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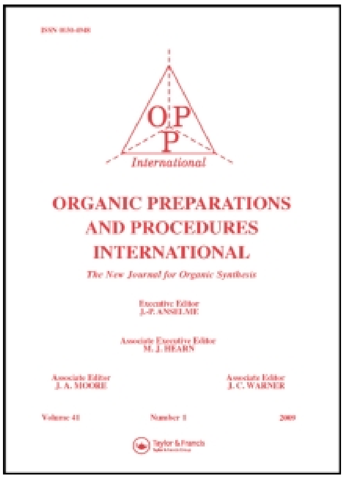

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AN IMPROVED SYNTHESIS OF (1α,6α)-8,8-DIOXABICYCLO[4.3.0]NONA-2,4-DIENE

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AN IMPROVED SYNTHESIS OF (1α,6α)-8,8-DIOXABICYCLO[4.3.0]NONA-2,4-DIENE

Submitted by
(04/25/88)

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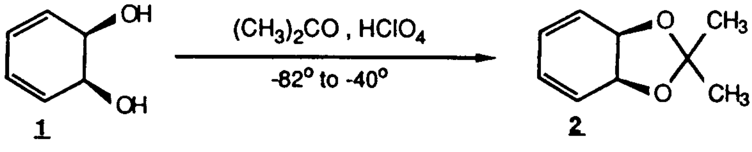
The title (2) has been used as an intermediate in the synthesis of benzene/anthracene cyclodimers[1] and a σ-homo-o-benzoquinone.[2] In addition, this compound is suitably functionalized for chemical elaboration to biologically active cyclitols[3] and aminocyclitols.[4,5] Unfortunately, the only existing route to diene 2 (prepared in four steps from cyclohexa-1,4-diene[1,6]) is inefficient (27% overall yield) and tedious. Given its synthetic potential, the development of a more efficient means for preparing 2 seemed warranted.

The recent discovery[7] of a microbial oxidant that allows the large scale conversion of benzene into cis-1,2-dihydroxyclohexa-3,5-diene (1), prompted us to consider means for the direct preparation of 2 from 1. We now report that, inspite of its inherent acid sensitivity, reaction of commercially available[8] 1 with acetone in the presence of perchloric acid catalyst



produces the desired compound in 61% yield. Crucial to the sucess of this conversion are the use of low reaction temperatures (-82° to -40°) and a base-quenching step (see Experimental Section). When the reaction is run at -25°, mixtures of diene 2 and phenol are produced, while at 20° phenol is the exclusive product of reaction.

EXPERIMENTAL SECTION

The ^{1}H and ^{13}C NMR spectra were obtained on JEOL JNM-GX400 and FX-90Q instruments, respectively. The MS was taken using a VG Micromass 7070F instrument. IR and UV spectra were recorded on Perkin Elmer 983G and Varian Super Scan 3 spectrophotometers, respectively.

(1α,6α)-8,8-Dimethyl-7,9-dioxabicyclo[4.3.0]nona-2,4-diene (2).- A vigorously stirred suspension of cis-1,2-dihydroxycyclohexa-3,5-diene (1) (5.0 g, 44.5 mmol) in acetone (120 mL, spectroscopic grade) maintained under nitrogen was cooled to -82° (internal temperature). A solution of 70% aqueous perchloric acid [**Caution - Strong Oxidant**] (600 mg) in acetone (10 mL) was then added to the reaction mixture in a dropwise fashion (syringe pump). After the completion of the addition (ca. 15 minutes), the reaction mixture was allowed to warm to ca. -40°. After stirring at this temperature for 2 hrs, the now homogenous reaction mixture was treated in a dropwise fashion with 1,5-diazabicyclo[4.3.0]non-5-ene (3.0 mL, 24 mmol) and the resulting solution was warmed to room temperature and then concentrated under reduced pressure (ca. 40 mm, no heating). The residual yellow oil was partioned between diethyl ether (50 mL) and aqueous KOH (50 mL of a 1.0 M solution). The separated aqueous phase was extracted with diethyl ether (1 x 50 mL) and the combined organic phases were then dried ($MgSO_4$), filtered and concentrated under reduced pressure (ca. 40 mm Hg) to give a colorless oil. Kugelrohr distillation (70°/5 mm) of this material gave spectroscopically pure diene **2** (4.15 g, 61%) as a clear colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.01 (m, 2H, vinylic H), 5.90 (m, 2H, vinylic H), 4.66 (t, J = 1.7Hz, 2H, H 1 and H 6), 1.43 (q, J = 1Hz, 3H, CH_3), 1.41 (q, J = 1Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 125.2, 123.5, 104.5, 70.2, 26.6, 24.6; IR(NaCl): 3044, 2984, 2933, 2887, 1378, 1370, 1240, 1209, 1158, 1031, 696 cm^{-1}; MS, m/e(70eV): 95(100 $[[M-CH_3COCH_2]^+]$, 94(45) $[[M-CH_3COCH_3]^+]$, 43(65) $[[CH_3CO]^+]$; UV (C_2H_5OH): λ 261 nm (ε = 4050). This material was identical (by ^{1}H NMR, TLC and IR) with an authentic sample of **2** prepared by the procedure of Yang and Mak.[1,6]

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