

lecular sieves (4 Å), and DBU (Aldrich Chemical Co.) was used as received.

**Reaction of Dimethyl 1-Chloro-3-methylcyclopropane-1,2-dicarboxylate (1) with DBU.** The chloro diester **1**<sup>1</sup> (4.13 g, 0.02 mol) in 50 mL of ethyl acetate was treated with DBU (9.15 g, 0.06 mol) in 20 mL of ethyl acetate with stirring. Progress of the reaction was examined by TLC (silica gel, iodine developer). After 7 days, no **1** could be observed. The white solid (2.10 g) that had formed was removed by filtration and identified as essentially pure DBU hydrochloride by its infrared spectrum (comparison with a known sample). The filtrate was concentrated by removal of ethyl acetate, and the residue was redissolved in a small volume of ethyl acetate. This solution was chromatographed on silica gel and eluted with ethyl acetate. A crystalline product (2.75 g, 47% assumed as **2**) was obtained. An analytical sample recrystallized from ethyl acetate had the following: mp 150–151 °C dec; IR 3010 (sh), 2958 (sh), 2930, 2855, 1715, 1615, 1550, 1510, 1205 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.54 (d, 3 H), 1.73–1.88 (m, 5 H), 2.07–2.15 (m, 2 H), 2.27 (d, 1 H), 2.42–2.48 (m, 2 H), 2.84 (t, 2 H), 3.25–3.36 (m, 4 H), 3.73 (s, 3 H); mass spectrum, *m/e* 290 (M<sup>+</sup>), 259 (M<sup>+</sup> – OCH<sub>3</sub>), 231 (M<sup>+</sup> – CO<sub>2</sub>CH<sub>3</sub>), 217, 203, 189, 175, 161, 147.

Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>: C, 66.18; H, 7.64; N, 9.65. Found: C, 66.56; H, 7.92; N, 9.45.

Repetition of the experiment with furan as a solvent and equimolar quantities of the chloro diester **1** and DBU showed no materials by TLC not previously observed, i.e., no adduct of furan and a cyclopropene.

**Reaction of Dimethyl 1-Bromocyclopropane-1,2-dicarboxylate with DBU.** Reaction of the bromo diester<sup>2c</sup> with DBU in ethyl acetate was carried out and worked up as in the chloro diester case above to give 3.51 g (63% assumed as **3**) of crystalline solid. An analytical sample recrystallized from ethyl acetate had the following: mp 139–140 °C; IR 3025 (sh), 2945, 2855, 1720, 1640, 1540–1560 (br), 1510, 1440, 1385, 1320, 1270, 1210, 1155, 1130, 1060, 1030, 980, 900 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.45 (dd, 1 H), 1.6–1.9 (m, 4 H), 1.95 (dd, 1 H), 2.11 (m, 2 H), 2.28 (dd, 1 H), 2.44 (t, 2 H), 2.80–2.99 (m, 2 H), 3.2–3.5 (m, 4 H), 3.68 (s, 3 H); mass spectrum, *m/e* 276 (M<sup>+</sup>), 245 (M<sup>+</sup> – OCH<sub>3</sub>), 244 (M<sup>+</sup> – HOCH<sub>3</sub>), 217 (M<sup>+</sup> – CO<sub>2</sub>CH<sub>3</sub>), 203, 189, 161, 80, 66.

Anal. Calcd for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>: C, 65.20; H, 7.30; N, 10.14. Found: C, 65.23; H, 7.22; N, 10.04.

**Registry No. 1**, 76010-95-2; **2**, 76010-96-3; **3**, 76010-97-4; dimethyl 1-bromocyclopropane-1,2-dicarboxylate, 76010-98-5; DBU, 6674-22-2.

### Hydration Constants of Pyridinecarboxaldehyde N-Oxides

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The knowledge of hydration constants is important in studies of reactions of carbonyl compounds, particularly those involving acid–base and metal ion catalysis.<sup>1–6</sup> In systems such as the pyridinecarboxaldehydes, the activation of the carbonyl group can be influenced by direct interactions at the oxygen atom or by remote effects of substituents and Lewis acids acting on the aromatic nitrogen. Both kinds of influence may be involved in the hydration of these compounds by metalloenzymes.<sup>7,8</sup> In

order to evaluate the role of remote interactions in the hydration of pyridinecarboxaldehydes, we have determined the hydration constants of a series of N-substituted derivatives in aqueous solution.

Most studies of hydration equilibrium have been made by using nuclear magnetic resonance spectroscopy (NMR). The ultraviolet (UV) spectrophotometry has been considered less convenient for the determination of hydration constants because of the disadvantage that the extinction coefficients should be previously known.<sup>9</sup> To circumvent the problem, values obtained in nonaqueous solvents, or from extrapolation of kinetics plots to zero time, have been used for these parameters. In some cases, when the absorption spectra of the carbonyl and the hydrated species differ appreciably, a simple spectrophotometric method can be applied, without requiring the previous knowledge of extinction coefficients, or the use of any reagent. Such a method is based on the systematic variation of the equilibrium constants with the temperature,<sup>10</sup> and, therefore, it requires that  $\Delta H \neq 0$ . One can start by choosing two wavelengths (here referred to as 1 and 2) where the absorption of the carbonyl (C) and of the hydrated (H) species has little overlap. The total concentration (*C<sub>T</sub>*) of the compound should be kept constant during the experiment. Then, by measuring the absorbances of the hydrated form (*A<sub>H,1</sub>*) and of the carbonyl (*A<sub>C,2</sub>*) compound at several temperatures, it is possible to calculate the ratio of the extinction coefficients ( $\epsilon_{H,1}/\epsilon_{C,2}$ ) from a plot of *A<sub>H,1</sub>* vs. *A<sub>C,2</sub>* according to eq 1. The hy-

$$A_{H,1} = C_T \epsilon_{H,1} - \frac{\epsilon_{H,1}}{\epsilon_{C,2}} (A_{C,2}) \quad (1)$$

dration constant is given by eq 2.

$$K_{\text{hydr}} = \frac{A_{H,1}/A_{C,2}}{\epsilon_{H,1}/\epsilon_{C,2}} \quad (2)$$

The method can also be extended to the situation where the absorption band of the carbonyl compound has some overlap with that of the hydrated form. In this case a Gaussian or log-normal analysis of the spectra provides a better estimate of the absorbance of the pure species. The alternative is to use eq 3 to obtain the ratio *R* ( $R = (\epsilon_{H,1}$

$$A_{H,1} = C_T \epsilon_{H,1} - \frac{(\epsilon_{H,1} - \epsilon_{C,1})}{\epsilon_{C,2}} (A_{C,2}) \quad (3)$$

–  $\epsilon_{C,2})/\epsilon_{C,2}$ ). Now, the expression of the hydration constant can be shown by eq 4.

$$K_{\text{hydr}} = \frac{(A_{H,1}/A_{C,2})\epsilon_{C,2} - \epsilon_{C,1}}{R\epsilon_{C,2} + \epsilon_{C,1}} = \frac{(A_{H,1}/A_{C,2})\epsilon_{C,2} - \epsilon_{C,1}}{\epsilon_{H,1}} \quad (4)$$

If the  $\epsilon_{C,1}$  term in eq 4 were neglected, then the calculated value of *K<sub>hydr</sub>* would be artificially increased. Therefore, by working at several wavelengths, one can test for the several experimental values of *R* which minimize *K<sub>hydr</sub>*. Such a procedure is essentially the same as varying the wavelength in order to locate the region of minimum overlap. Under these circumstances, if  $\epsilon_{C,1}$  is negligible, eq 4 becomes equivalent to eq 1.

We have tested the temperature variation method for 4-pyridinecarboxaldehyde, since in this case the hydration constants have been previously determined by Pocker et al.<sup>11</sup> The spectral changes with temperature, as shown

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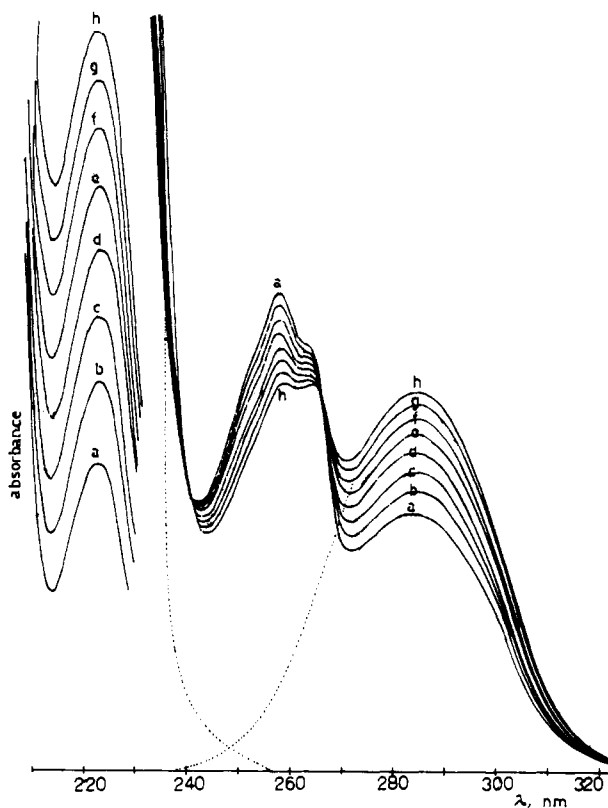
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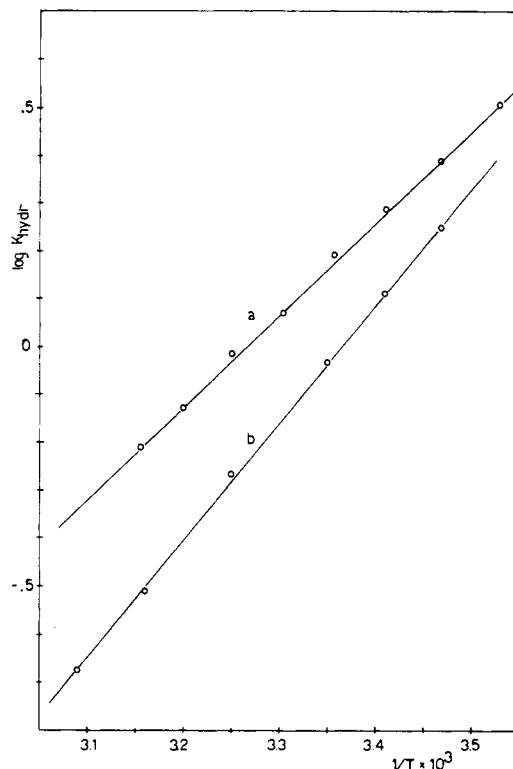


**Figure 1.** Variation with temperature of the UV spectrum of 4-pyridinecarboxaldehyde. Curves a-h refer to 9.4, 15.2, 20.1, 25.0, 29.7, 34.5, 39.2, and 44.0 °C; pH = 6.70, 0.50 M KCl.

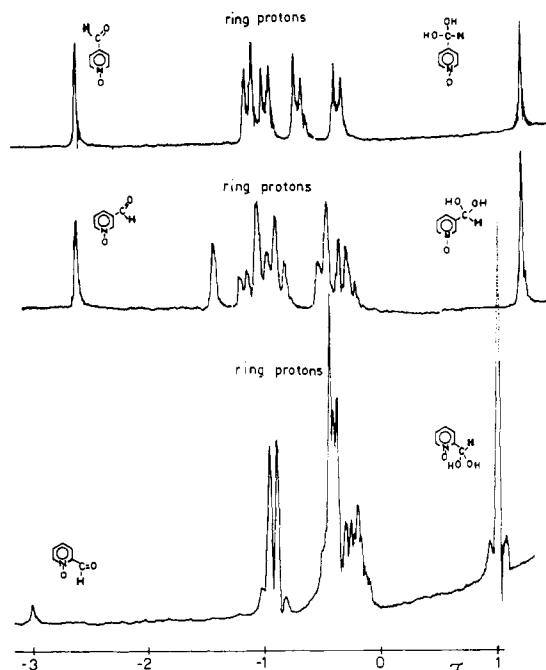
in Figure 1, are typical of a reversible system. As the absorption of the carbonyl compound increases at 284 and 222 nm, there is a concomitant decrease in the absorption of the hydrated form at 257 nm. The presence of an isosbestic point at 266 nm indicates that the extinction coefficients are rather independent of the temperature and that no decomposition reaction occurs.

Pocker et al.<sup>11</sup> have pointed out that the 4-pyridinecarboxaldehyde compound is not suitable for spectrophotometric work because its C and H forms absorb in a common spectral region. A Gaussian analysis reveals that interference of the C form should be minimal at approximately 250 nm. The ratio of the extinction coefficients for the C form at 250 and 290 nm can be estimated as 0.12. With this small correction, the plots of the absorbances of the hydrated and carbonyl species at 250 and 290 nm, respectively, yield a ratio  $\epsilon_{H,250}/\epsilon_{C,290}$  equal to  $0.85 \pm 0.04$ . By use of this value in eq 2, the calculated hydration constants show a remarkable agreement with those reported in the literature.<sup>11</sup>

In the case of the *N*-oxide derivative of the 4-pyridinecarboxaldehyde, the spectra are more favorable, showing absorption bands at 260 (hydrate) and 295 nm (carbonyl) well separated by an isosbestic point at 272 nm. For this reason a direct calculation of the hydration constants was attempted by using a simple minimization criterion. From the absorbance plot at 256 and 302 nm, the ratio of the extinction coefficients was calculated as 0.96, yielding  $K_{hydr}$  equal to 0.99 at 25 °C. This value remains practically constant as one increases the interval between the two wavelengths. The temperature dependence for the hydration constants is shown in Figure 2. The consistency of the spectrophotometric method was also checked in this case by a parallel determination of the equilibrium constant with the NMR method, based on the peaks of the hydrate and carbonyl forms, as shown in Figure 3.



**Figure 2.** Temperature dependence of the hydration constants of (a) 4-pyridinecarboxaldehyde and (b) 4-pyridinecarboxaldehyde *N*-oxide.



**Figure 3.** NMR spectra of 4-, 3-, and 2-pyridinecarboxaldehyde *N*-oxides in water at 25 °C, pH 6.7, 0.50 M KCl.

Figure 3 shows that  $K_{hydr}$  decreases as the distance separating the carboxaldehyde and *N*-oxide moieties increases. The values observed are  $16 \pm 4$ ,  $1.8 \pm 0.2$ , and  $0.95 \pm 0.05$  for the respective 2-, 3-, and 4-pyridinecarboxaldehyde *N*-oxides. The results obtained in this work are presented in Table I, along with some related systems from the literature. There is a dramatic increase in the hydration constant caused by the transformation of the 4-pyridinecarboxaldehyde into the 4-formyl-*N*-methylpyridinium ion. A similar behavior has also been observed for protonation<sup>11</sup> and *N*-coordination with hard

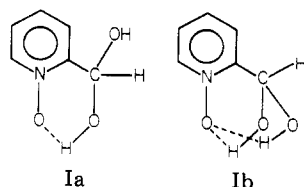
Table I. Hydration Constants of Some Pyridinecarboxaldehydes

compd	$K_{\text{hydr}}$	$\Delta H$ , kcal/mol	$\Delta S$ , cal/mol deg	observations
4-pyCHO	1.28			1.00 M KCl, 25 °C, UV <sup>13</sup>
	1.18	-4.2	-13.9	25 °C, D <sub>2</sub> O (NMR, UV) <sup>11</sup>
	1.21	-3.8	-12.3	this work, 25 °C, 0.5 M KCl, UV
CH <sub>3</sub> -4-pyCHO <sup>+</sup>	>30			this work, 30 °C, 0.5 M KCl, UV
Ru(NH <sub>3</sub> ) <sub>5</sub> (4-pyCHO) <sup>2+</sup>	0.20			37 °C, NMR <sup>12</sup>
Fe(CN) <sub>5</sub> (4-pyCHO) <sup>3-</sup>	0.61	-3.5	-12.7	25 °C, 0.10 M LiClO <sub>4</sub> , vis <sup>10</sup>
O-4-pyCHO	0.95			this work, 25 °C, 0.5 M KCl, NMR
	1.12	-4.9	-16.2	this work, 25 °C, 0.0 M KCl, UV
	0.98	-5.1	-17.0	this work, 25 °C, 0.5 M KCl, UV
	0.95	-4.7	-15.9	this work, 25 °C, 1.0 M KCl, UV
3-pyCHO	0.095			this work, 30 °C, D <sub>2</sub> O, NMR
O-3-pyCHO	1.80			this work, 25 °C, 0.5 M KCl, NMR
2-pyCHO	0.55	-3.8	-13.8	25 °C, D <sub>2</sub> O (NMR, UV) <sup>11</sup>
O-2-pyCHO	16			this work, 25 °C, 0.5 M KCl, NMR

metal ions.<sup>11,12</sup> This kind of evidence indicates that the aromatic nitrogen can have a strong participation in the activation of the carbonyl group, especially in metallo-enzyme catalysis. There are cases, however, of metal ions such as ruthenium(II) and low-spin iron(II), which can decrease the hydration constants by stabilizing the carbonyl species through backbonding interactions with the pyridine group.<sup>10,12</sup>

The way in which the *N*-oxide bond can influence the hydration of the pyridinecarboxaldehyde is rather interesting. The high electronegativity of the oxygen substituent is expected to enhance the electrophilic character of the carbonyl group, increasing the hydration constants. This kind of influence is transmitted mainly through  $\sigma$  bonds, from the nitrogen atom to the 2-, 3-, and 4-CHO substituents. At the same time, the oxygen atom can also act as  $\pi$ -donor group, using the available electron pairs to interact with the acceptor orbitals of the pyridine molecule. Now, the influence becomes more important at 2- and 4-positions rather than at 3-, since the lowest unoccupied orbital involved in  $\pi$ -backbonding has a nodal plane at this position. Therefore, the net effect will depend on the competition between the two opposing interactions. Along these lines, one can understand why the *N*-oxide bond produces a substantial increase of  $K_{\text{hydr}}$  for the 3-pyridinecarboxaldehyde *N*-oxide but leaves the analogous constant for the 4-pyridine derivative practically unchanged.

The behavior of the 2-pyridinecarboxaldehyde *N*-oxide cannot be explained in terms of donor-acceptor interactions, otherwise it would be comparable to that of the 4-pyridine derivative. The *N*-oxide bond has a pronounced effect on the hydration of the 2-pyridinecarboxaldehyde derivative, which seems to be related with the stabilization of the hydrated species through intramolecular hydrogen bonding, forming structures like Ia and Ib. This kind of



behavior has not been observed<sup>11</sup> for the 2-pyridinecarboxaldehyde compound. In that case, the hydration

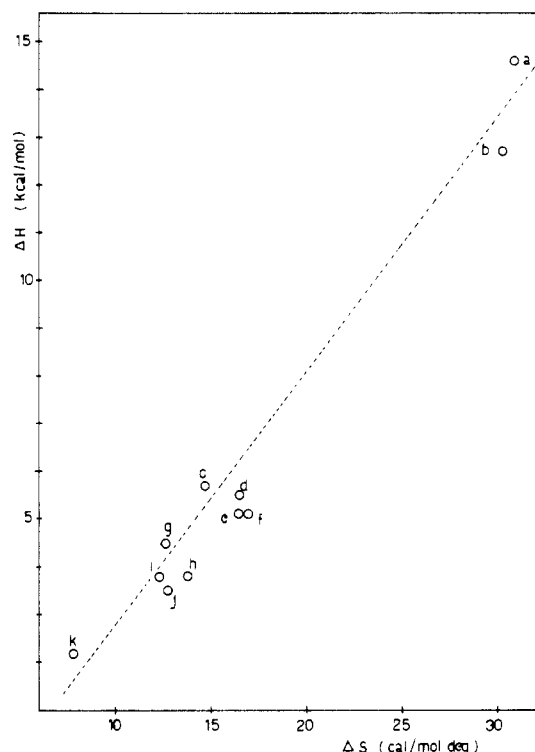


Figure 4. Enthalpy/entropy plot for the hydration of carbonyl compounds: (a) formaldehyde,<sup>22</sup> (b) chloral,<sup>23</sup> (c) *sym*-dichloroacetone,<sup>23</sup> (d) *asym*-dichloroacetone,<sup>23</sup> (e) acetaldehyde,<sup>24</sup> (f) 4-pyridinecarboxaldehyde *N*-oxide, (g) diacetyl,<sup>23</sup> (h) 2-pyridinecarboxaldehyde,<sup>11</sup> (i) 4-pyridinecarboxaldehyde, (j) pentacyanoferrate(II)(4-pyridinecarboxaldehyde),<sup>10</sup> and (k) monochloroacetone.<sup>23</sup>

constant is actually smaller than that in the 4-pyridine analogue. It seems that the main role of the *N*-O bond is to provide a close contact for hydrogen bonding between the interacting groups, which is not feasible in the case of the 2-pyridinecarboxaldehyde molecule.

The thermodynamic data available for the hydration of the carbonyl compounds show that the enthalpies and entropies are always negative. A compensation phenomenon<sup>14-16</sup> involving  $\Delta H$  and  $\Delta S$  seems to be implicated, as shown in Figure 4, with a correlation temperature of  $533 \pm 70$  K. It has been shown<sup>15</sup> that when the experimental

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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<sup>17,18</sup> 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.<sup>19,20</sup> 4-Formyl-1-methylpyridinium iodide was prepared as described in the literature<sup>21</sup> from the reaction of the 4-pyridinecarboxaldehyde and methyl iodide. Solutions of these reagents were prepared just prior to use. Reagent-grade KCl, Na<sub>2</sub>HPO<sub>4</sub>·H<sub>2</sub>O, and NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O 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.

**Acknowledgment.** We are grateful to Professor J. A. Vanin for help in obtaining the NMR spectra and to the Fundação de Amparo à Pesquisa do Estado de São Paulo for support.

**Registry No.** 4-Formyl-1-methylpyridinium iodide, 13441-53-7; 4-pyCHO, 872-85-5; Ru(NH<sub>3</sub>)<sub>6</sub>(4-pyCHO)<sup>2+</sup>, 19471-56-8; Fe(CN)<sub>6</sub>(4-pyCHO)<sup>3-</sup>, 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<sup>1</sup>

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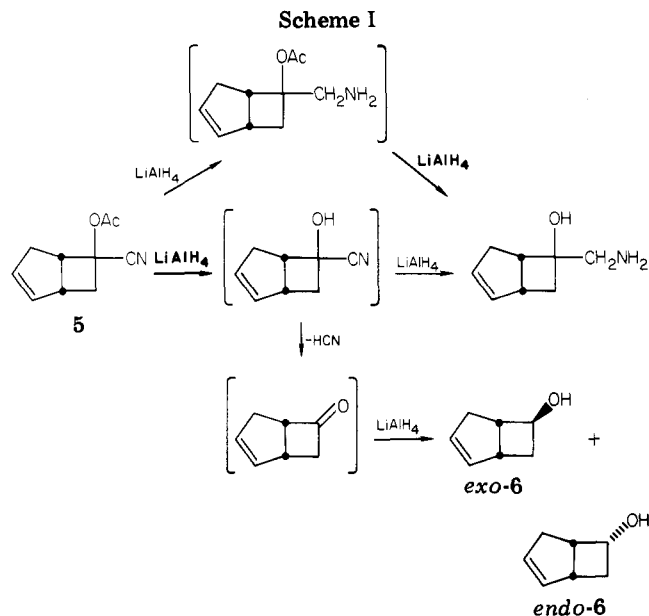
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As part of an early attempted synthesis of pentalene, it was reported in 1951<sup>2</sup> that the reaction of a mixture of stereoisomeric 6- and 7-bicyclo[3.3.0]-2-octenyl tosylates (1 and 2) with collidine (2,3,5-trimethylpyridine) and other tertiary amine bases appeared to form variable amounts of a yellow polyene, 3. This material had an ultraviolet absorption maximum at 260 nm (log  $\epsilon$  3.65) and a shoulder

(1) Contribution no. 6260. Supported by the National Science Foundation.

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at 250 nm (log  $\epsilon$  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.

There are seven possible C<sub>8</sub>H<sub>10</sub> tetraenes with conjugated or cross-conjugated double bonds. Of these, the linear *trans,trans*<sup>3</sup> and *cis,trans*<sup>4</sup> 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 octatetraene formation.

In a related investigation,<sup>5</sup> 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.<sup>2</sup> 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<sub>7</sub> trienes. Thus, acetolysis of 6-bicyclo[3.2.0]-2-heptenyl mesylate yields better than 30% 1,3,5-cycloheptatriene,<sup>7b</sup> and pyrolysis of the methyl xanthates of 6 also yields 7.<sup>7</sup> However, 7 is colorless with a  $\lambda_{\max}$  of 261 nm. A possible

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