

Reaction of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene with (Z)-butene-1,4-diol alcoholate

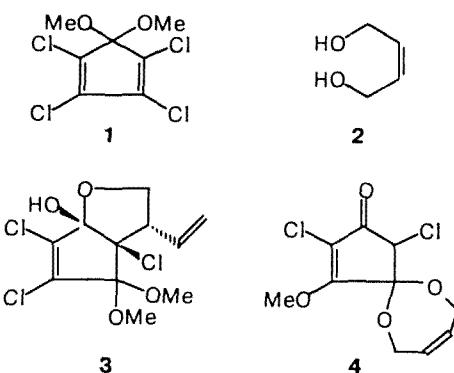
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5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene reacts with disodium (Z)-butene-1,4-diolate to give spiroketal in moderate yield.

Key words: 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene, (Z)-butene-1,4-diol, spiroketals.

Previously, we have shown¹ that bicyclic hemiketal **3**² is the product of a reaction between diene **1** and monosodium alcoholate of (Z)-butene-1,4-diol (**2**) in DMSO. The reaction of diene **1** with disodium alcoholate of diol **2** in DMSO-THF (1 : 4) results in spiroketal **4** in 30 % yield.



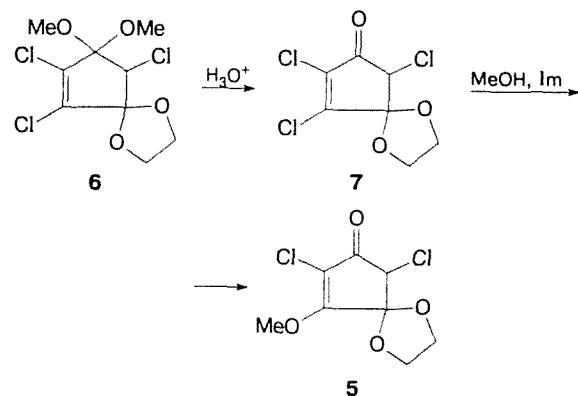
The structure of product **4** was established by comparing its spectral characteristics with those of ethylene ketal (**5**) synthesized from the known bisketal (**6**)³ following the chemically unambiguous route *via* enone (**7**) (Scheme 1).

Experimental

IR spectra were obtained on a UR-20 spectrophotometer in a thin layer or in suspension in Nujol. NMR spectra were recorded on a Bruker AM-300 spectrometer (¹H, 300, and ¹³C, 75.47 MHz, respectively) in CDCl₃ with SiMe₄ as the internal standard. Mass spectra were measured on a MKh-1306 instrument (70 eV), temperature of ionization chamber 75–100 °C.

(±)-Spiro-1,3-dichloro-4-methoxy-6,11-dioxa[4.6]undeca-3,8-dien-2-one (4). A solution of (Z)-butene-1,4-diol **2** (1.0 g, 11.9 mmol) in 2 mL of THF was added dropwise in the flow

Scheme 1



of Ar to a stirred suspension of NaH (0.48 g, 20 mmol) in a mixture of 4 mL of THF and 2 mL of DMSO. When the liberation of H₂ ceased, a solution of diene **1** (2.1 g, 8 mmol) in 2 mL of THF was slowly added to the mixture. The reaction mixture was stirred for 24 h at 20 °C, diluted with water (5 mL), and extracted with EtOAc. After the usual workup and chromatographic purification compound **4** (0.61 g, 30 %) was obtained, m.p. 98–100 °C. IR, ν/cm^{-1} : 1630, 1740. ¹H NMR, δ : 3.38 (s, 3 H, OMe); 4.45 (s, 1 H, CH); 4.40–4.70 (m, 4 H, 2 CH₂); 5.65 (m, 2 H, CH=CH). ¹³C NMR, δ : 60.75 (C-1); 60.83 (Me); 64.94 (C-10); 65.32 (C-7); 101.46 (C-5); 107.68 (C-3); 128.48 and 128.16 (C-8, C-9); 173.05 (C-4); 187.66 (C-2). Mass spectrum, *m/z*: 268 [M+4]⁺, 266 [M+2]⁺, 264 [M]⁺, 195 [M-C₄H₅O]⁺, 194

[M-C₄H₆O]⁺, 165 $\left[\begin{array}{c} \text{OCH}_2 \\ | \\ \text{M}-\text{CH} \\ | \\ \text{OCH}_2 \end{array} \right]^{+}$, 70 [C₄H₆O]⁺, 69 [C₄H₅O]⁺, 41 [C₃H₅]⁺ (max). Found (%): C, 45.50; H, 3.96; Cl, 27.07. C₁₀H₁₀Cl₂O₄. Calculated (%): C, 45.28; H, 3.77; Cl, 26.79.

(±)-Spiro-1,3-dichloro-4-methoxy-6,9-dioxa[4.4]non-3-en-2-one (7). To a stirred solution of bisketal **6** (3.0 g) in Me₂CO (20 mL), 15 % HCl (10 mL) was added dropwise, and after 2 h, 20 mL of a saturated aqueous solution of NaCl was

added. The product was extracted with EtOAc (3×50 mL). The combined organic extracts were washed with a saturated aqueous solution of NaCl, dried (MgSO_4), filtered, and concentrated; monoketal 7 was obtained in 82 % yield (2.06 g), m.p. 118–120 °C. IR, ν/cm^{-1} : 1610, 1750. ^1H NMR, δ : 4.15–4.35 (m, 4 H, 2 CH_2); 4.60 (s, 1 H, CH). ^{13}C NMR, δ : 62.19 (C-1); 67.45 and 67.57 (C-7, C-8); 107.71 (C-5); 134.37 (C-3); 157.19 (C-4); 186.11 (C-2).

(\pm)-Spiro-1,3-dichloro-4-methoxy-6,9-dioxa[4.4]non-3-en-2-one (5). A solution of ketone 7 (2 g) and imidazole (1.2 g) in MeOH (10 mL) was boiled for 3 h. The solvent was evaporated, the residue was dissolved in 15 mL of H_2O , and the product was extracted with EtOAc (3×20 mL). The combined organic extracts were dried with MgSO_4 , filtered, and concentrated. The oily residue was purified by column chro-

matography on SiO_2 . Compound 5 (1.22 g, 62 % yield) was obtained. IR, ν/cm^{-1} : 1630, 1745. ^1H NMR, δ : 4.15–4.30 (m, 4 H, 2 CH_2); 4.36 (s, 3 H, OMe); 4.52 (s, 1 H, CH). ^{13}C NMR, δ : 60.27 (C-1); 61.22 (Me); 106.69 (C-5); 109.60 (C-3); 170.84 (C-4); 187.09 (C-2).

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