

for 2 hr. The product was filtered, digested in dilute NaOH, filtered, washed, and dried, yielding 8.5 g (96%) of purple product, mp 202–203°. Crystallization from acetic acid, butyl acetate, or methylcyclohexane raised the melting point to 207–207.5°.

*Anal.* Calcd for  $C_{21}H_{12}OS_2$ : C, 73.3; H, 3.5; S, 18.6. Found: C, 73.4; H, 3.3; S, 18.4.

Pseudobase **22**, prepared similarly from 4-chloro-1-naphthol, crystallized from nitromethane as purple needles, mp 211.5–212°.

*Anal.* Calcd for  $C_{17}H_8OS_2Cl$ : C, 62.2; H, 2.7; Cl, 10.8; S, 19.5. Found: C, 62.1; H, 2.7; Cl, 10.7; S, 19.2.

Pseudobase **23**, prepared from 2-naphthol, contained a chlorinated by-product that was eliminated by chromatography of a methanol or nitromethane solution over alumina. The product was readily eluted, a reddish impurity being retained, and crystallized from methanol as purple needles, mp 162.5–163°.

*Anal.* Calcd for  $C_{17}H_{10}OS_2$ : C, 69.4; H, 3.4; S, 21.8. Found: C, 69.8; H, 3.2; S, 21.2.

**2-(Benzo-1,2-dithiol-3-ylidene)-4-methylcyclohexanone (24)**.—A mixture of 22.0 g (0.099 mol) of **18** and 15.0 ml (13.7 g, 0.124 mol) of 4-methylcyclohexanone in 75 ml of toluene was stirred at reflux for 50 min, filtered hot, cooled, and chilled in Dry Ice-acetone, yielding 9.7 g (38%) of red-brown solid, mp 122–126°. Crystallization from 55 ml of acetic acid gave 7.5 g of red solid, mp 130–131.5°.

*Anal.* Calcd for  $C_{14}H_{14}OS_2$ : C, 64.1; H, 5.3; S, 24.4. Found: C, 64.1; H, 5.3; S, 24.6.

4-*tert*-Butylcyclohexanone gave yellow-red **25**, mp 164.5–165.5° (ethanol or methylcyclohexane).

*Anal.* Calcd for  $C_{17}H_{20}OS_2$ : C, 67.1; H, 6.6; S, 21.0. Found: C, 66.9; H, 6.5; S, 20.8.

Cyclohexanone gave orange-red **26**, mp 114.5–115° (hexane).

*Anal.* Calcd for  $C_{13}H_{12}OS_2$ : C, 62.7; H, 4.8; S, 25.8. Found: C, 62.7; H, 4.7; S, 25.7.

Cyclopentanone gave brown **27**, mp 149–151° (methylcyclohexane).

*Anal.* Calcd for  $C_{12}H_{10}OS_2$ : C, 61.5; H, 4.3; S, 27.3. Found: C, 61.2; H, 4.1; S, 27.2.

**Thiothiophene 28**.—Phosphorus pentasulfide (4.50 g, 0.020 mol) was added to a refluxing solution of 4.18 g (0.016 mol) of **24** in 120 ml of toluene. The mixture was refluxed 1.5 hr, cooled, and filtered. The resulting olive-green solid was washed to a clear run-off with petroleum ether (bp 30–60°), dried, and stirred overnight in dilute alkali. Filtering, washing thoroughly with water, and drying gave 4.0 g of purple solid, mp 128–131°. Crystallization from methylcyclohexane or ethanol gave purple needles, mp 149.5–150°.

*Anal.* Calcd for  $C_{14}H_{14}S_3$ : C, 60.5; H, 5.0; S, 34.5. Found: C, 60.5; H, 5.1; S, 34.7.

**Naphtho[2,1-*b*]thiophene-1,2-dione (30)**.—A mixture of 30.0 g (0.19 mol) of 2-naphthalenethiol and 45 ml (67 g, 0.53 mol) of oxalyl chloride was heated under reflux for 3 hr in an oil bath at 110–120°. The condenser was then set for distillation and heating continued for 1 hr at 165–175°. The product was cooled, ground, and subjected to prolonged or repeated digestion at room temperature with 1 *N* NaOH, which left undissolved 8.4 g (24%) of crude 2-naphthyl dithioloxalate (**32**), mp 170–200°. Crystallization from 280 ml of trichloroethylene gave 5.2 g (15%), mp 225–227°. It could also be crystallized from toluene or butyl acetate.

*Anal.* Calcd for  $C_{22}H_{14}O_2S_2$ : C, 70.6; H, 3.7; S, 17.1. Found: C, 70.2; H, 3.8; S, 17.2.

Acidification of the orange NaOH solution gave 28.0 g (70%) of red-orange **30**, mp 156–158°. A specimen crystallized from butyl acetate or methylcyclohexane melted at 158–159° (lit.<sup>10</sup> mp 153°).

*Anal.* Calcd for  $C_{12}H_8O_2S$ : C, 67.3; H, 2.8; S, 14.9. Found: C, 67.1; H, 2.9; S, 14.7.

**2-Benzylthio-1-naphthaleneglyoxylic Acid 33**.—To a boiling solution of 2.14 g (0.0100 mol) of **30** in 20 ml of 5 *N* NaOH, 20 ml of water, and 20 ml of ethanol, was added 1.50 ml (1.65 g, 0.0130 mol) of benzyl chloride. The solution turned from orange to pale yellow in 1–2 min and was then cooled and acidified. An oil formed and slowly changed to 3.2 g (100%) of yellow crystals, mp 110–113°. Crystallization from toluene or methylcyclohexane raised the melting point to 115–118°.

*Anal.* Calcd for  $C_{19}H_{14}O_3S$ : C, 70.8; H, 4.3; S, 9.9. Found: C, 70.5; H, 4.2; S, 9.7.

Refluxing for 1 hr with thionyl chloride in benzene, both of which were then evaporated, gave **30**.

**Registry No.**—**3**, 35051-21-9; **4**, 35051-22-0; **5**, 35051-23-1; **6**, 35051-24-2; **7**, 35051-25-3; **8**, 35051-26-4; **9**, 35051-27-5; **10**, 35051-28-6; **11a**, 35051-29-7; **11b**, 35051-30-0; **11c**, 35051-31-1; **12**, 35051-32-2; **14**, 35051-33-3; **15**, 35096-47-0; **16**, 32003-89-7; **17**, 34180-78-4; **19**, 35051-36-6; **20**, 32741-87-0; **21**, 34294-68-3; **22**, 34192-52-4; **23**, 34192-54-6; **24**, 32003-88-6; **25**, 32041-16-0; **26**, 32003-84-2; **27**, 32003-83-1; **28**, 35051-45-7; **30**, 35051-46-8; **32**, 35051-47-9; **33**, 35051-48-0.

**Acknowledgment.**—The author is indebted to J. J. Kobliska and his staff for microanalyses.

## Kinetics of the Chromic Acid Oxidation of Deoxybenzoin<sup>1</sup>

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Received March 23, 1972

The kinetics of the chromic acid oxidation of deoxybenzoin has been examined in 91% acetic acid. The rate law is given by  $v = k_1k_2[\text{ketone}][\text{Cr}^{\text{VI}}][\text{H}^+]^2/(k_{-1}[\text{H}^+] + k_2[\text{Cr}^{\text{VI}}])$  where  $k_1$  was found to be equal to the rate of enolization. Benzoin was shown to be the intermediate in the reaction, and the source of the products, benzil, benzaldehyde, and benzoic acid. Substituent effects on the oxidation reaction and on enolization were found to be the same. When the concentration of chromium(VI) was maintained at a low level during the course of the reaction, bidesyl became a significant product. This suggests the formation of the desyl radical *via* a reaction involving an intermediate oxidation state of chromium.

The oxidation of ketones frequently provides a useful synthetic route to  $\alpha$ -hydroxy ketones,  $\alpha$  diketones, and carboxylic acids. As part of a continuing investigation of the mechanisms of chromic acid oxidations, we have studied the oxidation of deoxybenzoin. This is a convenient substrate in that the reaction site is localized

by the flanking phenyl rings thus minimizing secondary reactions. Further, the compound provides an opportunity to examine substituent effects.

The chromic acid oxidation of ketones has received previous study. Umeda and Tarama<sup>3</sup> as well as Best, Littler, and Waters<sup>4</sup> have investigated the kinetics of the oxidation of cyclohexanone and found the rate to

(1) This investigation was supported by a grant from the National Science Foundation.

(2) Taken in part from the Ph.D. Thesis of O. Aniline, 1968.

(3) K. Umeda and K. Tarama, *Nippon Kagaku Zasshi*, **83**, 1216 (1962).

(4) P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, 822 (1962).

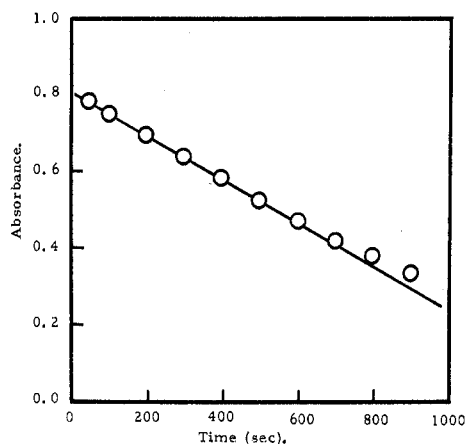


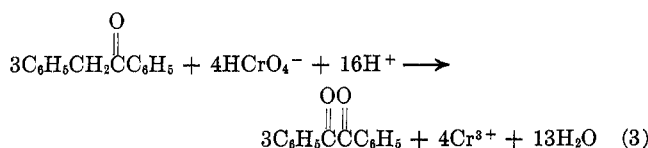
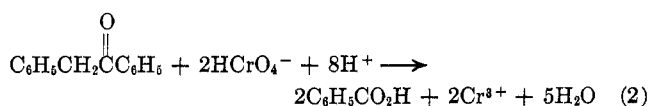
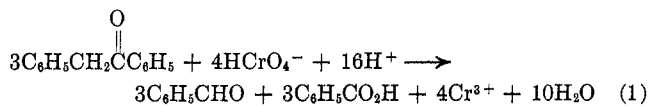
Figure 1.—Zero-order plot for the chromic acid oxidation of deoxybenzoin.

have a first-order dependence on the concentrations of ketone, chromium(VI), and hydrogen ion. The latter workers investigated kinetic isotope effects in the system and interpreted these results in terms of an enol intermediate.

Strong evidence for an enol intermediate was provided by Roček and Riehl<sup>5</sup> who found that the oxidation of  $\alpha$ -chlorocyclohexanone became independent of the concentration of chromium(VI) when the concentration of the oxidant was high. The limiting rate was close to the rate of enolization as measured by the rate of bromination.

### Results

The stoichiometry of the chromic acid oxidation of deoxybenzoin might reasonably be expected to correspond to any of eq 1–3. When deoxybenzoin was al-



lowed to react with chromium(VI) in 91% acetic acid in the presence of 1 *M* perchloric acid, and the products were determined gas chromatographically, it was found that 11% of the deoxybenzoin was consumed *via* reaction 1, 41% *via* reaction 2, and 48% *via* reaction 3. It is not unlikely that, in the actual reaction, process 2 arises *via* process 1 followed by oxidation of benzaldehyde. If that were the case, the oxidation of deoxybenzoin would proceed 52% *via* reaction 1 and 48% *via* reaction 3.

The products also were analyzed *via* isotope dilution using deoxybenzoin-*carbonyl*-<sup>14</sup>C as the reactant. In this case, 56% of the reaction proceeded *via* reaction 1

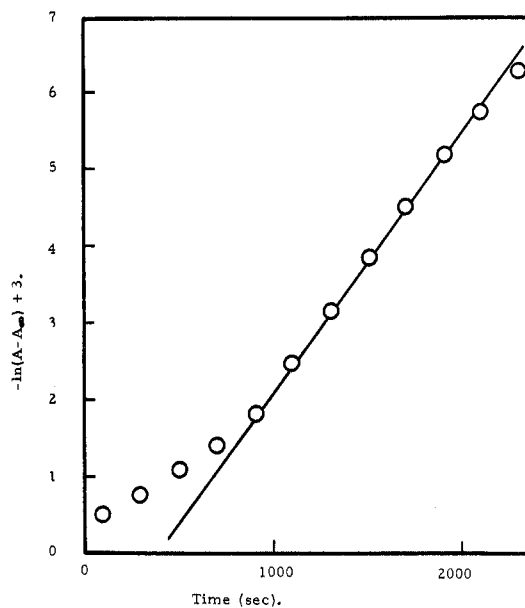
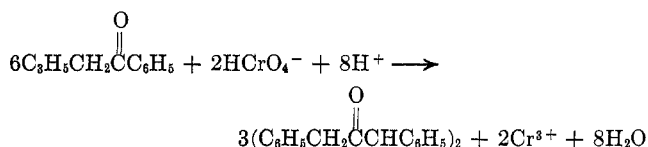


Figure 2.—First-order plot for the chromic acid oxidation of deoxybenzoin.

and 44% *via* reaction 3. The results *via* the two methods are in good agreement.

Another possible reaction is the one following.



Under the normal experimental conditions, no significant quantity of bidesyl is formed. However, when the reaction was carried out by the slow addition of chromium(VI) to the reaction mixture, 6% of the deoxybenzoin was converted to dibenzyl, as determined *via* isotope distillation. When a fivefold excess of manganous ion was added to the reaction mixture, the formation of benzil was decreased. However, the formation of bidesyl was not affected.

The kinetics of the reaction were studied spectrophotometrically at 340–420  $\mu\text{m}$  using degassed solutions to avoid interference by oxygen. An excess of deoxybenzoin was employed. Under these conditions, the disappearance of chromium(VI) appeared to be zero order through the first 50% of the reaction (Figure 1). The first-order plot had initial curvature followed by a relatively linear portion (Figure 2).

The slopes of the zero-order plots were dependent on the initial chromium(VI) concentration, and, thus, the apparent zero-order behavior results from a kinetic complication. This was identified as follows. To convert the apparent zero-order rate constants to units comparable with the first-order rate constants derived from the latter part of the reaction, they were divided by the chromium(VI) concentration giving the data summarized in Table I. The ratio of the first-order constants ( $k_i$ ) to this latter quantity (hereafter referred to as  $k_1$ ) was essentially constant, with a value of  $2.2 \pm 0.1$ .

The behavior observed in this case is characteristic of processes in which an intermediate builds up in concentration during the earlier part of the reaction and

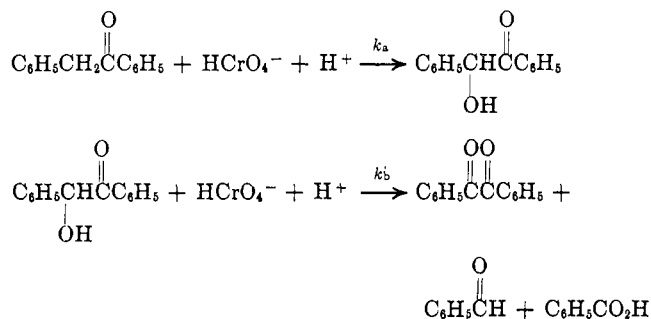
(5) J. Roček and A. Riehl, *J. Org. Chem.*, **32**, 3569 (1967); *J. Amer. Chem. Soc.*, **89**, 6691 (1967).

TABLE I  
EFFECT OF DEOXYBENZONIN CONCENTRATION ON THE RATE OF  
CHROMIC ACID OXIDATION<sup>a</sup>

Deoxybenzoin, $M$	$k_i \times 10^3, \text{sec}^{-1}$	$k_f \times 10^3, \text{sec}^{-1}$	$k_f/k_i$	$k_i/([\text{DSB}] \times 10^3), \text{l. mol}^{-1} \text{sec}^{-1}$
0.200	1.190	2.75	2.3	6.0
0.160	0.921	2.05	2.2	5.8
0.120	0.702	1.68	2.4	5.9
0.100	0.567	1.24	2.2	5.7
0.080	0.474	1.02	2.2	5.9
0.060	0.338	0.703	2.1	5.6
0.040	0.211	0.481	2.1	5.3
0.020	0.110			5.5
			$2.2 \pm 0.1$	$5.7 \pm 0.2$

<sup>a</sup>  $[\text{Cr}^{\text{VI}}] = 2.28 \times 10^{-3} M$ ;  $[\text{HClO}_4] = 0.412 M$ ;  $T = 30.0^\circ$ ;  $380 \text{ m}\mu$ . <sup>b</sup>  $k_i$  is the initial first-order rate constant obtained by dividing the apparent zero-order rate constant by  $[\text{Cr}^{\text{VI}}]$ . <sup>c</sup>  $k_f$  is the first-order rate constant observed in the later stages of the reaction.

then reaches a steady state. When the steady state has been reached, the reaction will show normal first-order behavior with a rate constant twice the initial rate constant. A reasonable possibility for such an intermediate is benzoin, which could further be oxidized to give the set of observed products. The kinetic scheme would be



If  $k_b \gg k_a$ , the observed rate constant after the steady state has been reached would be  $2k_a$ , whereas the initial rate constant would be  $k_a$ .

This explanation was tested by determining the rate of oxidation of benzoin ( $k = 1.78 \text{ l. mol}^{-1} \text{sec}^{-1}$ ,  $0.3 M \text{ HClO}_4$ ,  $0.0115 M$  benzoin, and  $2.44 \times 10^{-3} M \text{ Cr}^{\text{VI}}$ ) and calculating the change in absorbance with time for the oxidation of deoxybenzoin using the above kinetic scheme. A comparison of calculated and observed absorbance values is given in Figure 3 and it can be seen that good agreement is obtained.

When benzoin was oxidized in the presence of a two-fold excess of chromic acid and the products analyzed by vpc, it was found that 48% of the reactant was converted to benzil while the rest led to cleavage products. The agreement with the deoxybenzoin product study again indicates that benzoin is an intermediate, and indicates that  $k_i$  is the appropriate rate constant for use in the following discussion.

The initial first-order rate constants for the oxidation of deoxybenzoin divided by the ketone concentration gave a constant second-order rate coefficient (Table I) showing the reaction to have a first-order dependence on the ketone concentration. The effect of acid concentration on the rate of oxidation also was examined (Table II) and a plot of the logarithms of the rate constants against  $H_0$  gave a linear relationship with a slope of 1.20. This is quite similar to that found for the

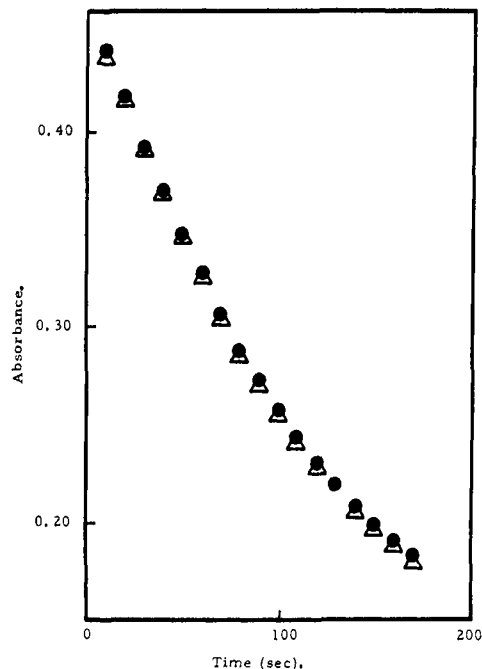


Figure 3.—Calculated ( $\Delta$ ) and observed ( $\bullet$ ) absorbance values for the chromic acid oxidation of deoxybenzoin.

TABLE II  
EFFECT OF ACID CONCENTRATION ON THE RATE OF  
OXIDATION OF DEOXYBENZONIN<sup>a</sup>

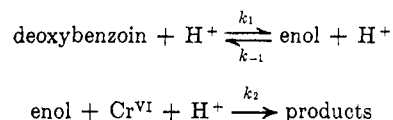
$[\text{HClO}_4], M$	$k_i \times 10^3, \text{sec}^{-1}$	$H_0$
0.050	0.14	+0.055
0.100	0.37	-0.270
0.150	0.67	-0.460
0.200	0.96	-0.600
0.250	1.34	-0.730
0.300	1.79	-0.830

<sup>a</sup>  $[\text{Deoxybenzoin}] = 0.200 M$ ;  $[\text{Cr}^{\text{VI}}] = 2.51 \times 10^{-3} M$ ;  $T = 30.0^\circ$ ;  $390 \text{ m}\mu$ .

oxidation of benzaldehyde (1.07)<sup>6</sup> and of diphenylmethane (1.25)<sup>7</sup> and is equivalent to a first-order dependence on the acid concentration.

The effect of chromium(VI) concentration on the rate of reaction also was studied. As the concentration was increased in the range  $0.00171$ – $0.0193 M$ , the apparent zero-order portion of the reaction increased in duration and the initial slopes of the first-order rate plots decreased by an amount greater than that which could be accounted for by the acid chromate-dichromate equilibrium.<sup>8</sup>

The decrease in rate coefficient might result from a process such as



This would be in accord with the observation of Roček and Riehl in their study of the chromic acid oxidation

(6) K. B. Wiberg and T. Mill, *J. Amer. Chem. Soc.*, **80**, 3022 (1958).

(7) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).

(8) The oxidation of alcohols and of related compounds have a kinetic dependence on the acid chromate ion rather than total chromic acid (cf. K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, p 159 ff). In view of the later conclusions concerning the nature of the oxidation step, it seemed appropriate to assume that only  $\text{HCrO}_4^-$  is involved in the rate expression in the present case also.

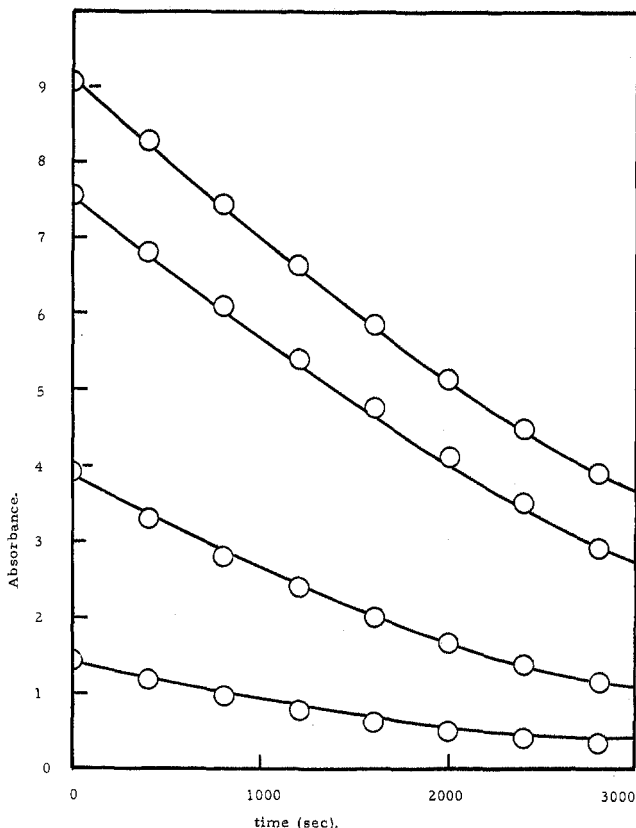


Figure 4.—Absorbance vs. time curves for four representative chromic acid concentrations (0.0193 *M*, 0.0171 *M*, 0.0113 *M*, and 0.0060 *M* from top to bottom). The circles are experimental points and the lines are values calculated as described in the text. [Deoxybenzoin] = 0.161 *M*; [HClO<sub>4</sub>] = 0.309 *M*; *T* = 30.0°; 420 m $\mu$ . A 1-cm cell was used for the lower concentrations, and a 0.2-cm cell was used for the higher concentrations.

of several aliphatic ketones.<sup>5</sup> The rate law for such a process would be

$$-d[\text{Cr}^{\text{VI}}]/dt = k_1 k_2 [\text{ketone}] [\text{Cr}^{\text{VI}}] [\text{H}^+]^2 / (k_{-1} [\text{H}^+] + k_2 [\text{Cr}^{\text{VI}}])$$

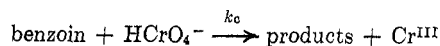
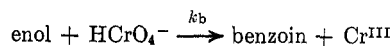
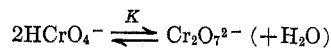
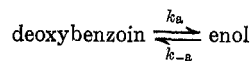
Thus, when  $k_2 [\text{Cr}^{\text{VI}}] \gg k_{-1} [\text{H}^+]$ , the rate constant should no longer depend on the concentration of oxidant. Because of the complexity of the system in which benzoin is an intermediate which only slowly reaches a steady state, and in which the absorbancy index of chromium(VI) is a function of the chromium(VI) concentration, the above rate law was tested by numerical integration of the rate expressions in Scheme I which apply to the case of a constant hydrogen ion concentration (*i.e.*, the dependence on acid concentration is absorbed into the rate constants).<sup>9</sup>

The rate of enolization of deoxybenzoin was determined by measuring the acid-catalyzed rate of bromination in 91% acetic acid. Using a 0.309 *M* perchloric acid, the rate constant was  $1.72 \times 10^{-5} \text{ sec}^{-1}$  (the zero-order rate constant divided by the ketone concentration). This value was used as the initial approximation of  $k_a$ .<sup>10</sup> As long as  $k_{-a} \gg k_a$ , only the

(9) The rate expressions are simplified in that the oxidation by chromium(V) or chromium(IV) is ignored. It is known that these species will come to their steady-state concentrations rapidly under the reaction conditions, and their effect will then appear largely in the stoichiometry rather than in the kinetics of the process. The four-order Runge-Kutta procedure was used in the numerical integration.

(10) Depending on the details of the stoichiometry involving the chromium species of intermediate valence, the apparent rate of enolization for the oxidation process could range from 0.67 to 2.00 times the true rate of enolization.<sup>5</sup>

## SCHEME I



$$d[\text{ketone}]/dt = -k_a[\text{ketone}] + k_{-a}[\text{enol}]$$

$$d[\text{enol}]/dt = k_a[\text{ketone}] + k_{-a}[\text{enol}] - k_b[\text{enol}][\text{HCrO}_4^-]$$

$$d[\text{benzoin}]/dt = k_b[\text{enol}][\text{HCrO}_4^-] - k_c[\text{benzoin}][\text{HCrO}_4^-]$$

$$d[\text{Cr}^{\text{VI}}]/dt = k_b[\text{enol}][\text{HCrO}_4^-] + k_c[\text{benzoin}][\text{HCrO}_4^-]$$

$$[\text{HCrO}_4^-] = (\sqrt{1 + 8K[\text{Cr}^{\text{VI}}]} - 1)/4K \quad K = 25^8$$

$$A = 1.77 \times 10^5 [\text{Cr}^{\text{VI}}]^3 + 1.33 \times 10^4 [\text{Cr}^{\text{VI}}]^2 + 153[\text{Cr}^{\text{VI}}] + 30[\text{Cr}^{\text{III}}]$$

ratio of  $k_b$  to  $k_{-a}$  is of significance in determining the rate of disappearance of chromic acid. The value of  $k_{-a}$  which was used (0.3)<sup>11</sup> was the largest which could conveniently be used in the numerical integration program. The value of  $k_c$  was found to be 1.78 l. mol<sup>-1</sup> sec<sup>-1</sup> (see above), and a value of  $k_b \sim 40$  was estimated from a plot of initial rates against the chromic acid concentration. Both  $k_a$  and  $k_b$  were adjusted so as to give a good fit to the experimental data (Figure 4 shows the results of four typical calculations; a total of ten chromic acid concentrations were used). The values of the rate constants follow:  $k_a = 1.5 \times 10^{-5}$  and  $k_b = 44$ . The value of  $k_b$ , as indicated above, depends on  $k_{-a}$  and, since the  $k_{-a}$  used is a minimum value, the true  $k_b$  is presumably greater than 45 l. mol<sup>-1</sup> sec<sup>-1</sup>. The rate of oxidation of the enol is therefore considerably greater than that for benzoin. This is in agreement with the results of Roček and Riehl.<sup>5</sup> At the highest chromic acid concentration (0.0193 *M*) the enol concentration was 35% of its equilibrium value making enolization largely rate determining, whereas at the lowest chromic acid concentration (0.00171 *M*) the enol concentration was 73% of its equilibrium value.

Substitution of the methylene protons in deoxybenzoin by deuterium caused a marked retardation of the rate of chromic acid oxidation. The ratio of the initial first-order constants obtained from the zero-order plots was 4.5. Similarly, the bromination of deoxybenzoin and desoxybenzoin-*d*<sub>2</sub> showed a kinetic isotopic effect of 4.0. Again, the results are in satisfactory agreement.

The effect of substituents on the rates of oxidation and enolization were determined giving the data summarized in Tables III and IV. The 4-methoxy and 4-ethoxy derivatives led to side reactions in both types of reactions (probably attack at the aromatic ring)<sup>12</sup> and could not be included in the study. When the substituent was attached to the benzoyl ring, a small negative  $\rho$  value was found for both oxidation ( $-0.42$ ) and

(11) The keto-enol equilibrium constant for cyclohexanone has been determined by R. P. Bell and P. W. Smith [*J. Chem. Soc. B*, 241 (1966)] to be  $4.1 \times 10^{-5}$ . If the constant were the same for deoxybenzoin,  $k_{-a}$  would be 4.2. It would not be surprising if the constant were somewhat larger for deoxybenzoin. Using  $k_{-a} = 0.3$ , satisfactory results were obtained in the numerical integration using a step size of 2 sec.

(12) S. G. Brandenberger, L. W. Maas, and I. Dvoretzky, *J. Amer. Chem. Soc.*, **83**, 2146 (1961).

TABLE III  
 RATES OF CHROMIC ACID OXIDATION OF DEOXYBENZOINS<sup>a</sup>

Substituent	$k \times 10^4, \text{sec}^{-1}$	$k_{\text{rel}}$
A. Benzyl Ring <sup>b</sup>		
H	0.93	1.00
<i>p</i> -Cl	1.03	1.10
<i>p</i> -NO <sub>2</sub>	1.11	1.19
<i>m</i> -CF <sub>3</sub>	0.58	0.62
<i>p</i> -CH <sub>3</sub>	1.05	1.13
B. Benzoyl Ring <sup>c</sup>		
H	0.57	1.10
<i>p</i> -C <sub>2</sub> H <sub>5</sub> O	0.74	1.30
<i>p</i> -CH <sub>3</sub>	0.61	1.07
<i>p</i> -Cl	0.49	0.86

<sup>a</sup> [Deoxybenzoin] =  $3 \times 10^{-2} M$ ; [HClO<sub>4</sub>] = 0.309 M;  $T = 30.0^\circ$ ; 420 m $\mu$ . <sup>b</sup> [Cr<sup>VI</sup>] =  $3.97 \times 10^{-3} M$ . <sup>c</sup> [Cr<sup>VI</sup>] =  $2.29 \times 10^{-3} M$ .

 TABLE IV  
 RATES OF ENOLIZATION OF DEOXYBENZOINS<sup>a</sup>

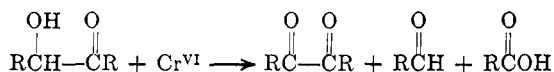
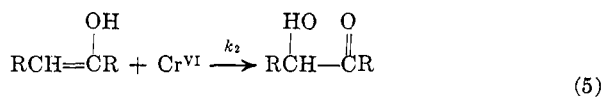
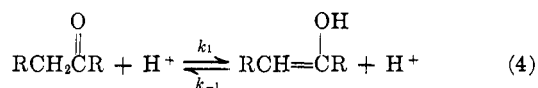
Substituents	$k \times 10^4, \text{sec}^{-1}$	$k_{\text{rel}}$
A. Benzyl Ring		
H	1.72	1.00
<i>p</i> -Cl	2.05	1.19
<i>p</i> -NO <sub>2</sub>	2.59	1.50
<i>m</i> -CF <sub>3</sub>	1.26	0.73
<i>p</i> -CH <sub>3</sub>	2.99	1.16
B. Benzoyl Ring		
H	1.72	1.00
<i>p</i> -C <sub>2</sub> H <sub>5</sub> O	2.84	1.65
<i>p</i> -CH <sub>3</sub>	2.09	1.21
<i>p</i> -Cl	0.83	0.48

<sup>a</sup> [Deoxybenzoin] =  $3 \times 10^{-2} M$ ; [Br<sub>2</sub>] =  $3 \times 10^{-3} M$ ; [HClO<sub>4</sub>] = 0.309 M;  $T = 30.0^\circ$ ; 450 m $\mu$ .

enolization ( $-1.0$ ).<sup>13</sup> On the other hand, when a para substituent was attached to the benzyl ring, both electron-releasing and -attracting groups accelerate the reaction. The 3-trifluoromethyl group retarded both oxidation and enolization. Clearly, no correlation with  $\sigma$  could be obtained. However, the effect of substituents on oxidation and on enolization were quite similar (Figure 5).

### Discussion

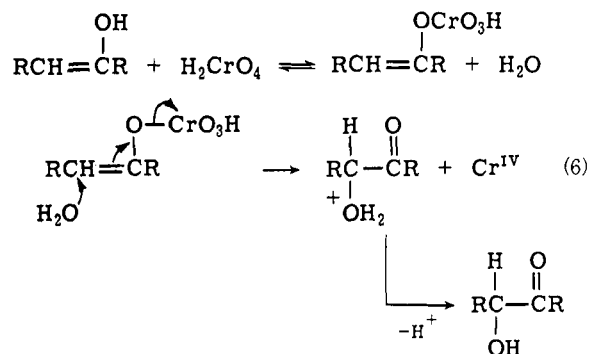
The kinetic data require that the enol be an intermediate in the oxidation and that benzoin be the first-formed product. Reaction 5 may occur either by for-



mation of the chromium(VI) ester of the enol followed by attack of water at the  $\alpha$  carbon, or by attack of chromium(VI) on the double bond. The chromic acid oxidation of isopropenyl acetate has been found to be quite slow, whereas its reaction with bromine is quite rapid. This leads us to believe that the attack by

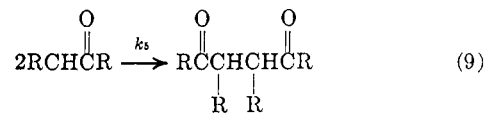
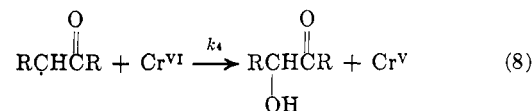
(13) A similar value of  $\rho$  was found for the enolization of acetophenone: D. P. Evans, V. G. Morgan, and H. B. Watson, *J. Chem. Soc.*, 1167 (1935).

chromium(VI) is not at the double bond. Thus, we favor reaction 6. As a result of the initial oxidation



step, chromium(VI) is formed. It is now known that chromium(VI) is an active oxidant in the chromic acid oxidation of alcohols.<sup>14</sup> Thus, it would not be surprising if it were also to react with deoxybenzoin with the formation of the desyl radical.

Under the usual reaction conditions in which the concentration of chromium(VI) is reasonably high during most of the reaction, the desyl radical would be expected to be readily oxidized to benzoin. However, if the concentration of chromium(VI) is maintained low *via* slow addition during the course of the reaction, there should be a good opportunity for the coupling of desyl radicals leading to bidesyl. The latter is found (6%) under these conditions and is absent under the more usual reaction conditions. It would be possible to generate bidesyl by an alternate route (such as by attack of a desyl cation on the enol) but this seems rather unlikely. Thus, the second reaction appears to be that shown in eq 7-9 where reactions 8 and 9 are



competitive. We cannot specify the mode of reaction of chromium(V), although it would not be surprising if it were to react in a fashion similar to chromium(VI). The fact that manganese(II) does not suppress the formation of bidesyl suggests that manganese(III) also effects the oxidation of deoxybenzoin to the desyl radical. This type of reaction has ample precedent.<sup>15</sup>

The oxidation of benzoin occurs at a rate 500 times as great as that of deoxybenzoin and is comparable with that of isopropyl alcohol. The reaction is almost certainly a typical alcohol oxidation in which the esterification of the hydroxy group is the first step. The formation of major amounts of cleavage products is ex-

(14) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1969); K. B. Wiberg and S. K. Mukherjee, *ibid.*, **93**, 2543 (1971).

(15) W. A. Waters and J. S. Littler, "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 185 ff.

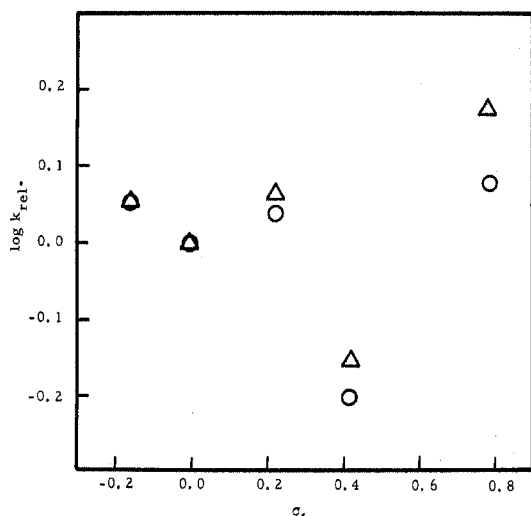


Figure 5.—Effect of substituents on the chromic acid oxidation (○) and enolization (△) of deoxybenzoin.

pected since this is the normal course of the reaction when a group which is able to bear a positive charge is attached to the alcohol carbon.<sup>16</sup> The normal product, benzil, is probably formed *via* oxidation by chromium(VI) whereas the cleavage products would be expected to arise *via* oxidation by the intermediate oxidation states of chromium. In view of the recent results of Roček and Rahman<sup>17</sup> on the chromium(VI) oxidation of alcohols, it seems clear that at least part of the cleavage results from oxidation by chromium(VI).

### Experimental Section

**Materials.**—Reagent grade glacial acetic acid was purified by treatment with chromic acid as previously described.<sup>6</sup> Reagent grade sodium dichromate hydrate was dried under vacuum at 100° over phosphorus pentoxide. Sodium perchlorate (G. F. Smith) was recrystallized from water and dried at 140° for 24 hr. Manganous perchlorate hexahydrate (G. F. Smith) was used directly without purification or drying. Reagent grade 70% perchloric acid was analyzed by titration with standard sodium hydroxide solution.

Deoxybenzoin (Eastman Kodak) was recrystallized twice from methanol and sublimed. 4-Methyl-, 4-chloro-, and 4-nitrodeoxybenzoin were prepared by the Friedel-Crafts reaction between benzene and the corresponding acyl chlorides using aluminum chloride as the catalyst. In all cases, the melting points agreed with the literature values. 4'-Methyl-, 4'-chloro-, and 4'-ethoxydeoxybenzoin were prepared in a similar fashion using phenylacetyl chloride and the appropriate reactant. Again, the melting points agreed with the literature values. All of the deoxybenzoin were sublimed before use.

**Deoxybenzoin-carbonyl-<sup>14</sup>C.**—Potassium cyanide-<sup>14</sup>C (50 μCi) was dissolved in 100 ml of water containing 115 g (1.77 mol) of potassium cyanide. A solution of 200 g of benzyl chloride (1.58 mol) in 240 ml of ethanol was added dropwise to the heated cyanide solution over 30 min. After heating to reflux for 2.5 hr, the reaction mixture was cooled and filtered. Distillation gave 131 g (71%) of benzyl cyanide-<sup>14</sup>C, bp 108–111° (13 mm). The benzyl cyanide was hydrolyzed to phenylacetic acid and converted to deoxybenzoin. The activity of the product was 1121 dpm/mg.

**Deoxybenzoin- $\alpha,\alpha$ -d<sub>2</sub>.**—A mixture of 8.0 g of deoxybenzoin, 150 ml of anhydrous ether and 30 g of acetic acid-*d* was treated with 1 drop of bromine and heated to reflux for 48 hr. The solvents were removed using a rotary evaporator and the procedure was repeated. The product was recrystallized twice

from benzene-heptane and sublimed. The nmr spectrum indicated 96% deuterium incorporation.

**3-Trifluoromethyldeoxybenzoin.**—3-Trifluoromethylphenylacetyl chloride was prepared by the addition of thionyl chloride to 3-trifluoromethylphenylacetic acid (PCR), and had bp 94–96° (15 mm). A solution of diphenylcadmium was prepared using the Grignard reagent formed from 1.5 g of magnesium turnings and 10.0 g of bromobenzene in 200 ml of dry ether, by the addition of 5.7 g of anhydrous cadmium chloride. Most of the ether was removed by distillation and 200 ml of benzene was added. To the diphenylcadmium solution was added 10 g of the acid chloride in 20 ml of benzene. The flask was heated with stirring for 3 hr. Following the usual work-up, the product was isolated by distillation giving 7.0 g (53%) of the ketone, bp 109–111° (0.3 mm). Final purification was effected by preparative vpc (20% neopentyl glycol sebacate on Chromsorb W).

*Anal.* Calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>O: C, 68.2; H, 4.2. Found: C, 68.1, 68.2; H, 4.2, 4.2.

**Kinetic Measurements.**—The disappearance of chromium(VI) was followed spectrometrically at 380–420 mμ. One solution contained sodium dichromate, sodium perchlorate, and perchloric acid in 91% acetic acid. The other solution contained deoxybenzoin in 91% acetic acid. Both solutions were made up a short time before the kinetic experiment. The solutions were degassed separately in two legs of a U cell attached to a spectrometer cell. The solutions were brought to the reaction temperature and were mixed at time zero by inverting the cell. The cell was placed in a spectrometer (Cary Model 15 or Beckman DU) and the transmittance was measured as a function of time.

The rates of enolization were determined in a similar fashion except that bromine replaced sodium dichromate and 450 mμ was used.

**Product Analysis.**—The products formed in the oxidation of deoxybenzoin were determined both by vpc analysis and by isotope dilution. In the former case the reaction was carried out in a fashion similar to the kinetic experiments except that benzophenone was included as an internal standard. After complete reaction, the reaction solution was treated with water and extracted with benzene. Benzoic acid was extracted from the benzene using sodium carbonate and was isolated by acidification. The amount of benzoic acid formed was determined by weighing after thorough drying. The amounts of unreacted deoxybenzoin and of benzil and benzaldehyde were determined by vpc by comparison of the areas for these compounds with that of benzophenone. Starting with 5.0 mmol of deoxybenzoin and 5.4 mmol of sodium dichromate there was obtained 1.8 mmol of deoxybenzoin, 2.5 mmol of benzoic acid, 1.3 mmol of benzil, 0.3 mmol of benzaldehyde, and 0.1 mmol of benzoin acetate.

The isotope dilution experiment was carried out under conditions similar to the kinetic experiments except that 2.0 g of deoxybenzoin-<sup>14</sup>C was the reactant. To the reaction product mixture was added 1.0 g of benzoic acid, 1.0 g of benzil, and 0.5 g of bidesyl along with water and benzene. Benzoic acid was isolated from the benzene solution as described above. The benzene solution was treated with heptane and concentrated whereupon crystals of bidesyl began to form. The bidesyl was separated by filtration and recrystallized from 10:1 benzene-heptane.

The filtrate was concentrated to 5 ml and was separated into its components by vpc on a 20% neopentyl glycol sebacate column. The benzil was recrystallized from methanol and dried under vacuum. The activities of the benzoic acid, bidesyl, and benzil were determined by liquid scintillation counting in toluene containing PPO and POPOP. Correction for quenching was effected by adding a known amount of deoxybenzoin-<sup>14</sup>C and recounting.

In each case the activity of the bidesyl was the same as the background (~40 dpm). In a typical experiment, 1.80 mmol of benzil was formed along with 4.82 mmol of benzoic acid.

**Slow Addition of Chromium(VI) to Deoxybenzoin-<sup>14</sup>C.**—To a solution of 2.06 g (10.5 mmol) of deoxybenzoin-<sup>14</sup>C in 50 ml of 1 M perchloric acid in 91% acetic acid was added dropwise with stirring at 85° a solution of 1.5 g of sodium dichromate (11.4 mmol) of 50 ml of 1 M perchloric acid in 91% acetic acid. The amount of bidesyl was determined by adding 0.5 g of unlabeled material followed by work-up as described above. Analysis of the bidesyl indicated that 0.3 mmol of bidesyl was formed in the reaction which corresponds to 0.6 mmol of deoxybenzoin. Thus, 6% of the reactant was converted into this product.

(16) J. J. Cawley and F. H. Westheimer, *J. Amer. Chem. Soc.*, **85**, 1771 (1963).

(17) M. Rahman and J. Roček, *ibid.*, **93**, 5455, 5462 (1971).

**Oxidation of Benzoin.**—The oxidation of 1.04 g (4.9 mmol) of benzoin with 1.35 g (10.3 mmol) of sodium dichromate was effected in the presence of benzophenone as an internal standard. After work-up as described above, the amount of benzil was determined by comparison of its vpc trace area with that of benzophenone. No benzaldehyde was found using this excess

of chromium(VI). The products were benzil (2.42 mmol, 48%) and benzoic acid (5.37 mmol, 52%).

**Registry No.**—Chromic acid, 7738-94-5; deoxybenzoin, 451-40-1; 3-trifluoromethyl deoxybenzoin, 30934-66-8.

## Oxymercuration-Demercuration of 6-Methylenebicyclo[3.1.1]heptane and 5-Methylenebicyclo[2.1.1]hexane<sup>1</sup>

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Received April 12, 1972

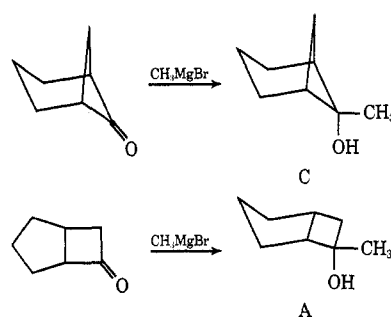
Oxymercuration followed by borohydride reduction has been applied to 6-methylenebicyclo[3.1.1]heptane (I) and 5-methylenebicyclo[2.1.1]hexane (II). The reaction of I led to 22% of 6-methylbicyclo[3.1.1]heptan-6-ols, 67% of 6-methylbicyclo[3.2.0]heptan-6-ols, 4% of 2-methylnorbornan-2-ol, and 6% of 2-methylenecycloheptanol. The rearrangements are analogous to those found in the solvolytic reactions of 6-substituted bicyclo[3.1.1]heptanes. The reaction of II led to 44% 2-methylenecyclohexanol, 28% of 3-methylenecyclohexanol, and 28% of 3-methylcyclohex-3-en-1-ol. An examination of the nmr spectrum of the reaction solution as a function of time indicated that a cyclopropane derivative was first formed and that this rearranged further to olefinic compounds. Corresponding product studies showed that the cyclopropane derivative, on reduction, gave 4-methylenecyclohexanol, whereas the other products were derived from the olefinic intermediates.

The oxymercuration of bicyclic olefins followed by *in situ* borohydride reduction of the organomercurial intermediate has been found to be a useful route to alcohols.<sup>3</sup> The reaction leads in effect to Markovnikov hydration, and generally gives little or no rearrangement. Because the reaction might provide a convenient route to alcohols which are epimeric with those formed by Grignard reagent addition to the corresponding ketones, the reaction has been explored with the strained methylenecyclobutane type compounds, 6-methylenebicyclo[3.1.1]heptane (I) and 5-methylenebicyclo[2.1.1]hexane (II).

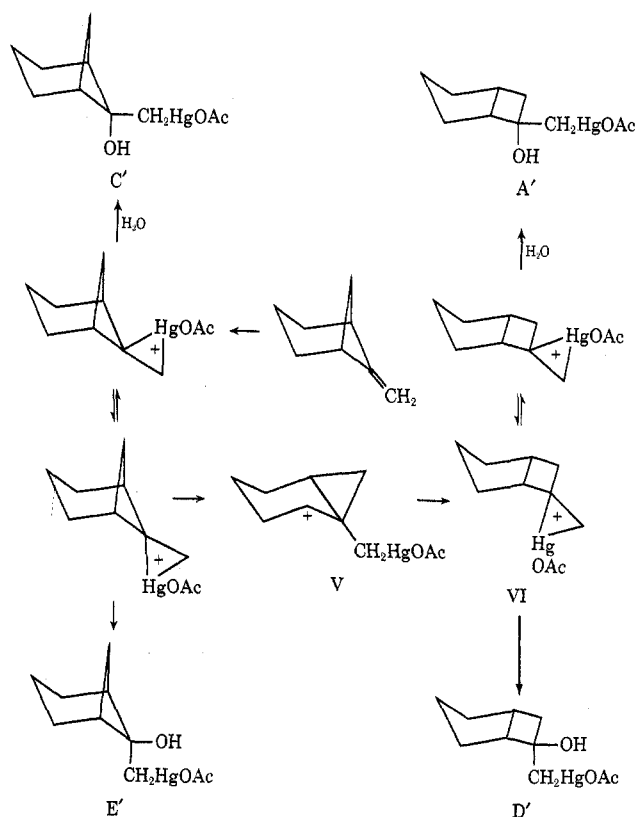
The reaction of I with mercuric acetate in aqueous tetrahydrofuran occurred readily and sodium borohydride reduction was essentially instantaneous. However, instead of producing only one alcohol, a mixture of six alcohols was obtained. They could be separated by gas chromatography, giving A (32%), B (4%), C (20%), D (36%), E (2%), and F (6%). The alcohols A–E all had methyl singlets in their nmr spectra at  $\tau$  8.6–8.8, indicating they were tertiary alcohols. The infrared spectrum of F showed bands at 1625 and 850  $\text{cm}^{-1}$ , suggesting an exocyclic double bond.

The alcohol C was found to be *endo*-6-methylbicyclo[3.1.1]heptan-6-ol by comparison with the nmr spectrum of an authentic sample prepared by the addition of the methyl Grignard reagent to bicyclo[3.1.1]heptan-6-one. The assignment of configuration is based on analogy with the lithium aluminum hydride reduction of the ketone, which gives 98% of *endo*-bicyclo[3.1.1]heptan-6-ol.<sup>4</sup>

Mechanistic considerations suggested that one of the alcohols might be 6-methylbicyclo[3.2.0]heptan-6-ol. The *endo* isomer was prepared by the addition of the



SCHEME I



(1) This investigation was supported by Public Health Service Grant GM12800 from the National Institute of General Medical Studies.

(2) Taken from part of the Ph.D. thesis of Wan-fang Chen, 1971.

(3) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967); H. C. Brown and W. J. Hammer, *ibid.*, **89**, 1525 (1967); H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1526 (1967).

(4) K. B. Wiberg and B. A. Hess, Jr., *ibid.*, **89**, 3015 (1967).