error is high, the slope of the compensation plot should be close to the harmonic mean of the temperatures of the several measurements. Since this is not the case, a true compensation phenomenon seems to be involved in the hydration of the carbonyl compounds.

Experimental Section

Materials. The pyridinecarboxaldehyde *N*-oxides were prepared as described in the literature[17,18] from conversion of the pyridinecarboxaldehydes to the diethyl acetal derivatives, followed by reaction with *m*-chloroperbenzoic acid at 0 °C. The compounds were recrystallized from benzene solutions, exhibiting melting points, and UV, infrared, and NMR spectra consistent with those reported in the literature.[19,20] 4-Formyl-1-methylpyridinium iodide was prepared as described in the literature[21] from the reaction of the 4-pyridinecarboxaldehyde and methyl iodide. Solutions of these reagents were prepared just prior to use. Reagent-grade KCl, $Na_2HPO_4 \cdot H_2O$, and $NaH_2PO_4 \cdot 2H_2O$ were employed without further purification.

Physical Measurements. Spectrophotometric measurements in the ultraviolet region were made with a Zeiss PMQ II or a Cary 14 instrument, fitted with thermostated cell compartments. Proton NMR spectra were recorded on a Varian XL-100 instrument, at room temperature. The concentration of the samples was typically 0.3 M.

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Registry No. 4-Formyl-1-methylpyridinium iodide, 13441-53-7; 4-pyCHO, 872-85-5; $Ru(NH_3)_5(4\text{-pyCHO})^{2+}$, 19471-56-8; $Fe(CN)_5(4\text{-pyCHO})^{3-}$, 37475-68-6; *O*-4-pyCHO, 7216-42-4; 3-pyCHO, 500-22-1; *O*-3-pyCHO, 22346-73-2; 2-pyCHO, 1121-60-4; *O*-2-pyCHO, 7216-40-2; pyridin-4-ylmethanediol *N*-oxide, 76037-07-5; pyridin-3-ylmethanediol *N*-oxide, 76037-08-6; pyridin-2-ylmethanediol *N*-oxide, 76037-09-7.

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Elimination Reactions of 6-Bicyclo[3.2.0]-2-heptenyl Tosylates[1]

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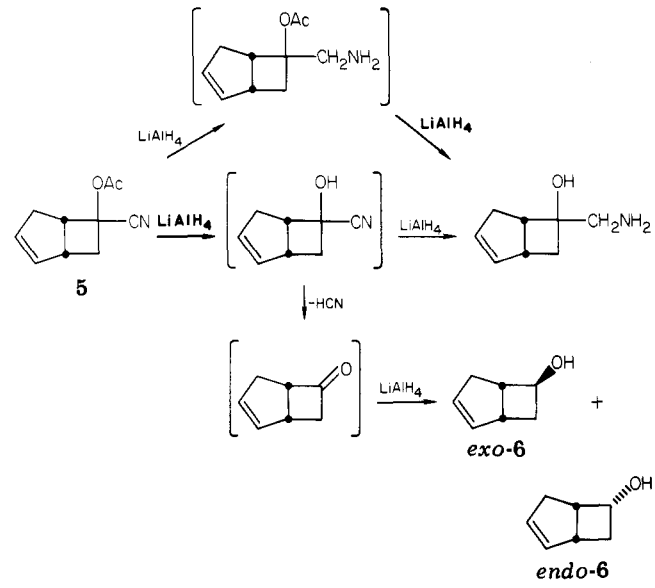
As part of an early attempted synthesis of pentalene, it was reported in 1951[2] that the reaction of a mixture of stereoisomeric 6- and 7-bicyclo[3.3.0]-2-octenyl tosylates (**1** and **2**) with collidine (2,3,5-trimethylpyridine) and other tertiary amine bases appeared to form variable amounts of a yellow polyene, **3**. This material had an ultraviolet absorption maximum at 260 nm (log ϵ 3.65) and a shoulder at 250 nm (log ϵ 3.62). On quantitative hydrogenation, the material absorbed more than 3, but less than 4, equiv of hydrogen and seemed best considered as an impure octatetraene. Variable and small yields in the preparation and lack of the powerful, later-developed separation and structural analysis techniques prevented resolution of the structural problem at the time.

Scheme I



There are seven possible C_8H_{10} tetraenes with conjugated or cross-conjugated double bonds. Of these, the linear trans,trans[3] and cis,trans[4] have been synthesized and have ultraviolet maxima about 40 nm toward shorter wavelengths than those of **3**, and this fact clouds the earlier assignment of octatetrene formation.

In a related investigation,[5] pure samples of the exo and endo isomers of **1** and **2** were prepared and subjected individually to elimination conditions with tertiary amines. However, despite a slight yellow cast occasionally observed for the elimination products, the infrared, proton NMR, and carbon-13 NMR spectra indicated formation of only bicyclo[3.3.0]-2,6-octadiene and bicyclo[3.3.0]-2,7-octadiene. That none of the tetraene was found suggested that the polyene arose from an impurity in the original tosylate mixture and, in fact, the culprits were ultimately found to be the stereoisomeric 6-bicyclo[3.2.0]-2-heptenyl tosylates, **4**. These tosylates were derived from the corresponding alcohols, **6** (Scheme I), formed in varying amounts in the reduction of the cyanohydrin acetate, **5**, which was a key intermediate in the formation of **1** and **2** in the earlier synthesis of these substances.[2] Reduction of the acetate group of **5** in competition with reduction of the cyano group would lead to the isomers of **6** along with the desired aminomethyl alcohol. Subsequent contamination of the tosylate mixture of **1** and **2** with the stereoisomeric tosylates, **4**, could lead to ring-opened C_7 trienes. Thus, acetolysis of 6-bicyclo[3.2.0]-2-heptenyl mesylate yields better than 30% 1,3,5-cycloheptatriene, **7**[6] and pyrolysis of the methyl xanthates of **6** also yields **7**.[7] However, **7** is colorless with a λ_{max} of 261 nm. A possible

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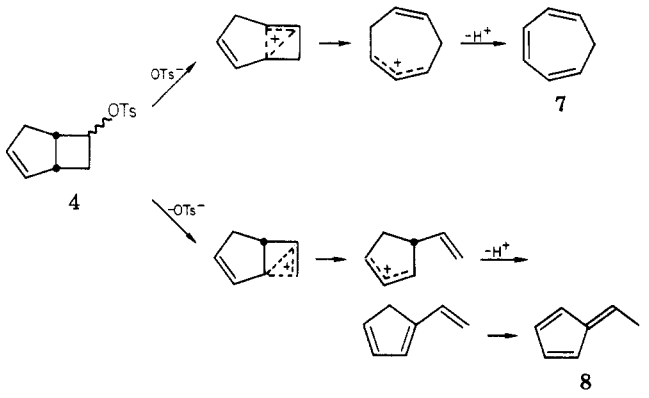
Scheme II



yellow C_7 triene is the fulvene 5-ethylidene-1,3-cyclopentadiene, 8, which can readily be envisioned as being formed from 4 by a mechanism similar to that postulated for formation of 7 (Scheme II).

Reduction of bicyclo[3.2.0]-2-hepten-6-one with lithium aluminum hydride at refluxing ether temperatures yielded a 70:30 mixture of *endo*- and *exo*-6, respectively. A corresponding mixture of the tosylates 4, heated with collidine, gave an intensely yellow product mixture which, before distillation, was found to be comprised of 70% 7, 15% 8, and 15% *exo*-4. The individual epimeric tosylates, *exo*-4 and *endo*-4, behave differently when heated with collidine. The *endo*-4 isomer undergoes clean elimination to yield only 7, while *exo*-4 did not react under the same conditions. However, when the ionizing power of the medium was increased by addition of 1.9 equivs of *p*-toluenesulfonic acid, then the exo isomer underwent elimination to produce a 1:4 mixture of 7 and 8, respectively. In the presence of *p*-toluenesulfonic acid epimerization can occur along with elimination[5] and *endo*-4, so formed from *exo*-4, could be the precursor of the 7 formed under these conditions. The substantially greater reactivity of *endo*-4 here compared to that of *exo*-4 is in full accord with the acetolysis rates.[8] Steric strain associated with having the bulky tosyl group in the endo position probably facilitates the ionization of *endo*-4.

The formation of both 7 and 8 accounts for the quantitative hydrogenation data when recalculated on the basis of a C_7 triene. Furthermore, the absorption maximum at 260 nm with a shoulder at 250 nm is reasonable, because 7, as mentioned, has a maximum at 261 nm (log ϵ 3.54)[9] and 5-ethylidene-1,3-cyclopentadiene has a maximum at 254 nm (log ϵ 4.16)[10] which tails off well into the visible region of the spectrum.

Experimental Section

The ^{1}H NMR spectra were taken on a Varian EM-390 spectrometer operating at 90 MHz.

The tosylate elimination reactions in collidine were carried out as previously described.[5]

Bicyclo[3.2.0]-2-hepten-6-one was prepared as previously described.[5]

***exo*- and *endo*-bicyclo[3.2.0]-2-hepten-6-ol, 6**, was prepared by lithium aluminum hydride reduction of bicyclo[3.2.0]-2-hepten-6-one in refluxing ether. From 14.4 g of bicyclo[3.2.0]-2-hepten-6-one was obtained 11.5 g of a 70:30 mixture of *endo*-6 and *exo*-6, respectively. The epimers were separated by preparative gas chromatography on a $^3/_8$ in × 16 ft Carbowax 20M column. *exo*-Bicyclo[3.2.0]-2-hepten-6-ol, *exo*-6: ^{1}H NMR (Me_2SO-d_6) δ 1.78–3.29 (m, 6 H), 3.50–3.82 (m, 1 H), 4.90 (d, 1 H, J = 6 Hz), 5.50–5.85 (m, 2 H). *endo*-Bicyclo[3.2.0]-2-hepten-6-ol, *endo*-6: ^{1}H NMR (Me_2SO-d_6) γ 1.30–3.28 (m, 6 H), 4.12–4.50 (m, 1 H), 4.68 (d, 1 H, J = 5 Hz), 5.73 (s, 2 H).

The *exo*- and *endo*-bicyclo[3.2.0]-2-hepten-6-yl tosylates, 4, were obtained individually or as a mixture from treatment of the corresponding alcohols for 1 h with 1.1 equiv of *p*-toluenesulfonyl chloride in the presence of excess pyridine at 0 °C. The reaction mixtures were stirred at room temperature for 15 h, diluted with ether, and then washed with 1 N hydrochloric acid, 5% sodium bicarbonate solution, and water. The ethereal layer was dried over potassium carbonate and the ether removed under reduced pressure. ***endo*-Bicyclo[3.2.0]-2-hepten-6-yl tosylate, *endo*-4**: ^{1}H NMR ($CDCl_3$) δ 1.62–3.30 (m, 6 H), 2.41 (s, 3 H), 4.90–5.18 (m, 1 H), 5.76 (br s, 2 H), 7.56 (d of d, 4 H). ***exo*-Bicyclo[3.2.0]-2-hepten-6-yl tosylate, *exo*-4**: ^{1}H NMR ($CDCl_3$) δ 1.95–3.28 (m, 6 H), 2.41 (s, 3 H), 4.37–4.60 (m, 1 H), 5.68 (br s, 2 H), 7.56 (d of d, 4 H).

Registry No. *exo*-4, 76036-47-0; *endo*-4, 76094-31-0; *exo*-6, 41524-25-8; *endo*-6, 13837-04-2; 7, 544-25-2; 8, 3839-50-7; bicyclo[3.2.0]-2-hepten-6-one, 13173-09-6.

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Synthetic Studies on Quassinoids: One-Step Transformation of α-Hydroxy Ketones into *O*-Methyl-Protected Diosphenols

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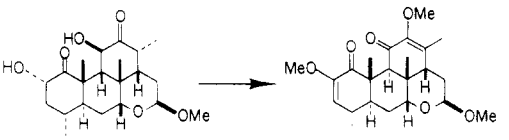
In conjunction with our efforts in the quassinoid area we required conditions for the direct one-step transformation of 1 into the fully protected bis(diosphenol) 2. Of



1 2

primary concern to us was the ability to simultaneously effect the inversion of configuration at C(9) (steroid numbering) so as to establish the trans,anti,trans arrangement of the ABC ring system common to the vast majority of quassinoids.

Examination of the literature reveals that numerous conditions have been developed over the years for the preparation of diosphenols from α-hydroxy ketones.[2-7] The majority of these procedures utilize either potassium carbonate or potassium hydroxide in aqueous methanol or ethanol in the presence of oxygen.[2] Many of these

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