

amount of chloroplatinic acid. The mixture was stirred for 16 hr at room temperature. The pentane was removed by distillation through a 24-in. spinning-band column yielding the product, 3.1 g (60%), bp 102°,  $n_D^{20}$  1.4288 (lit.<sup>8</sup> bp 103–105°,  $n_D^{20}$  1.4340).

**1,1,2-Trimethyl-1-silacyclohexane (1).** 1-(Trichlorosilyl)-5-chlorohexane.—To 20 g (0.16 mol) of 5-chloro-1-hexene in 250 ml of cyclohexane were added 60 g (0.50 mol) of trichlorosilane and 3.6 g of dibenzoyl peroxide catalyst. The temperature of the mixture was maintained at 65° for 90 hr. The solvent and excess trichlorosilane were removed by atmospheric distillation, and the product, bp 110–112° (0.12 mm), was isolated by vacuum distillation. The reaction yield was 21 g (87%). The product was converted to trimethyl-*n*-hexylsilane for characterization (see below).

**Trimethyl-*n*-hexylsilane.**—To 50 g of 1-(trichlorosilyl)-5-chlorohexane was added 50 ml of 3 *M* methylmagnesium bromide in ether. The mixture was stirred at ambient temperature for 1 hr, then poured over cracked ice, and extracted with two 50-ml portions of ether. The ether was removed by distillation, and the product, bp 195–197°,  $n_D^{20}$  1.4125, was distilled. The 1-(trimethylsilyl)-5-chlorohexane was treated with magnesium in ether, and the resulting Grignard reagent was hydrolyzed with H<sub>2</sub>O. The product was distilled and shown to be trimethyl-*n*-hexylsilane by comparison of its spectra (nmr, ir) with those of an authentic sample prepared from the reaction of *n*-hexylmagnesium bromide and trimethylchlorosilane.<sup>13</sup>

**Attempted Ring Closure of 1-(Trichlorosilyl)-5-chlorohexane.**—To a large excess of Mg in 500 ml of ether was added 20 g (0.063 mol) of 1-(trichlorosilyl)-5-chlorohexane. The mixture was heated at reflux overnight, and then 35 g (0.25 mol) of methyl iodide was added. The mixture was again heated at reflux for

(13) F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza, and G. T. Kerr, *J. Amer. Chem. Soc.*, **68**, 475 (1946).

24 hr. Water (100 ml) was then added and the organic material was extracted. The ether was removed by careful fractionation, and the volatile product was distilled. This material was shown to be trimethyl-*n*-hexylsilane by comparison of its spectra (nmr, ir) with those of an authentic sample.<sup>13</sup>

**1-Bromo-5-(dimethylchlorosilyl)hexane.**—Anhydrous HBr was bubbled through a mixture of 20 g (0.11 mol) of 5-(dimethylchlorosilyl)-1-hexene and 0.5 g of dibenzoyl peroxide in cyclohexane for 6 hr. During the reaction period, an oil separated from the cyclohexane solution. The ir of this oil showed a strong band at 9.5  $\mu$  (SiO). After separation of the oil and removal of the solvent, distillation yielded 18 g of product mixture, bp 80–100° (3 mm). Gpc analysis of this material showed it to be composed of equal amounts of two components. The material was taken into the ring-closure step without further purification.

**Ring Closure.**—A solution of 18 g of crude 1-bromo-5-(dimethylchlorosilyl)hexane in 500 ml of ether was added to an excess of Mg turnings, and the mixture was heated at reflux overnight. Water was then added and the ether phase was decanted and dried (Na<sub>2</sub>SO<sub>4</sub>). The ether was removed by distillation, and the product (bp 150–153°,  $n_D^{20}$  1.4410) was distilled. The product yield of the reaction was 3.8 g [23.6% from 5-(dimethylchlorosilyl)-1-hexene]: ir 8.0 (SiCH<sub>3</sub>), 7.25 (—CH<sub>2</sub>), 11.4  $\mu$  (silacyclohexane<sup>9</sup>); nmr  $\delta$  1.1 (d,  $\alpha$ -Me), 1.0–2.2 (m), 0.1 (SiCH<sub>3</sub>); there was no olefinic signal; mass spectrum *m/e* (rel intensity) 26 (19), 43 (12), 59 (35), 72 (25), 73 (25), 85 (35), 86 (25), 87 (11), 99 (base), 101 (15), 114 (35), 114 (35), 127 (60), 142 (65).

*Anal.* Calcd for C<sub>8</sub>H<sub>18</sub>Si: C, 67.51; H, 12.74. Found: C, 67.27; H, 12.59.

**Registry No.**—1, 30102-80-8; 2a, 36982-63-5; 2b, 36982-64-6; 5-chloro-1-hexene, 927-54-8; 5-(chloromethylsilyl)-1-hexene, 36982-66-8; 5-(dimethylsilyl)-1-hexene, 36982-67-9.

## One-Electron vs. Two-Electron Oxidations. The Vanadium(V) and Manganese(III) Oxidations of Cyclobutanol

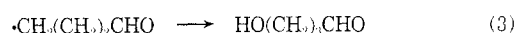
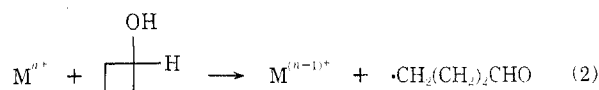
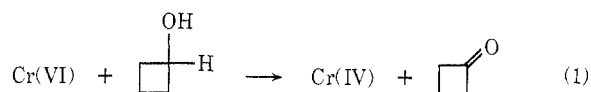
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*Received August 4, 1972*

Vanadium(V) oxidizes cyclobutanol in high yields to the ring cleavage product,  $\gamma$ -hydroxybutyraldehyde. The observations that 1-methylcyclobutanol reacts about nine times faster than cyclobutanol, that the oxidation of 1-deuteriocyclobutanol is accompanied by a low deuterium isotope effect ( $k_H/k_D = 1.21$ ), and that cyclobutanol is about 1000 times more reactive than cyclohexanol, all support the mechanism consisting of a rate-limiting ring opening reaction leading to the  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$  radical as the first reaction product. The presence of manganese(II) in chromic acid oxidations of cyclobutanol has a strong accelerating effect on the reaction, and leads to a large decrease in the deuterium isotope effect and to a large increase in the reactivity of 1-methylcyclobutanol. The yield of cyclobutanone decreases and that of hydroxybutyraldehyde increases with increasing concentration of manganese(II) in the system. These observations are consistent with a mechanism in which the effective oxidant is manganese(III), formed probably by the reaction  $\text{Cr(VI)} + \text{Mn(II)} \rightleftharpoons \text{Cr(V)} + \text{Mn(III)}$ , reacting *via* the same free radical intermediate as vanadium(V). Both results strongly indicate that cyclobutanol reacts rapidly and smoothly with one-electron oxidizing agents under ring cleavage, and can be successfully employed as a probe for one-electron oxidants.

Cyclobutanol reacts with chromium(VI), which is a two-electron oxidant, to yield, by carbon-hydrogen bond breaking, the corresponding ketone, cyclobutanone<sup>2</sup> (eq 1), while cleavage of the carbon-carbon bond occurs in the reaction with one-electron oxidants like chromium(IV)<sup>2</sup> or cerium(IV)<sup>3</sup> (eq 2 and 3). It has been proposed<sup>3</sup> that the property of cyclobutanol to react by either carbon-hydrogen or carbon-carbon cleavage could make it a valuable tool for determining the ability of oxidants to react as either one- or two-electron re-



agents. However, before one can use cyclobutanol oxidations as a diagnostic tool, one has to gain more confidence that the observed pattern is indeed generally valid.

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(2) J. Roček and A. E. Radkowsky, *J. Amer. Chem. Soc.*, **90**, 2986 (1968).

(3) K. Meyer and J. Roček, *ibid.*, **94**, 1209 (1972).

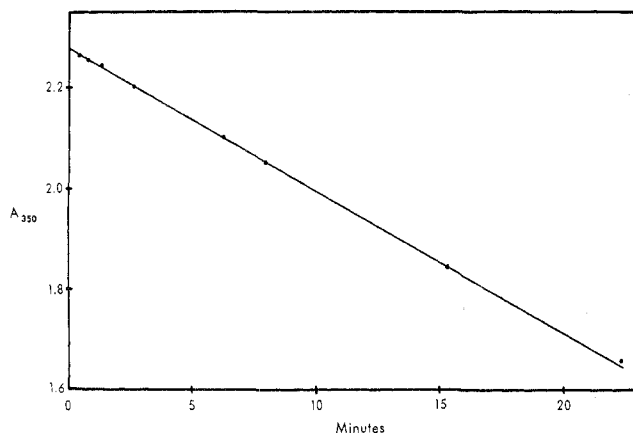


Figure 1.—Example of zero-order plot for the chromic acid oxidation of cyclobutanol in the presence of manganese(II) at 30°: cyclobutanol = 0.0128 *M*, chromium(VI) =  $2.09 \times 10^{-3}$  *M*,  $\text{MnSO}_4 = 3.35 \times 10^{-3}$  *M*,  $\text{Na}_2\text{SO}_4 = 0.196$  *M*.

Both vanadium(V)<sup>4</sup> and manganese(III)<sup>4</sup> are one-electron oxidants. They are known to oxidize unstrained alcohols, like cyclohexanol, to the corresponding ketones in a reaction in which the breaking of the carbon-hydrogen bond occurs in the rate-limiting step. We have therefore examined their reaction with cyclobutanol in order to determine whether this strained alcohol would react differently.

### Experimental Section

**Materials.**—The preparation and/or purification of the organic compounds used in this work will be described elsewhere.<sup>5</sup>

A solution of manganic sulfate,  $\text{Mn}_2(\text{SO}_4)_3$ , in 6.3 *M* sulfuric acid was prepared from potassium permanganate and manganese sulfate, using an excess of the latter.<sup>6</sup> The solution was diluted to lower acidities with a manganese sulfate solution. With decreasing acidity, a shift<sup>7</sup> of the absorption maximum to shorter wavelengths was observed.

Commercially available ammonium vanadate (Fisher Certified Reagent) was used without purification.

**Kinetic Measurements.**—The reaction rates were followed spectrophotometrically<sup>8</sup> at 350 nm for both the vanadium(V) and the chromium(VI)-manganese(II) oxidation systems. In all cases at least a threefold excess of substrate over oxidant was employed. For the vanadium(V) oxidations, pseudo-first-order rate constants were calculated from the slopes of the plots of the logarithm of the absorbance *vs.* time. In the chromium(VI)-manganese(II) system good straight line plots were obtained for absorbance *vs.* time plots (Figure 1). The slopes of the lines were used to compute reaction rates and pseudo-zero-order rate constants. Only at very low manganese concentrations, the absorbance *vs.* time plots were curved and better straight line plots could be obtained from  $\log(\text{absorbance})$  *vs.* time plots. The pseudo-first-order constants obtained from the logarithmic plots were converted to initial rates by multiplication with the initial chromium(VI) concentration. The agreement between the rate data obtained from the two types of treatment of the experimental data was usually within 10%, with the logarithmic plots leading to somewhat higher figures. In view of the large amount of kinetic data investigated, only random duplicate runs were made. The deviations from the multiple results were within 3%. For the chromium(VI)-manganese(II)-cyclobutanol system, the molar absorptivity of chromium(VI) at 350 nm was  $1.090 \times 10^3$ .

(4) For an extensive review of vanadium(V) and manganese(III) oxidations, cf. W. A. Waters and J. S. Littler in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 185-241.

(5) J. Roček and A. Radkowsky, to be published; cf. also A. E. Radkowsky, Ph.D. Thesis, The Catholic University of America, Washington, D. C., 1967.

(6) A. R. J. P. Ubbeholde, *J. Chem. Soc.*, 1605 (1935).

(7) R. G. Selim and J. J. Lingrove, *Helv. Chim. Acta*, **21**, 536 (1959).

(8) J. Roček and Sr. A. Riehl, *J. Amer. Chem. Soc.*, **89**, 6691 (1967).

In determining the rate dependence on the various components of the reaction medium, corrections were made to account for the uncatalyzed chromic acid oxidation of cyclobutanol. The  $\Delta v_0$  referred to in all cases is the difference between the observed overall rate and the rate of the uncatalyzed chromium(VI) oxidation, and is therefore equivalent to the rate attributable to the manganese-catalyzed chromium(VI) oxidation. However, rate determinations were not made for chromium(VI) oxidations in which all the variations in substrate and chromium(VI) concentrations of the manganese(II) studies were duplicated. The contributions of the uncatalyzed oxidation were estimated, assuming a first-order dependence.

**Reaction Products. Gravimetric Determinations.**—In a typical experiment, 0.0795 g (0.680 mmol) of ammonium metavanadate, 0.0224 g (0.3114 mmol) of cyclobutanol, and 1 ml of 5 *M* sulfuric acid were diluted with water to 5 ml and allowed to react at room temperature in the dark. After completion of the reaction, the solution was allowed to react overnight with a slight excess of a solution of 2,4-dinitrophenylhydrazine. The precipitate was collected, washed, dried, and weighed. The aqueous layer was extracted three times with chloroform, which was then neutralized, dried, and evaporated. The residue and precipitate were analyzed by tlc (ether-benzene, 3:1). The major product, 4-hydroxybutanaldehyde 2,4-dinitrophenylhydrazone, was isolated by preparative tlc and further identified by ir and nmr comparisons with an authentic sample.

**Glpc Determination of Cyclobutanone.**—Isoamyl alcohol (0.01592 g, 0.1806 mmol) was added to a reaction mixture obtained as indicated above. Aliquots (0.2 ml) were extracted under standardized conditions (2 min extraction time) with carbon disulfide (0.2 ml) and analyzed by glpc (Aerograph Hy-Fi Model 600D, 0.125  $\times$  60 in. Carbowax column). A calibration curve was used to determine cyclobutanone yields.

### Results and Discussion

**Vanadium(V).**—Table I gives the results of the kinetic study of the vanadium(V) oxidation of cyclobutanol, 1-deuteriocyclobutanol, and 1-methylcyclobutanol. The vanadium(V) oxidation of all alcohols was found to be first order in both the oxidant and the alcohol.

The data for cyclobutanols can be compared with those obtained for vanadium(V) oxidations of a non-strained alcohol, cyclohexanol, by earlier investigators.<sup>9</sup> Littler and Waters obtained for somewhat different conditions (50°, 5.59 *M*  $\text{HClO}_4$ ,  $\mu$  6) a second-order rate constant,  $k = 5.85 \times 10^{-4}$   $\text{M}^{-1} \text{sec}^{-1}$ . Comparing this figure with the figure for cyclobutanol given in Table I, one can estimate that cyclobutanol is about 1000 times more reactive than cyclohexanol toward vanadium(V) oxidation. This huge difference in reactivity clearly suggests that the two alcohols are oxidized by different mechanisms. As cyclohexanol is oxidized with carbon-hydrogen cleavage to the corresponding carbonyl compound, cyclohexanone, the much higher reactivity of cyclobutanol suggests that it undergoes a carbon-carbon cleavage, facilitated by the release of ring strain in the rate-limiting step.

The high reactivity of the tertiary 1-methylcyclobutanol (Table I) provides strong additional evidence

TABLE I  
SECOND-ORDER RATE CONSTANTS FOR VANADIUM(V)  
OXIDATIONS IN 1.0 *M* PERCHLORIC ACID AT 30°<sup>a</sup>

Substrate	10 <sup>3</sup> <i>k</i> , $\text{M}^{-1} \text{sec}^{-1}$	<i>k</i> / <i>k</i> <sub>cyclobutanol</sub>
Cyclobutanol	0.458	
1-Deuteriocyclobutanol	0.377	0.82
1-Methylcyclobutanol	4.22	9.22

<sup>a</sup>  $[\text{VO}_2^+] = 5.8 \times 10^{-3}$  *M*; [alcohols] = 0.056–0.065 *M*.

(9) J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 4046 (1959).

TABLE II  
 PRODUCTS OF VANADIUM(V) OXIDATION OF CYCLOBUTANOLS AT 30°

Substrate	Mmol	[V(V)], mmol	Yield, % <sup>a</sup>			Total
			Cyclobutanone	HO(CH <sub>2</sub> ) <sub>3</sub> CR	HC(CH <sub>2</sub> ) <sub>2</sub> CR	
Cyclobutanol <sup>b</sup>	0.311	0.678	0.3	57.0 <sup>d</sup>	14.0 <sup>d</sup>	71.0
Cyclobutanol <sup>c</sup>	0.647	0.640	1.5	93.7 <sup>d</sup>		95.2
Cyclobutanol-1- <i>d</i> <sup>b</sup>	0.323	0.673	~0	80.0 <sup>e</sup>	11.0 <sup>e</sup>	91.0
1-Methylcyclobutanol <sup>b</sup>	0.260	0.658		43.0 <sup>f</sup>		43.0
1-Methylcyclobutanol <sup>c</sup>	0.619	0.644		76.0 <sup>f</sup>	4.9 <sup>f</sup>	80.4

<sup>a</sup> Calculated on basis of available V(V). <sup>b</sup> [H<sub>2</sub>SO<sub>4</sub>] = 0.97 M. <sup>c</sup> [HClO<sub>4</sub>] = 1 M. <sup>d</sup> R = H. <sup>e</sup> R = D. <sup>f</sup> R = CH<sub>3</sub>.

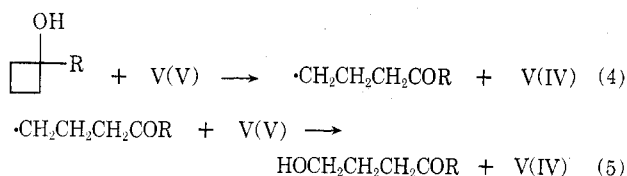
for a mechanism involving carbon-carbon bond cleavage. The nine times higher reactivity of the tertiary alcohol makes it obvious that the presence of an  $\alpha$ -hydrogen atom is entirely unnecessary for an oxidation to take place. Also, the low value<sup>10</sup> of the deuterium isotope effect ( $k_H/k_D = 1.22$ ), which is within the range usually observed for secondary isotope effects,<sup>11</sup> indicates that no carbon-hydrogen bond cleavage is taking place in the rate-limiting step.

Table II gives the result of the product analysis. Except for a minute amount of cyclobutanone, all products result from carbon-carbon bond cleavage. In the experiments in which a slight excess of the oxidant was used, the total yield is lower, and a substantial amount of higher oxidation products was identified. As we analyzed only for carbonyl compounds, substantial amounts of products, *e.g.*, hydroxy acids and lactones, were not determined, and their formation may account for the lower yields.

The nature of the products clearly confirms the conclusion reached from rate studies, that the oxidation proceeds by carbon-carbon bond cleavage. In particular, it should be noted that in this case the secondary cyclobutanol and the tertiary 1-methylcyclobutanol yield the same type of product, and thus obviously react by the same mechanism. This is quite different from the mechanism observed in chromium(VI) oxidations.<sup>12</sup>

All these results indicate that the vanadium(V) oxidation of cyclobutanols proceeds by a carbon-carbon bond cleavage (Scheme I).

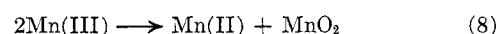
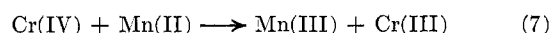
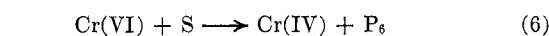
SCHEME I



**Manganese(III).**—The oxidation of cyclobutanol by manganese(III) was observed, unexpectedly, during an attempt to carry out a chromic acid oxidation of cyclobutanol in the presence of manganese(II).

When a chromic acid oxidation of a simple alcohol like isopropyl alcohol is carried out in the presence of manganese(II), a precipitate of manganese dioxide is formed, and the rate of oxidation may be reduced to a limiting value of one-half of its normal magnitude. This is due to the following set of reactions (Scheme II),

SCHEME II



where S represents the substrate and P<sub>6</sub> the product formed by its oxidation with chromium(VI).

In the oxidation of cyclobutanol in the presence of manganese(II) entirely different results were obtained. Neither precipitate formation nor the transient appearance of the cherry red color of manganese(III), clearly noticeable in control experiments with cyclohexanol, could be observed. Further, the oxidation rate in the presence of manganese(II) increased rather than decreased. Table III shows the effect of the con-

TABLE III

 OXIDATION RATES<sup>a</sup> OF CYCLOBUTANOL AS A FUNCTION OF [Mn(II)]/[Cr(VI)] RATIO<sup>b</sup> AT 30°

[Mn(II)]/[Cr(VI)]	10 <sup>7</sup> v <sub>0</sub> , M sec <sup>-1</sup>	10 <sup>7</sup> Δv <sub>0</sub> , M sec <sup>-1</sup>
0	3.85	0
0.65	3.98	0.13
3.23	4.45	0.60
16.30	6.60	2.75
50.20	22.80	18.95
82.30	47.70	43.85
99.40	69.40	65.55

<sup>a</sup> v<sub>0</sub> oxidation rates extrapolated to the starting time of the reaction; Δv<sub>0</sub> is the rate increase caused by the presence of manganese(II). <sup>b</sup> Conditions: [Cr(VI)] = 2.037 × 10<sup>-3</sup> M, [H<sub>2</sub>SO<sub>4</sub>] = 0.954 M, [cyclobutanol] = 0.0127 M, [MnSO<sub>4</sub>] + [Na<sub>2</sub>SO<sub>4</sub>] = 0.1998 M.

centration of manganese(II) sulfate on the oxidation rate of cyclobutanol at constant ionic strength. As the rate law of the oxidation changes as the concentration of manganese(II) is increased, initial rates (v<sub>0</sub>) are used.

Table IV shows the effect of added manganese(II) on (a) the magnitude of the kinetic isotope effect and (b) the relative reactivity of 1-methylcyclobutanol and cyclobutanol.

The magnitude of the deuterium isotope effect decreases rapidly as the concentration of manganese(II) in the solution is increased. At high manganese(II):chromium(VI) ratios it reaches a value which is much closer to those typically associated with secondary rather than with primary isotope effects. This decrease in the value of the isotope effect is thus highly indicative of a change in mechanism. It is obvious that the transfer of the  $\alpha$ -hydrogen atom which takes place in the rate-limiting step of the chromium(VI) oxidation of cyclobutanol does not take place during the rate-limiting step of the oxidation in the presence of manganese(II).

(10) This low value stands in strong contrast to the value of  $k_H/k_D = 3.6$ , which was obtained for the oxidation of cyclohexanol to cyclohexanone.<sup>9</sup>

(11) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(12) J. Roček and A. E. Radkowsky, *Tetrahedron Lett.*, 2835 (1968).

TABLE IV  
COMPARATIVE RATES<sup>a</sup> IN THE MANGANESE(II) CATALYZED CHROMIC ACID OXIDATION OF CYCLOBUTANOLS<sup>b</sup>

[MnSO <sub>4</sub> ], M	[Mn(II)]/[Cr(VI)]	10 <sup>3</sup> v <sub>0</sub> , M sec <sup>-1</sup>		1-Methyl- cyclobutanol	(v <sub>0</sub> ) <sub>H</sub> /(v <sub>0</sub> ) <sub>D</sub>	(v <sub>0</sub> ) <sub>OH</sub> /(v <sub>0</sub> ) <sub>H</sub>
		Cyclobutanol	1-Deuterio- cyclobutanol <sup>c</sup>			
0 <sup>d</sup>	0	5.43	0.88		6.2	0.0046 <sup>e</sup>
0.0267 <sup>d,f</sup>	12.3	6.13	1.37	0.60	4.5	0.1
0.099	49	20.98	14.32	17.35	1.46	0.83
0.1332	66	32.6	23.8	32.3	1.37	1.0
0.1998	99	67.5	54.8	76.2	1.23	1.13

<sup>a</sup> v<sub>0</sub> oxidation rates extrapolated to the starting time of the reaction. <sup>b</sup> Conditions: [Cr(VI)] = 1.971–2.175 × 10<sup>-3</sup>M; [alcohol] = 0.01217–0.01396 M; [H<sub>2</sub>SO<sub>4</sub>] = 0.954 M 30°. <sup>c</sup> Uncorrected for actual deuterium content. <sup>d</sup> v<sub>0</sub> from logarithmic plots of absorbance. <sup>e</sup> In 1 M HClO<sub>4</sub>. <sup>f</sup> 25°.

The effect of manganese(II) on the relative oxidation rate of 1-methylcyclobutanol leads to the same conclusion. While in the absence of manganese(II) cyclobutanol is oxidized by chromium(VI) about 200 times faster than 1-methylcyclobutanol, the tertiary alcohol actually becomes more reactive than the secondary alcohols at high manganese(II) concentrations. Again, this clearly demonstrates that the breaking of the carbon–hydrogen bond in the rate-limiting step is replaced by another process, most probably the breaking of a carbon–carbon bond.

The conclusions about the effect of added manganese(II) on the nature of oxidation of cyclobutanol by chromic acid which were derived from the rate studies discussed above are fully supported by the product studies, which are summarized in Table V. The yield

TABLE V  
PRODUCT COMPOSITION IN MANGANESE(II)–CHROMIUM(VI)  
OXIDATION OF CYCLOBUTANOLS<sup>a</sup>

R	[Mn(II)]/[Cr(VI)]	Cyclobutanone, % yield <sup>b</sup>	HO(CH <sub>2</sub> ) <sub>3</sub> C=O,
			% yield <sup>c</sup>
H	0	38.1	
H	3.2	27.7	
H	9.5	11.5	73
H <sup>d</sup>	12.6	18.3	
H	25.4	3.7	88
D	12.7	3	95
CH <sub>3</sub>	12.7		68

<sup>a</sup> Conditions: [H<sub>2</sub>SO<sub>4</sub>] = 1 M; K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> = 0.0263 mmol; alcohol (R = H, 0.312 mmol; R = D, 0.310 mmol; R = CH<sub>3</sub>, 0.255 mmol); 30°. <sup>b</sup> Analyzed by glpc. <sup>c</sup> Gravimetric determination. <sup>d</sup> 0°.

of cyclobutanone, which corresponds to about 40% of the products in the chromic acid oxidation in the absence of manganese, decreased to the low value of 3.7% when a Mn(II):Cr(VI) ratio of 25:1 was reached. At the same time, the yield of the cleavage product,  $\gamma$ -hydroxybutyraldehyde, increased considerably. In the presence of less than a 13-fold excess of manganese(II) over chromium(VI), the oxidation of cyclobutanol-1-d give a 95% yield of the deuteriohydroxyaldehyde and the oxidation of 1-methylcyclobutanol gives an almost 70% yield of the corresponding hydroxy ketone, whereas no identifiable products could be isolated from the oxidation of the latter alcohol in the absence of manganese(II).<sup>12</sup>

The results of both kinetic studies and product studies thus show that in the presence of manganese(II) the oxidation of cyclobutanol assumes a completely

different character than corresponds to a rate-limiting two-electron oxidation of chromium(VI) and becomes in all respects very similar to one-electron oxidations by oxidants like vanadium(V) or cerium(IV)<sup>8</sup>. We therefore conclude that the actual oxidant in the chromic acid–manganese(II) system is manganese(III) and not chromium(VI), and that the rate-limiting step of the oxidation consists in a carbon–carbon bond cleavage leading to a free radical intermediate (reaction 2). This conclusion can be made with a great deal of confidence, even though a fully satisfactory detailed reaction mechanism cannot be offered at the present time and further work will be required before the reaction can be fully understood.

The conclusion that manganese(III) is very reactive toward cyclobutanol and is in all probability responsible for the observed oxidation cleavage reaction is also supported by the observation of an instantaneous reduction, upon the addition of cyclobutanol, of a manganese(III) solution in 1.1 M sulfuric acid. Strain-free alcohols react only slowly under these conditions.

A more detailed investigation of the oxidation of cyclobutanol by chromic acid in the presence of manganese(II) led to the following results.

(1) The order of the reaction in chromium(VI) decreases to zero order with increasing manganese(II) concentrations, although in the absence of manganese(II) the oxidation is strictly first order in chromium(VI). Individual runs gave fairly good zero-order plots over almost the entire range of manganese(II) concentrations studied (Figure 1). The dependence of the experimental pseudo-zero-order rate constants on the initial chromium(VI) concentrations is more complex, but a decrease of the order with respect to chromium(VI) down to zero is clearly evident, particularly at higher concentrations of manganese(II) (Figure 2).

(2) The rate increase,  $\Delta v_0$ , is proportional to [Mn(II)] at lower manganese(II) concentrations and to [Mn(II)]<sup>2</sup> at higher manganese(II) concentrations (Figure 3).

(3) The reaction is first order in cyclobutanol throughout the whole set of conditions, regardless of the manganese(II) concentration (Figure 4).

(4) The rate is independent of the concentration of chromium(III) (Table VI).

For the regions in which the reaction is first order in manganese(II), these findings, together with the convincing evidence that a one-electron oxidation involving manganese(III) is taking place, can be accommodated by Scheme III.

Reaction 9 is typical for the oxidation of metal ions which can undergo a one-electron reaction, for ex-

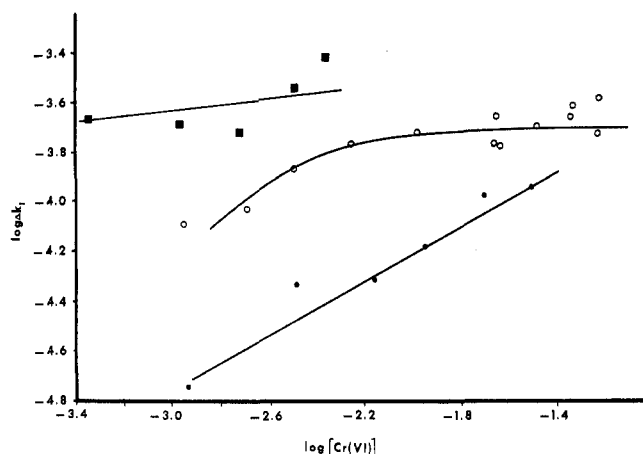


Figure 2.—Dependence of the manganese(II) catalyzed oxidation of cyclobutanol on the concentration of chromium(VI) at 30°: ■,  $[\text{MnSO}_4] = 0.1332 \text{ M}$ ,  $[\text{cyclobutanol}] = 0.03621\text{--}0.1300 \text{ M}$ ; ○,  $[\text{MnSO}_4] = 0.0999 \text{ M}$ ,  $[\text{cyclobutanol}] = 0.0752\text{--}0.2103 \text{ M}$ ; ●,  $[\text{MnSO}_4] = 0.0333 \text{ M}$ ,  $[\text{cyclobutanol}] = 0.072 \text{ M}$ ;  $[\text{H}_2\text{SO}_4] = 0.954 \text{ M}$ ,  $\Delta k_1 = \Delta v_0/[\text{CB}]$ .

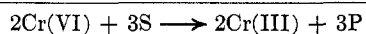
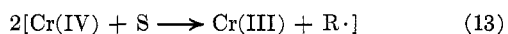
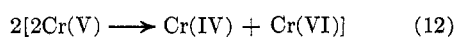
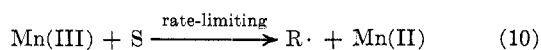
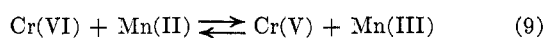
TABLE VI

DEPENDENCE OF THE MANGANESE(II) CATALYZED OXIDATION OF CYCLOBUTANOL ON CHROMIUM(III)<sup>a</sup>

Chromium(III), M	$10^4 v_0$ , M sec <sup>-1</sup>
0	0.851
0.0520	0.874
0.1039	0.864

<sup>a</sup> Conditions:  $[\text{MnSO}_4] = 0.1996 \text{ M}$ ,  $[\text{Mn(II)}] + [\text{Cr(III)}] + [\text{Na}_2\text{SO}_4] = 0.3038 \text{ M}$ ,  $[\text{Cr(VI)}]_{\text{avg}} = 2.02 \times 10^{-3} \text{ M}$ ,  $[\text{cyclobutanol}] = 0.0133 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.954 \text{ M}$ , 30°.

## SCHEME III



ample, vanadium(IV), iron(II), and neptunium(IV).<sup>13</sup> We assume that the oxidation of the substrate by manganese(III) (reaction 10) constitutes the rate-limiting step. The free radical formed in this reaction can be oxidized further by any of the oxidants which are available, chromium(VI), chromium(V), chromium(IV), or manganese(III). In Scheme III we assume that the most likely reaction of the free radical is its oxidation by the oxidant which is present in the highest concentration. However, reaction with other oxidants would not alter the overall results. Since chromium(V) is a product of both reactions 9 and 11 in the above sequence, a reaction in which it is consumed has to be included in the scheme. We propose that chromium(V) may undergo a disproportionation reaction into chromium(IV) and chromium(VI) (reaction 12). We have shown earlier<sup>14</sup> that this reaction should have an equilibrium constant of about  $2.5 \times 10^{13}$ , and should thus be thermodynamically highly favored. Con-

(13) J. K. Beattie and G. P. Haight, Jr., in "Mechanisms of Inorganic Relations," J. A. Edwards, Ed., Wiley, New York, N. Y., 1972.

(14) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5462 (1971).

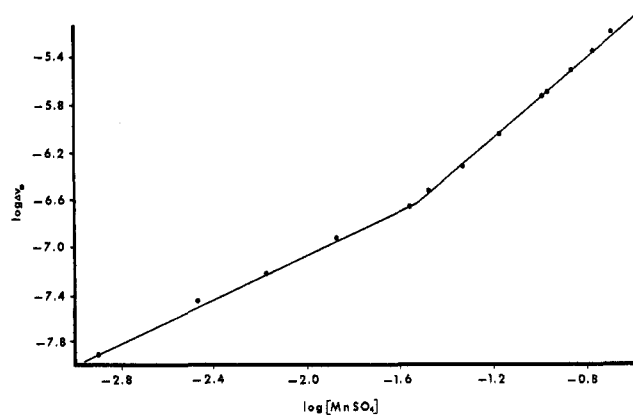


Figure 3.—Dependence of the manganese(II) catalyzed oxidation of cyclobutanol on the concentration of manganese(II):  $[\text{Cr(VI)}] = 2.073 \times 10^{-3} \text{ M}$ ,  $[\text{cyclobutanol}] = 0.0127 \text{ M}$ ,  $[\text{MnSO}_4] + [\text{Na}_2\text{SO}_4] = 0.1998 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.954 \text{ M}$ .

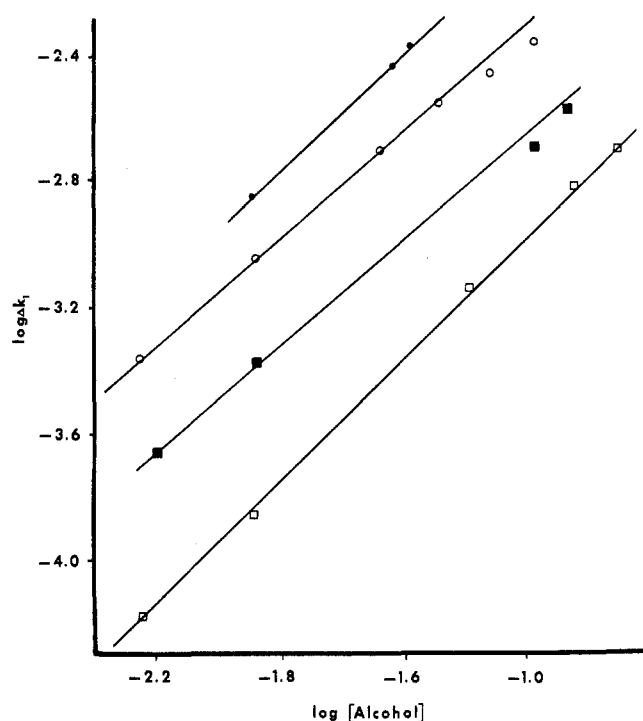


Figure 4.—Dependence of the manganese(II) catalyzed oxidation of cyclobutanol concentration at 30°:  $\Delta k_1 = \Delta v_0/[\text{Cr(VI)}]$ ;  $[\text{Cr(VI)}]_{\text{avg}} = 2.07 \times 10^{-3} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.954 \text{ M}$ ,  $[\text{MnSO}_4] + [\text{Na}_2\text{SO}_4] = 0.1332 \text{ M}$ ; □,  $[\text{MnSO}_4] = 0.0333 \text{ M}$ ; ■,  $[\text{MnSO}_4] = 0.0666 \text{ M}$ ; ○,  $[\text{MnSO}_4] = 0.0999 \text{ M}$ ; ●,  $[\text{MnSO}_4] = 0.1332 \text{ M}$ .

siderable evidence that reaction 12 does indeed play an important role in the chromic acid oxidation is now becoming available.<sup>15,16</sup> Reaction 13 represents the chromium(IV) oxidation of cyclobutanol, which is discussed in detail elsewhere.<sup>2,5,17</sup>

The rate of the reaction, according to Scheme III, is governed by step 10, and is therefore given by eq 14.

$$v = k_{10}[\text{S}][\text{Mn(III)}] = k_{10}K_9[\text{S}][\text{Mn(II)}] \frac{[\text{Cr(VI)}]}{[\text{Cr(V)}]} \quad (14)$$

If one can make the fairly plausible assumption that the steady-state concentration of chromium(V) which will be established rapidly during the reaction

(15) P. M. Nave and W. S. Trahanovsky, *ibid.*, **92**, 1120 (1970).

(16) J. C. Drozd, Ph.D. Thesis, University of Illinois at Chicago Circle, Chicago, Ill., 1971.

(17) M. Rahman and J. Roček, *J. Amer. Chem. Soc.*, **93**, 5455 (1971).

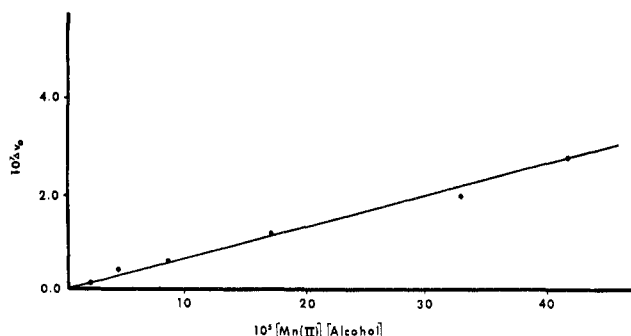
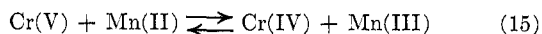


Figure 5.—Determination of rate constant for manganese(II) catalyzed oxidation of cyclobutanol at low manganese(II) concentrations at 30°: [cyclobutanol] = 0.0127 M, [Cr(VI)] =  $2.073 \times 10^{-3}$  M, [Mn(II)] = 0–0.0333 M, [MnSO<sub>4</sub>] + [Na<sub>2</sub>SO<sub>4</sub>] = 0.1998 M, [H<sub>2</sub>SO<sub>4</sub>] = 0.954 M;  $\Delta v_0 = (v_0)_{\text{expt}} - k_A[\text{Cr(VI)}] \cdot [\text{alcohol}]$ .

will be approximately proportional to the concentration of chromium(VI), then the reaction should be first order in both the substrate and manganese(II) and approximately zero order in chromium(VI). This is indeed observed at higher manganese concentrations.<sup>18</sup>

At high manganese(II) concentrations, the steady-state concentration of chromium(V) would increase, and an additional reaction (eq 15) may become important.



This reaction may be responsible for the shift from first- to second-order dependence on the concentration of manganese(II) at high concentrations (Figure 3).

The oxidation rates for cyclobutanol by chromium(VI) and manganese(II) can be expressed very crudely by an empirical rate law (eq 16). The first term corre-

$$v_0 = [\text{alcohol}] \{k_A[\text{Cr(VI)}] + k_B[\text{Mn(II)}] + k_C[\text{Mn(II)}]^2\} \quad (16)$$

sponds to the oxidation of cyclobutanol in the absence of manganese(II). The second and third terms reflect the dependence of the oxidation rate on manganese(II) at low and high manganese(II) concentrations, respectively. The values of the rate constants in eq 16 as estimated from the experimental data from the appropriate plots (Figures 5 and 6) are

$$k_A = 1.49 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$$

$$k_B = 6.5 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$$

$$k_C = 9.2 \times 10^{-3} \text{ M}^{-2} \text{ sec}^{-1}$$

One can attempt to estimate the magnitude of  $k_{10}$ , the second-order rate constant for the manganese(III) oxidation of cyclobutanol. From the reduction potentials of the Cr(VI)/Cr(V) couple (0.55 V)<sup>19</sup> and the Mn(III)/Mn(II) couple (1.51 V)<sup>20</sup> one can estimate the value of the equilibrium constant of reaction 9:  $k_9 \cong 5 \times 10^{-17}$ . At the beginning of the reaction, when [Mn(III)] = [Cr(V)], the concentration of manganese(III) will be approximately  $10^{-10}$  M {for [Mn(II)] = 0.1, [Cr(VI)] =  $10^{-3}$  M} and will in the course of the reaction decrease further as the concentration of chrom-

(18) At low manganese(II) concentrations, the dependence on chromium(VI) is not reduced to zero but is of an apparent one-half order (Figure 2). No reasonable interpretation for this observation can be offered at this time. It is unfortunate that an attempt to derive a more precise rate law for Scheme III leads to a fourth-order equation, which is too complex to permit direct experimental verification.

(19) L. J. Csanyi, *Magy. Kem. Foly.*, **65**, 415 (1959).

(20) W. M. Latimer, "Oxidation Potentials," 2nd ed. Prentice-Hall, Englewood Cliffs, N. J., 1952.

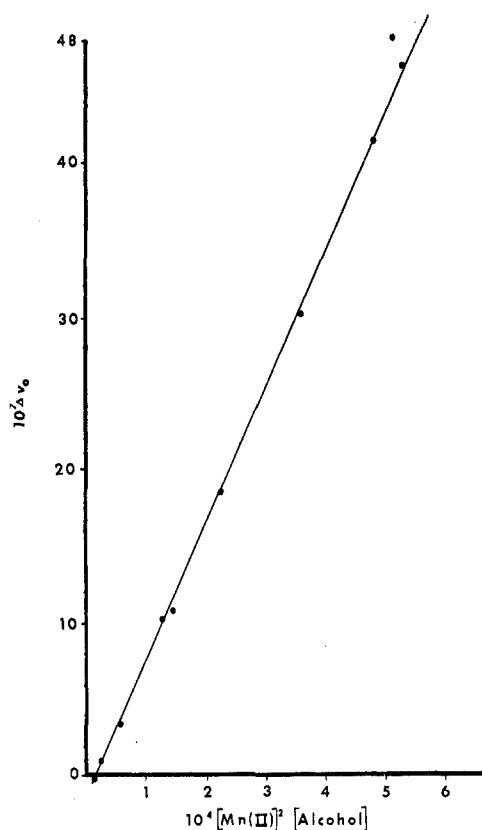


Figure 6.—Determination of rate constant for manganese(II) catalyzed oxidation of cyclobutanol at high manganese(II) concentrations at 30°: [cyclobutanol] = 0.0127 M, [Cr(VI)] =  $2.03 \times 10^{-3}$  M, [Mn(II)] = 0.0333–0.1998 M, [MnSO<sub>4</sub>] + [Na<sub>2</sub>SO<sub>4</sub>] = 0.1998 M, [H<sub>2</sub>SO<sub>4</sub>] = 0.954 M;  $\Delta v_0 = (v_0)_{\text{expt}} - k_A[\text{Cr(VI)}][\text{alcohol}] - k_B[\text{Mn(II)}][\text{alcohol}]$ .

ium(V) increases. As  $k_B = k_{10}[\text{Mn(III)}]/[\text{Mn(II)}]$  the value of  $k_{10}$  must be at least  $10^5 \text{ M}^{-1} \text{ sec}^{-1}$ . Manganese(III) thus appears to be an extremely reactive oxidant toward cyclobutanol. This reactivity, which is clearly by many orders of magnitude higher than the reactivity toward unstrained secondary alcohols,<sup>4</sup> strongly supports the assumption that cyclobutanols react by a completely different mechanism, namely, by way of carbon-carbon cleavage.

Kemp and Waters<sup>21</sup> have described a study of the effect of manganese(II) on the chromic acid oxidation of  $\alpha$ -hydroxyisobutyric acid. Their results parallel our findings in many respects, and it is therefore quite probable that a similar mechanism may be operative in both cases. However, these authors proposed a mechanism (Scheme IV) in which the rate-limiting step is the decomposition of a reversibly formed manganese(III)-substrate complex.

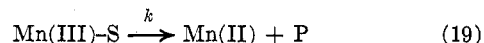
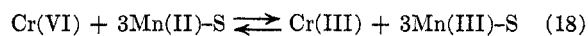
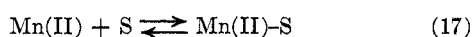
This mechanism would lead to the rate law (eq 20),

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{-d[\text{Mn(III)-S}]}{dt} = \frac{kK^{1/3}[\text{Cr(VI)}]^{1/3}[\text{Mn(II)}](\text{S})}{[\text{Cr(III)}]^{1/3}} \quad (20)$$

where  $K$  is the overall equilibrium constant for the formation of Mn(III)-S from the substrate, manganese(II) and chromium(VI) (reactions 17 and 18). This rate law requires that chromium(III) should have a retarding effect on the reaction. Kemp and Waters did not examine the effect of added chromium(III).

(21) T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 3193 (1969).

## SCHEME IV



However, in our study chromium(III) definitely did not exhibit any influence on the reaction rate. Therefore, any mechanism which would require an equilibrium involving chromium(III) to be established prior to the rate-limiting step of the oxidation has to be rejected, and we therefore cannot apply the mechanism proposed by Kemp and Waters to rationalize our results. Further, while the formation of a complex

between manganese and an  $\alpha$ -hydroxy acid was an entirely plausible assumption, it would be much less justified to propose the formation of an intermediate complex in the case of the oxidation of cyclobutanol.

**Registry No.**—Vanadium, 7440-62-2; manganese, 7439-96-5; cyclobutanol, 2919-23-5; 1-deuteriocyclobutanol, 22696-02-2; 1-methylcyclobutanol, 20117-47-9.

**Acknowledgment.**—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the U. S. Army Research Office, Durham, for generous support of this research.

## The Synthesis of Substituted Hydroazulenes

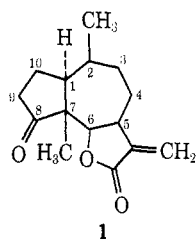
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Received June 30, 1972

The conversion of 1(9)-octalin-2-one derivatives to isomeric 9-octalin-2-one derivatives by way of ketal formation and subsequent acid hydrolysis has been examined. Construction of substituted diketo hydroazulenes from these 9-octalin-2-one derivatives has been studied, and the chemistry of the resulting compounds investigated.

A large variety of techniques are currently available for the stereoselective construction of substituted decalins and hydrindanes. In addition, conformational analysis is useful in predicting the relative stability of isomers in such systems.<sup>1</sup> Unfortunately, a similar body of information is not available for the stereoselective construction of substituted hydroazulenes, and the application of conformational analysis to substituted seven-membered rings is relatively difficult.<sup>2</sup> Recently, a large and relatively important group of sesquiterpenes, the pseudoguaianolides, has been shown to possess the hydroazulene ring system.<sup>3</sup> Damsin (**1**) is a typical representative of this family of



compounds.<sup>4</sup> As a result of our interest in these sesquiterpenes, this work was initiated to develop stereoselective methods for the preparation of substituted and functionalized hydroazulenes, with particular reference to the substitution patterns typical of the pseudoguaianolides.

(1) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962.

(2) (a) N. L. Allinger, *J. Amer. Chem. Soc.*, **81**, 5727 (1959); (b) R. Pauncz and D. Ginsburg, *Tetrahedron*, **9**, 40 (1960); (c) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); (d) J. B. Hendrickson, *Tetrahedron*, **19**, 1387 (1963); (e) J. B. Jones, J. M. Zander, and P. Price, *J. Amer. Chem. Soc.*, **89**, 94 (1967).

(3) J. Romo and A. R. de Vivar, *Progr. Chem. Org. Natur. Prod.*, **25**, 90 (1967).

(4) (a) L. Bernardi and G. Büchi, *Experientia*, **13**, 466 (1957); (b) W. Herz, H. Watanabe, M. Miyazaki, and Y. Kishida, *J. Amer. Chem. Soc.*, **84**, 2601 (1962); (c) M. Suchy, V. Herout, and F. Šorm, *Collect. Czech. Chem. Commun.*, **28**, 2257 (1963).

In order to provide a method for direct introduction of oxygen functionality at C-6 and C-8 of the hydroazulene ring system, we have examined the transannular condensation of two unstable 1,3,6-cyclodecatrienes **5a** and **5b**, which are conveniently prepared by ozonolysis of the corresponding  $\beta,\gamma$ -unsaturated ketones **4a** and **4b**<sup>5</sup> (Scheme I).

The methods available in the literature for construction of  $\beta,\gamma$ -unsaturated ketones, such as **4**, are essentially twofold: kinetic protonation of the enolate anion derived from the corresponding  $\alpha,\beta$ -unsaturated ketone<sup>6</sup> and Birch reduction of a suitably substituted 6-methoxytetralin followed by careful hydrolysis.<sup>7</sup> Unfortunately, these methods require vigorous and strongly basic reaction conditions, which are not compatible with a variety of functional groups. It is well known, however, that conversion of an  $\alpha,\beta$ -unsaturated ketone to a ketal affords a product in which the double bond has moved to a  $\beta,\gamma$  position.<sup>8</sup> We, therefore, chose to examine the possibility of careful hydrolysis of such a ketal to the corresponding  $\beta,\gamma$ -unsaturated ketone.

Treatment of octalone **2a** with ethylene glycol in the presence of *p*-toluenesulfonic acid afforded ketal **3a** as the only product. Careful hydrolysis of **3a** with oxalic acid in aqueous methanol then afforded an 81% yield of **4a**. Ozonolysis of **4a** followed by a reductive work-up would be anticipated to yield triketone **5a**. This compound proved to be extremely reactive, however, and could not be isolated. Hydroazulene **6a** was obtained instead, presumably by way of spon-

(5) Cf. L. Velluz, G. Muller, J. Mathieu, and A. Poittevin, *C. R. Acad. Sci.*, **252**, 4084 (1961).

(6) (a) H. J. Ringold and S. K. Malhotra, *Tetrahedron Lett.*, 669 (1962); (b) J. A. Marshall and S. F. Brady, *ibid.*, 1387 (1969); (c) J. Meinwald and L. Hendry, *J. Org. Chem.*, **36**, 1446 (1971).

(7) Cf. A. J. Birch, *J. Chem. Soc.*, 593 (1946).

(8) (a) J. A. Zderic, D. C. Limon, H. J. Ringold, and C. Djerassi, *J. Amer. Chem. Soc.*, **81**, 3120 (1959); (b) C. Djerassi and M. Gorman, *ibid.*, **75**, 3704 (1953).