 3.46 (dd, 1 H, *J* 8), 3.33 (d, 1 H, *J* 9), 3.19 (d, 1 H, *J* 12), 3.15 (d, 1 H, *J* 13), 2.6 (m, 1 H), 2.52 (br m, 1 H), 2.35 (br m, merged 2 H), 1.81 (br m, 2 H), 1.35 (dd, 1 H, *J* 7 Hz), 0.77 (br d, 1 H). δ_C (75 MHz, CDCl₃) 61.63 and 58.58 (two COH), 48.88, 48.66 (epoxide carbons), 48.28, 44.55, 39.87 and 39.11 (CH=, 29.58 and 26.95 (CH₂) *m/z* 164.08373 (M⁺).

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