to the Co(III) nucleus as the acetato ligand (since it is derived from the stronger acid).[1] Dissociation of the type described in eq 12 allows for (partial) exchange of acetato ligands, which are less dissociated when the complex is diluted with glacial acetic acid, and leads to less reactive cobalt(III) species.

The effect of acetic acid was determined in TFA-A solutions containing 10, 20, and 30% (v) acetic acid. A 10-ml stock solution of cobalt(III) trifluoroacetate (0.2068 g) was prepared. A 2-ml aliquot of this solution was diluted to 10 ml with the appropriate mixed solvent and allowed to equilibrate for 4 hr. One milliliter of this solution was mixed with 2 ml of a stock solution of 8.1×10^{-2} M benzene in TFA-A. The times for half-disappearance of benzene were 10, 31, and 194 min in solutions consisting of 10, 20, and 30%

(v) acetic acid, respectively. The kinetic isotope effect in the oxidation of benzene was carried out with stock solutions of $1.8 \times 10^{-2} M$ cobalt(III) and separate stock solutions of $1.1 \times 10^{-2} M$ benzene and benzene-d_6 in TFA-A.

The charge-transfer spectra of arenes were measured in methylene chloride solutions containing $5 \times 10^{-3} M$ tetracyanoethylene(resublimed).

Mechanism of the Chromic Acid Oxidation of Cyclobutanol[1]

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Abstract: Cyclobutanol is oxidized to a mixture of cyclobutanone, 4-hydroxybutyraldehyde, and higher oxidation products derived from further oxidation of the hydroxyaldehyde. The existence of a large deuterium isotope effect in the oxidation of 1-deuteriocyclobutanol (8.9) and the low reactivity of 1-methylcyclobutanol strongly suggest that cyclobutanone is the product of a chromium(VI) oxidation of cyclobutanol with the ketone being formed in the rate-limiting step of the reaction. Using an induced chromic acid oxidation of cyclobutanol by vanadium-(IV) and an induced oxidation of 1-methylcyclobutanol by secondary alcohols, it is shown that the reaction leading to the opening of the cyclobutane ring is due to chromium(IV). This reaction leads to a free radical which is further oxidized to the corresponding hydroxycarbonylic compound. Chromium(V) seems to react with cyclobutanol to yield cyclobutanone rather than a cleavage product in a reaction which is slow enough to permit accumulation of chromium(V) to sufficient concentrations to make its bimolecular disproportionation to chromium(IV) and chromium(VI) important. Heats of combustion were used to calculate enthalpies of formation for cyclobutanol (34.6 kcal/mol) and cyclobutanone (21.9 kcal/mol). From these values it is shown that cyclobutanol and cyclobutanone have very similar strain energies (25.1 and 24.5 kcal/mol, respectively), contrary to the general expectation that a change from an sp^3- to an sp^2-hybridized carbon in a strained small ring compound should lead to a major increase in strain energy.

Small ring compounds and other strained structures often react very differently from their unstrained analogs. Their study has led not only to the discovery of new reactions and effects, but also to a deeper and more intimate understanding of many previously known reactions.

Although the chromic acid oxidation of alcohols is a reaction which has been investigated by numerous investigators over a period of many years,[2] important aspects concerning the nature of the transition state of the rate-limiting step and the role of unstable chromium compounds formed during the reaction remain poorly understood.[3] We therefore decided to investigate in detail the chromic acid oxidation of cyclobutanol in order to gain a better insight into the nature of the reaction.

(1) (a) Preliminary communication: *J. Amer. Chem. Soc.*, 90, 2986 (1968). (b) Address correspondence to J. Roček, Graduate College, University of Illinois at Chicago Circle, Chicago, Ill. 60680.

(2) (a) F. W. Westheimer, *Chem. Rev.*, 45, 419 (1949); (b) J. J. Cawley and F. H. Westheimer, *J. Amer. Chem. Soc.*, 85, 1771 (1963); (c) D. Bretzger, Ph.D. Dissertation, University of Delaware, 1964; (d) K. B. Wiberg in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, pp 159 and 164.

(3) Several important contributions have been made[4] since the preliminary account of this work was published.[1a]

(4) (a) P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, 92, 1170 (1970); 93, 4536 (1971); (b) K. B. Wiberg and S. K. Mukherjee, *ibid.*, 93, 2543 (1971); (c) M. Rahman and J. Roček, *ibid.*, 93, 5455, 5462 (1971).

Experimental Section

Materials. Cyclobutanone was synthesized from pentaerythritol, *via* pentaerythrityl tetrabromide, 1-hydroxymethyl-1-cyclobutanol, and methylenecyclobutane, by methods reported in the literature.[5] In addition, some was obtained commercially (Columbia Chemical Co.). Final purification by glpc was done on the F & M Model 500 gas chromatograph using a 0.25 in. × 144 in. Carbowax 20M column.

For the determination of heats of combustion, cyclobutanone was purified by distillation on a spinning band column (Nester-Faust), distillation through a tube filled with Linde molecular sieve (4A), purification by preparative glpc, using a polyester cross-linked diethylene glycol adipate column, and by vacuum line distillation. The final product was 99.94% pure and contained two unknown impurities (0.02 and 0.03%, respectively) and a very small amount of ether (0.006%). Physical constants: $d^{24}_4 = 0.924$, n^{25}D 1.4188 (lit. 1.4189), bp 99–100° (lit.[3] bp 98–100°).

Cyclobutanol was prepared by lithium aluminum hydride reduction of cyclobutanone followed by isolation through a spinning band column and final purification by glpc. 1-Deuteriocyclobutanol was prepared in the same manner, using lithium aluminum deuteride (Metal Hydrides Inc. 96.2% D). The analytically determined deuterium content of the product was 0.928 atom deuterium per molecule; the analysis was carried out by J. Nemeth, Urbana, Ill.

For the determination of heats of combustion, cyclobutanol was purified in the same manner as cyclobutanone, except that several glpc purifications were required (Carbowax 20M column). The final product was 99.92% pure. The impurities were water (0.04%), ether (0.01%), and two unknown impurities (0.01 and 0.02%,

(5) J. D. Roberts and R. H. Mazur, *ibid.*, 73, 2509, 3542 (1951).

respectively). The physical constants were $d^{24}_4 = 0.921$, $n^{25}D$ 1.4338 (lit. 1.4347), bp 124.6° (lit.[5] bp 125°).

1-Methylcyclobutanol. Methylenecyclobutane (14.8 g, Columbia Chemical Co.) was allowed to react with a mixture of 98% formic acid (15 ml) and 11 N sulfuric acid (2.5 ml), first under cooling and later by refluxing the mixture for 30 min. The reaction mixture was then saponified with sodium hydroxide added in a 30% solution to the phenolthalein end point. 1-Methylcyclobutanol was isolated by extraction and purified by distillation on a spinning band column and glpc.

4-Hydroxybutyraldehyde was prepared by the lead tetraacetate oxidation of 1,2,5-pentanetriol.[6] The triol was prepared through hydroxylation of 4-penten-1-ol with hydrogen peroxide in formic acid. The aldehydic compound was isolated as the dinitrophenylhydrazone derivative which was twice recrystallized from ethyl alcohol: mp 122°; nmr of aliphatic part (CH_2Cl_2) δ 1.91 (m, 2), 2.58 (m, 2), 3.77 (t, 2, $J = 6.0$ Hz), 7.68 (t, 1, $J = 5.0$ Hz). 4-Hydroxybutyraldehyde-1-d was isolated from the reaction mixture of the chromic acid oxidation of cyclobutanol-1-d as the 2,4-dinitrophenylhydrazone which was recrystallized from ethyl alcohol and methylene chloride (at $-20°$): mp 118-120°; nmr of aliphatic part (CH_2Cl_2) δ 1.91 (m, 2), 2.47 (t, 2, $J = 6.6$ Hz), 3.76 (t, 2, $J = 6.6$ Hz). Atom-% D 8.10 (Calcd for $C_{10}H_{11}DN_4O_5$ atom-% D, 8.02 (based on 96.2% D in $LiAlD_4$). *Anal.* Calcd for $C_{10}H_{11}D-N_4O_5$: C, 44.61; H, 4.86; N, 20.81. Found: C, 44.59; H, 4.79; N, 20.77.

5-Hydroxy-2-pentanone (K & K Lab. Inc.) was converted to the dinitrophenylhydrazone which was recrystallized from benzene: mp 149.5-150°; nmr (CH_2Cl_2) δ 1.95 (m, 2), 2.07 (s, 3), 2.55 (t, 2, $J = 7.5$ Hz), 3.71 (t, 2, $J = 6.0$ Hz).

4-Keto-1-pentanal was obtained through the chromic acid oxidation of 5-hydroxy-2-pentanone and was isolated as the dinitrophenylhydrazone. The very insoluble derivative was purified by removing all contaminants with appropriate solvents, mp 230-231°. *Anal.* Calcd for $C_{17}H_{16}N_8O_8$ C, 44.35: H, 3.50; N, 24.34; Found: C, 44.52; H, 3.64; N, 24.03.

Cyclohexanol (Fisher reagent), 1-methylcyclohexanol (Aldrich Chemical Co.), and δ-butyrolactone (Aldrich Chemical Co.) were purified through glpc. Levulinic acid (K & K Lab., Inc.) was purified through its dinitrophenylhydrazone derivative. 2-Propanol (Fisher reagent) was used without further purification.

All solvents were reagent grade. Chloroform and benzene were redistilled when needed for column chromatography.

Perchloric acid (70.8%) and concentrated sulfuric acid, both Baker reagents, were diluted as needed and standardized against 0.1 N NaOH (Fisher certified standard reagent).

Potassium dichromate, chromic acid, ammonium metavanadate, all Fisher reagents, and sodium perchlorate anhydrous, G. F. Smith Chem. Co., were used without further purification. Solutions of vanadyl perchlorate were prepared from barium perchlorate (Dessichlora) and vanadyl sulfate (Fisher reagent) according to the procedure of Espenson.[7]

Reaction Products. Determination of Carbonylic Products as 2,4-Dinitrophenylhydrazones. Cyclobutanol (3.529 mmol) and potassium dichromate (0.542 mmol) made up to 50 ml in 1 M aqueous perchloric acid were kept in the dark for 4.5 hr until completion of the oxidation. The solution was then treated overnight with an excess (110 ml) of a freshly filtered saturated solution of 2,4-dinitrophenylhydrazine in 2 M hydrochloric acid. The precipitated dinitrophenylhydrazones were collected by filtration and extracted with hot chloroform. The residue was identified as succindialdehyde bis-2,4-dinitrophenylhydrazone. The ethereal solution from the continuous extraction of the aqueous layer was neutralized with a sodium bicarbonate solution and combined with the chloroform extract. The solid residue from these solutions after evaporation was chromatographed on an acid-washed alumina (Merck, activity III) column using a 100:1 weight ratio of alumina to product and separated into the 2,4-dinitrophenylhydrazones of cyclobutanone and 4-hydroxybutyraldehyde. The alkaline layer from the ether washings was acidified and extracted with chloroform. In the oxidation of cyclobutanol-1-d, succinaldehydic acid was isolated from this fraction.

The most useful method of identification of dinitrophenylhydrazones was by ir comparison (KBr pellets) with authentic samples. The degree of purity of the products could be estimated ($\pm 3\%$) by nmr and tlc when solubility was not a problem. The use of melting points as a criterion of purity was limited by the wide range of values that a dinitrophenylhydrazone exhibits, depending on the ratio of syn/anti isomers in the sample.[8]

γ-Butyrolactone. Cyclobutanol (0.176 mmol) and a potassium dichromate solution (0.0548 M in 1 M perchloric acid, 0.5 ml), made up to 10 ml with additional 1 M perchloric acid, were allowed to react to completion. (The alcohol to oxidant ratio is the same as in the preceding experiment.) Propylene glycol (0.404 mmol) was added; 0.1 ml of the solution was saturated with sodium sulfate and extracted with ethyl acetate (0.3 ml). The extract was analyzed by glpc. A calibration curve was prepared to convert peak area ratios of propylene glycol and γ-butyrolactone to mmol ratios. No attempt was made to isolate and identify succinic acid from the reaction solutions.

Yield of Cyclobutanone as a Function of Oxidation Conditions. A calibration curve was prepared of the glpc (Aerograph Hy-Fi Model 600D, $\frac{1}{8}$ in. $\times$ 60 in. Carbowax column) peak area response factor of cyclobutanone and isoamyl alcohol as a function of mmol ratio. In a typical oxidation procedure cyclobutanol (0.361 mmol), 0.5 ml of potassium dichromate solution (0.0523 M in 1 M perchloric acid), and 2.0 ml of 1 M perchloric acid were diluted with water to 5 ml in a volumetric flask and allowed to react to completion in the dark. After the addition of isoamyl alcohol (0.183 mmol) as an internal standard, a 0.2-ml aliquot was extracted for 2 min with carbon disulfide (0.2 ml), and the extract was analyzed by glpc.

In the irradiation experiments, the thermostated (30°) reaction flask was exposed to a 1000-W tungsten lamp to determine the effect of longer wavelength light ($\lambda > 350$ nm). To determine the effect of uv light ($\lambda > 325$ nm), the reaction mixture in a quartz cell was rotated at room temperature before a Hanau high-pressure immersion lamp in a water-cooled quartz condenser.

Yield of Cyclohexanone in the Presence of Tertiary Alcohols. (a) By Glpc Analysis. A weighed portion (1.0135 g $\pm$ 0.06%) of potassium dichromate solution (0.1404 mmol of chromium(VI)), 2.5 ml of 2 M perchloric acid, 25-230 μl of 1-methylcyclobutanol, and 25 μl (0.02372 g $\pm$ 1.69%) of cyclohexanol (0.2368 mmol) were diluted with water to 5 ml in a volumetric flask. (When 1-methylcyclohexanol was used as the tertiary alcohol, the concentration range was limited because of the low solubility of this alcohol in aqueous solutions.) After the completion of the oxidation, 0.1 ml of the reaction solution was extracted with 0.2 ml of ether for 2 min, and the extract was analyzed by glpc. The yield of cyclohexanone was derived from the ratio in peak area of cyclohexanone product and unreacted cyclohexanol converted to mmol ratio through a calibration curve. In the calculation of the yields, the possibility of overoxidation of cyclohexanone was taken into account.[9,10]

(b) By Gravimetric Determination. To the oxidized reaction mixtures in which 1-methylcyclohexanol was the tertiary alcohol, enough dinitrophenylhydrazine solution was added until a positive test for excess, using acetone, was obtained. The collected precipitate, washed and dried, was analyzed by tlc (benzene-ether 1:1) and consisted of cyclohexanone 2,4-dinitrophenylhydrazone (95%), unreacted reagent (3.4%), and a trace amount of an unidentified product. Yield ranged from 77 to 73.2%.

Yield of Acetone in the Presence of 1-Methylcyclobutanol. Potassium dichromate (0.172 mmol), 1-methylcyclobutanol (3.154 mmol), and 2-propanol (0.591 mmol), made up to 25 ml in 1 M perchloric acid, reacted to completion in the dark at room temperature. The addition of dinitrophenylhydrazine, the work-up, and the product identification followed the procedure outlined in the section on the oxidation products of cyclobutanol, except that the aqueous layer was extracted with small portions of ether instead of continuously. The products were identified as 2,4-dinitrophenylhydrazones of acetone (52%), acetaldehyde (2%), 5-hydroxy-2-pentanone (10%), 4-ketopentanal (21%), and levulinic acid (8%). The acetaldehyde contamination of the acetone was estimated by tlc, using a petroleum ether (bp 30-50°)-ethyl acetate-nitromethane (12:2:1) solvent system and a partially opened tank.[11]

Yield of Organic Product in Chromium(VI)-Vanadium(IV)-Cyclobutanol System. A solution of vanadyl perchlorate (0.259 mmol), perchloric acid (0.45 mmol), cyclobutanol (4.505 mmol), and potassium dichromate (0.0433 mmol) in 5 ml was prepared in a volumetric flask and allowed to react at room temperature for 10

(6) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, 197 (1948).

(7) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 5101 (1964).

(8) G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. J. Fleming, and J. S. Rotka, *ibid.*, **85**, 2784 (1963).

(9) F. Mares, J. Roček, and J. Sicher, *Collect. Czech. Chem. Commun.*, **26**, 2355 (1961).

(10) For details *cf.* A. E. Radkowsky, Ph.D. Thesis, The Catholic University of America, 1966.

(11) D. C. Hoare and W. A. Waters, *J. Chem. Soc.*, 2252 (1964).

min, which was the reaction time required to complete the reduction of chromium(VI) in a parallel experiment in the absence of cyclobutanol. The yield of vanadium(V) was evaluated from the spectrophotometric absorbances at 432 nm and estimated to be 58.7 ± 3.5%, on the basis of absorbances recorded for the reference sample. Ferrous sulfate[12] (0.0885 g) and dinitrophenylhydrazine solution (7 ml) were added, the reaction mixture was stored overnight in a refrigerator, and the precipitate was collected, washed, dried, and identified as 4-hydroxybutyraldehyde dinitrophenylhydrazone by comparison with the ir and nmr spectra of an analytical sample, yield 0.0565 mmol (43.5%), mp 112–113°. Tlc indicated no impurities. The aqueous layer was extracted with three portions of chloroform; the chloroform extracts were neutralized with sodium bicarbonate and evaporated. The residue consisted of unreacted dinitrophenylhydrazine and some decomposition products.

Yield of Vanadium(V). The yield of vanadium(V) was determined in two ways spectrophotometrically: by measuring the gain of vanadium(V) at 350 nm and the loss of vanadium(IV) at 764 nm from the expressions $[V^v]$ (mmol) = $\{((A_{350})_\infty/\epsilon_{V^v}) - [V^v]_0\}$ volume and $[V^v]$ (mmol) = $\{[V^v]_0 - ((A_{764})_\infty/\epsilon_{V^{iv}})\}$ volume where $[V^v]_0$ and $[V^{iv}]_0$ are the initial concentrations. Espenson's[7] values for molar absorptivities were used, and no correction for influence of organic substrates[4c] was applied. Chromium(III) absorbs slightly at 350 nm, but at the concentrations used in this work, its contribution to the absorbance was negligible. Vanadium(IV) is the only species absorbing at 764 nm but the low concentrations and absorptivity made it necessary to use an expanded 0–0.1 reading scale, which resulted in an increase in recorder noise and introduced an uncertainty in absorbance readings. Both the yield of vanadium(V) and kinetic data were obtained from the same runs.

In a typical set of experiments, an aqueous stock solution was prepared with perchloric acid (0.0628 M), ammonium metavanadate (0.00195 M), and vanadyl perchlorate (0.00258 M). Aliquots of this solution were weighed into glass-stoppered 1-cm spectrophotometric quartz cells and the volume was calculated by using the density value of 0.9995 g cm^{-3} for a 0.5% perchloric acid solution at 25°. Weighed volumes of cyclobutanol were injected (0–0.63 mmol). After thermally equilibrating the cells at 25 ± 0.05°, a uniform amount of chromic acid solution (1.36 × 10^{-3} mmol in chromium(VI), ±0.1%) was quickly injected, the cell was shaken, and readings were begun. The average deviation in the yield of vanadium(V) as calculated from measurements at 350 and 764 nm was 2.2%.

However, the uncertainties in the V^v yields were considerably greater (up to ±11%) in those experiments in which the effect of V^{iv} was determined and where larger amounts of V^{iv} therefore had to be added.

Kinetic Measurements. Chromium(VI) Oxidations. The rates of chromium(VI) oxidation of organic substrates, at specified temperatures, were determined by the procedure outlined by Roček and Riehl.[13]

Chromium(VI) Oxidation of Vanadium(IV). The preparation of the kinetic runs was described above. All stock solutions which involved varying ratios of vanadium(IV) and vanadium(V) were 1 M in sodium perchlorate. Initial absorptions, A_0, rates of change of the absorbance, and final absorptions, A_∞, measured after 1 hr, were recorded at 350 and 764 nm.

In all the kinetic studies of this work, the product of the concentration of chromium(VI) and hydrogen ions ([Cr(VI)][H$^+$]) had a value of 3.1 × 10^{-5}. Experience has shown that under these conditions the complete rate expression (eq 1) has to be used. However, it can be redefined in terms of a new rate constant as given by eq 2 and 3.[7]

$$-d[Cr^{vi}]/dt = [V^{iv}]^2/[V^v]\{k[HCrO_4^-] + k'[H^+][HCrO_4^-]^2\} \quad (1)$$

$$k_{app} = \frac{[V^v]}{[V^{iv}]^2[Cr^{vi}]}\frac{1}{dt}\frac{d[Cr^{vi}]}{} \quad (2)$$

$$k_{app} = [HCrO_4^-]/[Cr^{vi}]\{k + k'[H^+][HCrO_4^-]\} \quad (3)$$

a. In the Absence of an Organic Substrate. The stoichiometry of the inorganic reaction is given by

$$Cr^{vi} + 3V^{iv} = Cr^{iii} + 3V^v \quad (4)$$

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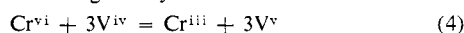
(12) It was previously established that the ferric compound formed by vanadium(V) oxidation of ferrous sulfate does not oxidize cyclobutanol or chromium(III) even in 2 M acid solution.

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

At 350 nm the absorption of these species has to be considered (eq 5).

$$A_{350} = \epsilon_{Cr^{vi}}[Cr^{vi}] + \epsilon_{V^v}[V^v] + \epsilon_{Cr^{iii}}[Cr^{iii}] \quad (5)$$

From the stoichiometry (eq 4) and assuming $[Cr^{vi}]_\infty = 0$, the instantaneous concentration of chromium(VI) is given by eq 6 and the rate of disappearance of chromium(VI) by eq 7. The appro-

$$[Cr^{vi}]_t = \frac{A_t - A_\infty}{\epsilon_{Cr^{vi}} - 3\epsilon_{V^v} - \epsilon_{Cr^{iii}}} \quad (6)$$

$$-\left(\frac{d[Cr^{vi}]}{dt}\right)_t = \left(\frac{dA_{350}}{dt}\right)_t (1/(\epsilon_{Cr^{vi}} - 3\epsilon_{V^v} - \epsilon_{Cr^{iii}})) \quad (7)$$

priate absorbance data were obtained graphically from A_{350} vs. time plots.

At 764 nm only vanadium(IV) absorbs so that the rate of vanadium(IV) oxidation can be determined independently from the 350-nm measurements. The decrease in the vanadium(IV) concentrations at time t is given by

$$[V^{iv}]_0 - [V^{iv}]_t = (A_0 - A_t)_{764}/\epsilon_{V^{iv}} \quad (8)$$

and is equal to the increase in the concentration of vanadium(V). One third of this amount is the decrease in the concentration of chromium(VI). The rate of vanadium(IV) oxidation, at time t, as given by eq 9, is equal to three times the rate of consumption of

$$\left(\frac{d[V^{iv}]}{dt}\right)_t = \left(\frac{dA_{764}}{dt}\right)_t \bigg/ \epsilon_{V^{iv}} \quad (9)$$

chromium(VI). These values were determined graphically from A_{764} vs. time plots.

Thus both the instantaneous concentrations and the rates of disappearance of chromium(VI) could be determined from two independent measurements, eq 7 or 9, and these values were used to calculate k_{app} according to eq 2.

The values of k and k' were then determined from eq 3 for reactions with and without added sodium perchlorate. The required values for [HCrO$_4^-$] were derived from the equilibrium relationship

$$[Cr_2O_7^{2-}]/[HCrO_4^-] = 98 \ M^{-1} \quad (10)$$

b. In the presence of an organic substrate, the stoichiometry of eq 4 no longer holds and eq 6 and 7 therefore have to be modified. Equations 8 and 9, which are still valid, can be used to determine the contribution of vanadium(V) to the total absorption at 350 nm (eq 11 and 12). ϵ_{V^v} and $\epsilon_{V^{iv}}$ are the molar absorptivities of vanadium-

$$(A_{V^v}^{350})_t = \epsilon_{V^v}[V^v]_0 + (\epsilon_{V^v}/\epsilon_{V^{iv}})(A_0 - A_t)^{764} \quad (11)$$

$$(dA_{V^v}/dt)_t^{350} = \epsilon_{V^v}/\epsilon_{V^{iv}}(dA^{764}/dt)_t \quad (12)$$

(V) at 350 nm and of vanadium(IV) at 764 nm, respectively. Hence the concentration of chromium(VI) at time t and its rate of disappearance were evaluated using the expressions of eq 13 and 14.

$$[Cr^{vi}]_t = \frac{1}{\epsilon_{Cr^{vi}}}(A - A_{V^v})_t^{350} \quad (13)$$

$$-\left(\frac{d[Cr^{vi}]}{dt}\right)_t = \frac{1}{\epsilon_{Cr^{vi}}}\left\{\left(\frac{dA^{350}}{dt}\right)_t - \left(\frac{\epsilon_{V^v}}{\epsilon_{V^{iv}}}\right)\left(\frac{dA^{764}}{dt}\right)_t\right\} \quad (14)$$

respectively. The contribution to the absorbance by the chromium(III) species was neglected.

To test the reliability of deriving the chromium(VI) data at 350 nm from the absorbances at 764 nm, the rate of consumption of chromium(VI) was calculated, in the absence of cyclobutanol, by eq 14 and 7. The average agreement between the two methods was within 4%.

The mmol ratio of cyclobutanol to vanadium(IV) was not always duplicated in the runs at both wavelengths. Calibration curves were prepared which correlated this ratio to the rates of consumption and to the concentrations of vanadium(IV). Hence, the expressions of eq 11–14 could be evaluated by interpolation for any concentration of cyclobutanol or other variations in solution composition. In this phase of the study, only k_{app} (eq 2) was evaluated and no further work was done to calculate k and k'.

Results

Oxidation Products. A. Chromic Acid Oxidation of Cyclobutanol.

The products formed in the oxidation of cyclobutanol and of 1-deuteriocyclobutanol are summarized in Table I. In both cases, the main oxidation

Table I. Products of the Chromic Acid Oxidation of Cyclobutanol[a] and 1-Deuteriocyclobutanol[b]

	Yield, %, from	
Product	Cyclobutanol	1-Deuterio-cyclobutanol
Cyclobutanone	48 (25)[c]	20
4-Hydroxybutyraldehyde	31 (23)	32[d]
Succinaldehyde	Trace (4)	9
γ-Butyrolactone	13 (e)	14
Succinaldehydic acid	0 (9)	10
Cyclopropyl-carboxaldehyde	0 (0)	0
% total yield based on Cr^{vi}	92 (61)	85

[a] Cyclobutanol, 3.529 mmol, $K_2Cr_2O_7$, 0.542 mmol, [$HClO_4$], 1 M. [b] Cyclobutanol-l-d, 3.865 mmol, K_2CrO_7, 0.517 mmol, [$HClO_4$], 1 M. [c] Values in parentheses refer to conditions used by Demjanov and Dojarenko:[14] cyclobutanol, 3.51 mmol, CrO_3, 2.14 mmol, [H_2SO_4], 0.84 M, 50° and then reflux. [d] 4-Hydroxy-1-deuteriobutyraldehyde. [e] Not determined.

products are cyclobutanone and 4-hydroxybutyraldehyde. These two compounds are of the same oxidation level with respect to cyclobutanol and are not interconvertible under the reaction conditions. In the oxidation of the deuterated alcohol, the deuterium label is retained by the hydroxyaldehyde and is located at the aldehydic carbon. All other compounds which were isolated are higher oxidation products, which were obviously formed by further oxidation of 4-hydroxybutyraldehyde; cyclobutanone is essentially stable toward chromic acid and to the acidic medium under the reaction conditions employed (cf. Table IX).

Demjanov and Dojarenko[14] reported the formation of large amounts of cyclopropanecarboxaldehyde in the oxidation of cyclobutanol. We therefore paid special attention to the detection of this compound among the oxidation products, but with completely negative results, despite the fact that we were able to get a practically quantitative yield of this aldehyde by chromic acid oxidation of cyclopropylcarbinol. The determination of reaction products was carried out both under the standard conditions used throughout this study as well as under the conditions employed by Demjanov and Dojarenko.[15]

The results of a study of the yields of cyclobutanone under a wide range of reaction conditions are given in Table II. The yields are quite insensitive to the substrate to oxidant ratio (except for the extreme value where overoxidation of primary reaction products becomes important) and are not markedly influenced by the presence of fairly large amounts of chromium(III) sulfate (up to Cr^{iii}/Cr^{vi} ratio of 12:2). The yields of

(14) N. J. Demjanov and M. Dojarenko, Ber., 41, 43 (1908).

(15) The formation of cyclopropanecarboxaldehyde observed by Demjanov and Dojarenko[14] in their chromic acid oxidation of cyclobutanol can be traced back to their use of an impure sample of the substrate. These authors used cyclobutanol synthesized by the Simonini method, which is contaminated by large amounts of cyclopropylcarbinol.[16]

(16) N. J. Demjanov and M. Dojarenko, Ber., 40, 2594 (1907).

Table II. Yield of Cyclobutanone in the Chromic Acid Oxidation of Cyclobutanol under Different Reaction Conditions[a]

Temp, °C	Cr^{vi}, M	$HClO_4$, M	Cyclobutanone yield, %
20	0.0041	1.0	49.1
20	0.0106	1.0	46.5 (34.8)[b]
20	0.021	1.0	48.0
20	0.041	1.0	50.8
20	0.064	1.0	34.9
20	0.0106	1.0	45.4 (34.1)[b]
30	0.0106	1.0	45.8 (33.9)[b]
40	0.0106	1.0	45.0
50	0.0106	1.0	39.0 (31.8)[b]
60	0.0106	1.0	37.7
20	0.0106	0.1	32.5
20	0.0106	0.5	43.3
20	0.0106	1.0	46.3
20	0.0106	1.78	55.2
20	0.0106	2.2	50.2
20	0.0106	3.25	50.3
20	0.0106	4.3	57.3
20	0.0106	5.3	71.4
20	0.0106	6.4	74.5
20	0.0106	0.95[c]	41.8
20	0.0106	2.39[c]	49.1
20	0.0106	4.77[c]	47.0 (35.3)[b]

[a] Cyclobutanol, 0.064 M. [b] 1-Deuteriocyclobutanol. [c] H_2SO_4.

cyclobutanone obtained in sulfuric acid are somewhat lower than those in perchloric acid, but the difference is not large. There is some decrease in the ketone yield with increasing temperature, but the most important trend which we observe is the increase in the yield of cyclobutanone with increasing acidity, especially in perchloric acid.

We have also determined the effects of light on the reaction. While reaction rates were greatly accelerated by irradiation of the reaction mixture with visible light (tungsten lamp) or with uv light (Hanau high-pressure Hg lamp), the yields of cyclobutanone decreased only moderately from 45.3% in the dark to 39.3% in visible light and to 37.2% in uv light. The yield of cyclobutanone from 1-deuteriocyclobutanol decreased from 35.3% in the dark to 33.5% in visible light. The most significant result of these studies is that the yield of cyclobutanone never fell below 33%.

It should be noted that in the oxidation of 1-deuteriocyclobutanol the yield of cyclobutanone is consistently lower than for cyclobutanol, and that larger amounts of higher oxidation products of 4-hydroxybutyraldehyde-l-d are formed (Table I).

B. Vanadium(IV) Induced Oxidation of Cyclobutanol.

Chromium(VI) oxidizes vanadium(IV) to vanadium(V) quite readily at conditions[7] under which the oxidation of cyclobutanol by either chromium(VI) or by vanadium(V) is slow. However, when a mixture of vanadium(IV) and cyclobutanol is oxidized by chromium(VI), there is a marked decrease in the yield of vanadium(V), down to 43%, with increasing cyclobutanol concentrations (Table III). In addition, the data of Table IV show that there is a competition between vanadium(IV) and cyclobutanol for the oxidant, since the yield of vanadium(V) increases from 40 to 61% for a threefold increase in the ratio of vanadium(IV) to cyclobutanol. The only organic oxidation product which was isolated from the reaction mixture was the carbon–carbon bond cleavage product 4-hydroxybutyraldehyde.

Table III. Effect of Cyclobutanol on Vanadium(V) Yields Reaction Rates[a]

Cyclobutanol, M	$-d[V^{iv}]/dt,^b$ %	% Cr^{vi} used after 150 sec	% yield V^v
0.0	100	55.8	100
0.0052	78		
0.0077		58.8	70.5
0.0090	76		
0.0111		59.8	64.5
0.0141	64		
0.0244		59.0	60.5
0.0284	60		
0.0333		58.5	58
0.0382	57		
0.0660		57.2	55
0.0793	52		
0.118		57.7	50
0.133	39		
0.141	48		
0.216		55.7	43.5
0.262	40		
0.395	38		

[a] Conditions: 25°, $[V^{iv}]$, 2.58×10^{-3} M, $[V^v]$, 1.95×10^{-3} M, $[Cr^{vi}]$, 0.470–0.490 $\times$ 10^{-3} M, $[HClO_4]$, 0.0628 M. [b] Relative initial rates determined at 764 nm.

Table IV. Vanadium(IV) to Cyclobutanol Concentrations and Yield of Vanadium(V)[a]

$10^3[V^{iv}]$, M	10^2[Cyclobutanol], M	% yield vanadium(V)[b]
2.66	0	98
2.66	2.5	40
7.55	0	97
7.55	2.5	61

[a] Conditions: 25°, $[V^v]$, 2.09×10^{-3} M, $[Cr^{vi}]$, 0.47×10^{-3} M, $[HClO_4]$, 0.066 M, $\mu(NaClO_4)$, 1 M. [b] Data recorded at 350 nm.

Table V. Oxidation of Organic Substrates in the Chromium(VI)–Vanadium(IV) System[a] at 25°

Alcohol	M	$[HClO_4]$, M	V^v yield,[b] %	4-Hydroxybutanal yield,[c] %
None	0	0.10	100	
Cyclobutanol	0.045	0.09	59	43.5
Cyclobutanol	0.062	0.063	52	
Cyclobutanol-1-d	0.066	0.063	56	
2-Propanol	0.058	0.063	78	

[a] $[V^{iv}]$, 2.3×10^{-3} M, $[Cr^{vi}]$, 5.6×10^{-4} M. [b] Spectrophotometric determination. [c] Gravimetric determination of dinitrophenylhydrazone.

$$\text{H—OH} \xrightarrow{Cr^{v}-V^{iv}} HO(CH_2)_3CHO \qquad (15)$$
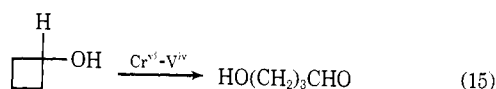
Table V and Figure 1 give additional data comparing the effect of cyclobutanol on the yields of vanadium(V) in the chromic acid oxidation of vanadium(IV) with the effect exerted by other substrates. The much smaller effect of 2-propanol shows that this alcohol is obviously less efficient in competing with vanadium(IV) than cyclobutanol. The similarity between the effects of cyclobutanol and 1-deuteriocyclobutanol indicates that the oxidation of cyclobutanol taking place under these conditions is subject to only a small isotope effect.

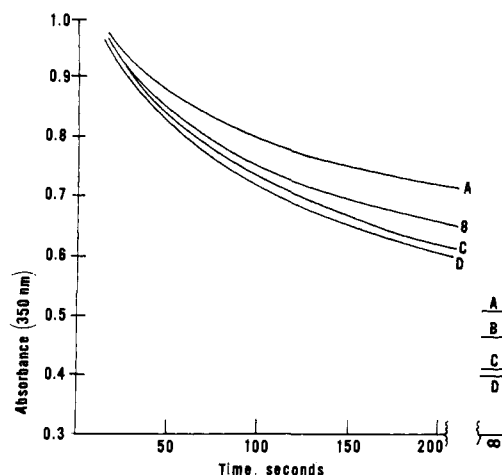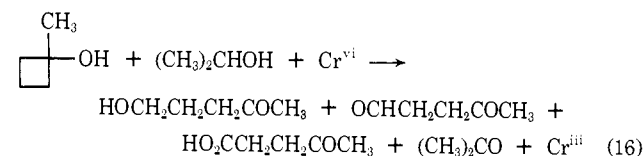**C. Oxidation of 1-Methylcyclobutanol in the Pres-**

Figure 1. Rate of oxidation of vanadium(IV) by chromium(VI) and yield of vanadium(V) in presence of organic substrates at 25°: (A) no organic substrate; (B) 2-propanol; (C) 1-deuteriocyclobutanol; (D) cyclobutanol. Concentrations: $[Cr^{vi}]_0$, 0.56 $\times$ 10^{-3} M, $[VO^{2+}]_0$, 0.23 $\times$ 10^{-2} M, $[H^+]$, 0.0628 M, alcohols, 0.06 M.

ence of Secondary Alcohols. As we reported earlier, 1-methylcyclobutanol, unlike most other tertiary alcohols, is directly oxidized by chromic acid.[17] However, as its reactivity is relatively low compared with those of the oxidation products formed in the reaction, a far-reaching degradation is taking place, and no simple oxidation products can be isolated.

An entirely different situation is observed if 1-methylcyclobutanol is subjected to chromic acid in the presence of a secondary alcohol. In order to determine qualitatively and quantitatively whether 1-methylcyclobutanol under these conditions was indeed oxidized, we determined its effect on the yield of cyclohexanone formed in the chromic acid oxidation of cyclohexanol in the presence of increasing amounts of 1-methylcyclobutanol. The results are given in Table VI and show clearly that the yields of cyclohexanone are drastically reduced in the presence of larger amounts of 1-methylcyclobutanol. Table VII shows that no similar reduction in the yield of cyclohexanol is produced if 1-methylcyclohexanol is used instead of 1-methylcyclobutanol.

The products which are formed in the oxidation of 1-methylcyclobutanol in the presence of a secondary alcohol (cyclohexanol or isopropyl alcohol) are entirely analogous to the cleavage products formed in the oxidation of cyclobutanol. In an experiment using a 5.3:1 ratio of 1-methylcyclobutanol–2-propanol, we were able to isolate and identify 5-hydroxy-2-pentanone and its oxidation products 4-keto-1-pentanal and levulinic acid (Table VIII).

$$\text{CH}_3\text{—OH} + (CH_3)_2CHOH + Cr^{vi} \longrightarrow$$
$$HOCH_2CH_2CH_2COCH_3 + OCHCH_2CH_2COCH_3 +$$
$$HO_2CCH_2CH_2COCH_3 + (CH_3)_2CO + Cr^{iii} \qquad (16)$$

Reaction Rates. Chromic Acid Oxidation of Cyclobutanols. Table IX summarizes the oxidation rates for cyclobutanols and their related compounds. Our

(17) J. Roček and A. E. Radkowsky, *Tetrahedron Lett.*, No. 24, 2835 (1968).

Table VI. Effect of 1-Methylcyclobutanol on the Chromic Acid Oxidation of Cyclohexanol[a]

[1-Methylcyclobutanol]/[cyclohexanol]	0	1.2	2.0	3.2	4.4	5.6	8.0	9.2
Cyclohexanone, % yield	80.2	66.4	52.2	52.4	44.8	43.7	35.1	39.1

[a] [HClO$_4$], 1 M, [K$_2$Cr$_2$O$_7$], 1.40 × 10^{-2} M, [cyclohexanol], 4.74 × 10^{-2} M; cyclohexanone determined by glpc.

Table VII. Effect of 1-Methylcyclohexanol on the Chromic Acid Oxidation of Cyclohexanol[a]

[1-Methylcyclohexanol]/[cyclohexanol]	0	0.76	1.76	2.74	3.43
Cyclohexanone, % yield[b]	81.0	80.2	80.0	80.4	78.4
Cyclohexanone, % yield[c]	77.0	75.5		73.2	

[a] Conditions: [HClO$_4$], 1 M; [K$_2$Cr$_2$O$_7$], 1.40 × 10^{-2} M; [cyclohexanol], 4.82 × 10^{-2} M. [b] Determined by glpc. [c] Determined by gravimetric analysis of dinitrophenylhydrazones.

Table VIII. Reaction Products in the Chromic Acid Oxidation of a Mixture of 1-Methylcyclobutanol and Isopropyl Alcohol[a]

Product	Yield, %
Acetone	51.8
5-Hydroxy-2-pentanone	10.1
4-Keto-1-pentanal	20.6
Levulinic acid	8.2
Total	90.7

[a] Conditions: 3.15 mmol of 1-methylcyclobutanol, 0.591 mmol of isopropyl alcohol, 0.172 mmol of K$_2$Cr$_2$O$_7$ in 1 M HClO$_4$ at room temperature.

Table IX. Second-Order Rate Constants[a] for Chromic Acid Oxidations at 29.6°

Substrate	M	10^2k, M^{-1} sec^{-1}	$k_{cyclobutanol}/k_{substrate}$
Cyclobutanol	0.15	4.24	
	0.097	4.46	
Cyclobutanol-1-d	0.097	0.646	8.9[b]
1-Methylcyclobutanol	0.119	0.018	220
Cyclobutanone	0.117	3.57 × 10^{-3}	1.2 × 10^3
5-Hydroxy-2-pentanone	0.102	1.27	3.4
2-Propanol	0.095	1.39	3.1
Cyclohexanol	0.101	2.73	1.63

[a] Concentrations: [Cr^{vi}], 0.6 × 10^{-3} M, [HClO$_4$], 1 M. [b] Experimental value, 6.9, corrected for 96.29% D content of LiAlD$_4$ used in synthesis of 1-deuteriocyclobutanol.

results confirm earlier observations that the oxidation of cyclobutanol is faster than that of cyclohexanol.[18] The results given in the table also show that cyclobutanone is quite unreactive toward chromic acid. The reaction exhibits a sizable deuterium isotope effect, k_H/k_D = 8.9. It should be noted that 5-hydroxy-2-pentanone is oxidized at a rate comparable to cyclobutanol and faster than the deuterated analog. It is likely that the oxidation rate of 4-hydroxybutyraldehyde is in the same range, so that its overoxidation is competitive with the oxidation of cyclobutanol.

Oxidation of Mixtures of Cyclobutanol and Vanadium(IV) by Chromic Acid. Vanadium(IV) is readily oxidized by chromic acid. The reaction mechanism of the oxidation is given by Scheme I. The rate of the

(18) (a) H. G. Kuivila and W. J. Becker III, *J. Amer. Chem. Soc.*, 74, 5329 (1952); (b) J.-C. Richer and N. T. T. Hoa, *Can. J. Chem.*, 47, 2479 (1969).

Scheme I

$$Cr^{vi} + V^{iv} \underset{}{\overset{fast}{\rightleftarrows}} Cr^{v} + V^{v} \qquad (17)$$

$$Cr^{v} + V^{iv} \xrightarrow[limiting]{rate} Cr^{iv} + V^{v} \qquad (18)$$

$$Cr^{iv} + V^{iv} \longrightarrow Cr^{iii} + V^{v} \qquad (19)$$
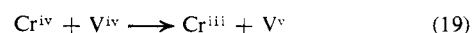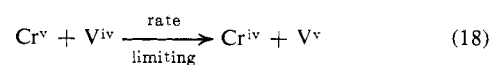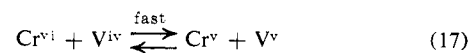
reaction is determined by the rate (eq 20) of reaction 18

$$v = k[Cr^{v}][V^{iv}] \qquad (20)$$

from which the complete rate law (eq 1) can be derived.

As both chromium(VI) and vanadium(V) are too unreactive to be responsible for the oxidation of cyclobutanol under the low acidities under which the experiments were carried out, either chromium(V) or chromium(IV) must be responsible for the observed induced oxidation of cyclobutanol.[19]

The effect of cyclobutanol on the chromium(VI)–vanadium(IV) rate law (eq 1) was examined in detail. Table III indicates that both the rates of vanadium(IV) oxidation and the yields of vanadium(V) show a marked decrease as the concentration of cyclobutanol is increased, the decrease in vanadium(IV) oxidation rates approximately paralleling the decreases in vanadium(V) yield. The data in the third column show that there is little variation in the amount of chromium(VI) consumed during the first half-life of the reaction, that is, cyclobutanol does not affect the rate of reduction of chromium(VI).[20] The rate law for the inorganic reaction (eq 1) involves a second-order dependence on vanadium(IV) and a minus first-order dependence on vanadium(V). Part A of Table X shows that, independent of cyclobutanol concentrations, the consumption of chromium(VI) decreases with increasing vanadium(V) concentrations; in part B the opposite trend is observed as the concentration of vanadium(IV) increases. In each case, the value of the rate constant, k_{app}, is within close range of the value, 1.30 M^{-1} sec^{-1}, obtained for the inorganic oxidation reaction,[21] indicating that the reaction, in the presence of cyclobutanol, retains the same dependency on vanadium(V) and vanadium(IV) as the inorganic reaction.

Discussion

Chromium(VI) Oxidation Step. The kinetics of the chromic acid oxidation of cyclobutanol does not differ from that of other alcohols. The oxidation is first order in chromic acid, first order in the alcohol, and has a

(19) No kinetic evidence was found for either a vanadium(V)–vanadium(IV) or a chromium(VI)–vanadium(V) complex of unusual reactivity toward cyclobutanol. The addition of cyclobutanone to the reaction mixture had no effect on the reaction kinetics.

(20) Because of the complexity of the rate law, it was more convenient and reliable to compare the amounts of chromium(VI) remaining after a given standard time interval than to compare initial rates obtained from extrapolation of curved plots to zero time. In later work a more elaborate computer method was used.[4c]

(21) The rate constants k_{app} of Table X are derived only from initial slope measurements. The value of k_{app}, 1.30 M^{-1} sec^{-1}, in the absence of cyclobutanol, was calculated in a more rigorous manner according to eq 3.

Table X. Effect of Vanadium(V) and Vanadium(IV) Concentrations[a]

$10^3[V^v]$, M	$10^3[V^{iv}]$, M	10^2[Cyclo-butanol], M	$10^5 v_0$, M sec^{-1}	k_{app}, M^{-1} sec^{-1}
A. Effect of [Vanadium(V)]₀				
0.549	2.74	0	0.78	1.24
1.07	2.64	0	0.57	1.87
1.84	2.65	0	0.25	1.45
3.14	2.90	0	0.18	1.42
0.549	2.74	2.8	0.89	1.40
1.07	2.64	2.8	0.60	1.87
1.84	2.65	2.8	0.29	1.68
3.14	2.90	2.8	0.17	1.37
0.549	2.74	9.0	0.84	1.33
1.07	2.64	9.0	0.58	1.94
1.89	2.65	9.0	0.33	1.87
4.14	2.90	9.0	0.16	1.28
B. Effect of [Vanadium(IV)]₀				
2.09	2.66	0	0.20	1.53
2.09	5.25	0	0.89	1.46
2.09	7.55	0	2.19	1.75
2.09	2.66	2.8	0.24	1.53
2.09	7.55	2.8	2.34	1.87

[a] $25 \pm 0.05°$; concentrations: $[Cr^{vi}]$, 0.43×10^{-3} M, [HClO₄], 0.006 M, μ(NaClO₄), 1 M; $v_0 = -d[Cr^{vi}]/dt$ at time 0; $k_{app} = v_0[V^v]/[V^{iv}]^2[Cr^{vi}]$ (eq 2).

first- and second-order term in hydrogen ions. The oxidation is subject to a large primary kinetic deuterium isotope effect ($k_H/k_D = 8.9$). The corresponding tertiary alcohol, 1-methylcyclobutanol, is relatively unreactive, giving additional evidence for the involvement of the α-hydrogen atom in the rate-limiting step of the oxidation. Further, the ring-cleavage product of the oxidation of the deuterated analog, cyclobutanol-1-d, retains the deuterium atom in the aldehydic group. This leads to the conclusion that the product formed in the rate-limiting step is cyclobutanone and not the cleavage compound. As the rate-limiting step must involve the reduction of chromium(VI), one can conclude that cyclobutanone is formed by chromium(VI) oxidation of cyclobutanol.

The low reactivity of 1-methylcyclobutanol toward chromium(VI) stands in sharp contrast to its high reactivity toward one-electron oxidants like manganese-(III),[22] vanadium(V),[22] or cerium(IV).[23] This difference in behavior suggests strongly that the chromium-(VI) oxidation of cyclobutanol is a two-electron process.

There is therefore little reason to doubt that the first stage of the reaction proceeds by the same mechanism

Scheme II

$$\text{(21)}$$
$$\text{(22)}$$
$$\text{(23)}$$
$$\text{(24)}$$
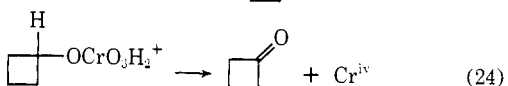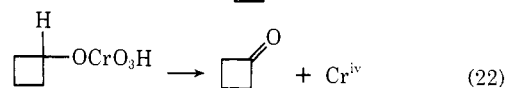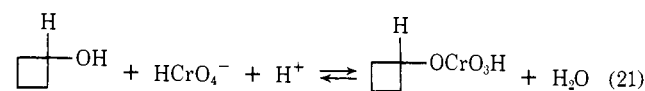
(22) J. Roček and A. E. Radkowsky, J. Org. Chem., 38, 89 (1973).
(23) K. Meyer and J. Roček, J. Amer. Chem. Soc., 94, 1209 (1972).

which has been well established for other chromic acid oxidations of primary and secondary alcohols (Scheme II).

Chromium(IV) Oxidation Step. The chromium(IV) compound formed in the rate-limiting step of the chromium(VI) oxidation (eq 22) can either react with chromium(VI) to undergo oxidation to chromium(V) (eq 25) or it can oxidize an organic substrate (eq 26).

$$Cr^{iv} + Cr^{vi} \longrightarrow 2Cr^{v} \qquad (25)$$

$$Cr^{iv} + S \longrightarrow Cr^{iii} + R\cdot \qquad (26)$$
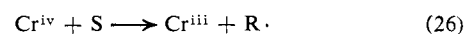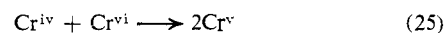
Reaction 25 had for a long time been widely accepted as the most probable next step in chromic acid oxidations. However, this is most unlikely on thermodynamic grounds, as the estimated equilibrium constant ($K = 4 \times 10^{-14}$) for the reaction makes this process highly unfavorable.[4c, 24]

It would be impossible to distinguish between the oxidation of the chromium(IV) intermediate (reaction 25) or its reduction reaction (reaction 26) from chromic acid oxidation studies alone. However, a clear distinction can be drawn from the following results reported in the preceding section.
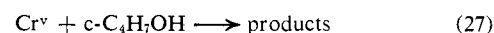
(a) In the chromic acid oxidation cyclobutanol forms two products of the same oxidation level (with respect to cyclobutanol). One, cyclobutanone is formed in an oxidation involving carbon–hydrogen bond cleavage, while the second product, 4-hydroxybutyraldehyde, results from a ring opening reaction involving the cleavage of a carbon–carbon bond (Tables I and II).

(b) Only 4-hydroxybutyraldehyde is formed in the induced oxidation in the presence of vanadium(IV) (eq 15).

(c) The presence of cyclobutanol in the chromic acid oxidation of vanadium(IV) reduces the yield of vanadium(V) and the rate of the vanadium(IV) oxidation, but has no effect on either the rate or on the rate law governing the reduction of chromium(VI) (Tables III, IV, and X).

(d) Cyclobutanone is formed in the rate-limiting chromium(VI) oxidation. The last point eliminates chromium(VI) and makes it clear that either chromium(V) or chromium(IV) must be responsible for the cleavage reaction.

In Scheme I it was shown that chromium(V) is formed in an equilibrium step (reaction 17) preceding the rate-limiting step (reaction 18). If chromium(V) could oxidize both vanadium(IV) (reaction 18) and cyclo-

$$Cr^{v} + c\text{-}C_4H_7OH \longrightarrow products \qquad (27)$$

butanol (reaction 27) at comparable rates, then the rate of the reaction would be given by

$$v = [Cr^{v}](k_{18}[V^{iv}] + k_{27}[S]) \qquad (28)$$

The overall rate of the chromic acid reduction thus would increase in proportion to the concentration of the substrate (cyclobutanol).[25]

On the other hand, as chromium(IV) is formed in the rate-limiting step (reaction 18), oxidation of cyclo-

(24) E. A. M. Wetton and W. C. E. Higginson, J. Chem. Soc., 5890 (1965).
(25) An example of a chromium(V) oxidation is the induced oxidation of iodide ions by chromic acid in the presence of vanadium(IV) as inductor.[7] The induction of chromic acid by the iodide ion–vanadium(IV) system is practically instantaneous for conditions under which vanadium(IV) alone reacts at moderate rates and iodide ions practically not at all.
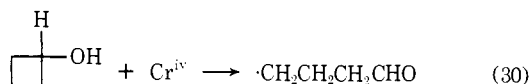
butanol by this valence state (reaction 29) will be with-

$$Cr^{iv} + c\text{-}C_4H_7OH \longrightarrow products \qquad (29)$$
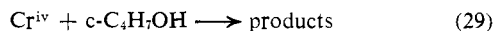
out effect on the rate of induction of chromium(VI), although it will reduce the amount of vanadium(V) formed by diverting chromium(IV) from the oxidation of vanadium(IV) (reaction 19) to the oxidation of cyclobutanol (reaction 29).

The observation that the oxidation of cyclobutanol to 4-hydroxybutyraldehyde takes place without any effect on the rate or rate law of the reduction of chromium(VI) by vanadium(IV) thus permits us to identify chromium(IV) as the oxidant responsible for the ring-cleavage oxidation. We can further conclude that chromium(V) is not very reactive toward cyclobutanol.

The chromium(IV) oxidation of cyclobutanol (reaction 30) leads to a free radical which, in all probability,

$$\cdot CH_2CH_2CH_2CHO + H_2CrO_4 \longrightarrow$$
$$H_2O_3CrOCH_2CH_2CH_2CHO \quad (31)$$
$$H_2O_3CrOCH_2CH_2CH_2CHO + H_2O \longrightarrow$$
$$H_3CrO_4 + HOCH_2CH_2CH_2CHO \quad (32)$$

is further oxidized by chromium(VI) to yield, after hydrolysis, a chromium(V) compound and 4-hydroxybutyraldehyde (reactions 31 and 32).
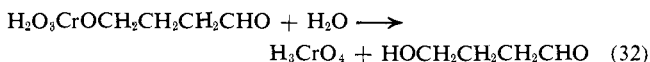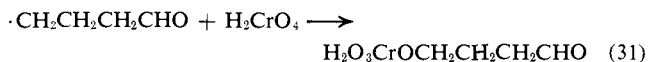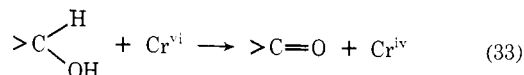
It should be noted that chromium(IV) reacts with unstrained aliphatic alcohols by carbon–hydrogen and not by carbon–carbon cleavage.[4c] The reason for the carbon–carbon bond cleavage in the oxidation of cyclobutanol can obviously be found in the strain present in the four-membered ring which is partially relieved in a transition state involving the breaking of one of the carbon–carbon bonds of the ring. Oxidative cleavage of the cyclobutane ring occurs also in all other one-electron oxidations of cyclobutanol investigated so far.[22,23]

The nature of the chromium(IV) oxidation of cyclobutanol is in full agreement with the quite similar effectiveness of cyclobutanol and of 1-deuteriocyclobutanol in reducing the yields of vanadium(V), which points to a very low deuterium isotope effect for the chromium(IV) oxidation of cyclobutanol.

As the chromium(IV) oxidation of cyclobutanol does not involve any breaking of the carbon–hydrogen bond, it was expected that the usually unreactive tertiary alcohols should be able to undergo quite easily a similar type of oxidative cleavage as the secondary cyclobutanol. This reaction, however, cannot be observed directly in the chromic acid oxidation of a tertiary cyclobutanol because of the very low reactivity of the alcohol toward chromium(VI). However, as we have shown in an earlier section of this paper, an induced oxidation of 1-methylcyclobutanol is easily observed in the presence of a secondary alcohol, cyclohexanol or isopropyl alcohol, which serves to supply the chromium(IV) necessary for the reaction. Scheme III indicates the reactions taking place in induced chromic acid oxidation of 1-methylcyclobutanol, using a secondary alcohol as inductor. We believe that chromium(IV) oxidation is also responsible for other types of cleavage reactions which have been observed in the course of chromic

Scheme III

$$>C\overset{H}{\underset{OH}{\diagdown}} + Cr^{vi} \longrightarrow >C=O + Cr^{iv} \qquad (33)$$

$$\underset{CH_3}{\square}\text{—OH} + Cr^{iv} \longrightarrow \cdot CH_2CH_2CH_2COCH_3 + Cr^{iii} \quad (34)$$

$$\cdot CH_2CH_2CH_2COCH_3 + Cr^{vi} \longrightarrow HOCH_2CH_2CH_2COCH_3 + Cr^{v} \qquad (35)$$
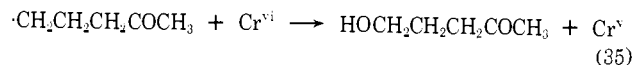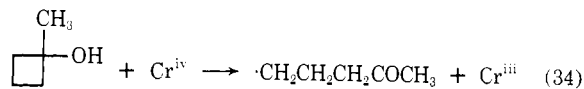
acid oxidations, e.g., the cleavage of phenyl-tert-butylcarbinol to benzaldehyde and tert-butyl alcohol (reaction 36).[1b]

$$C_6H_5CHOHC(CH_3)_3 \longrightarrow$$
$$C_6H_5COC(CH_3)_3 + C_6H_5CHO + (CH_3)_3COH \quad (36)$$
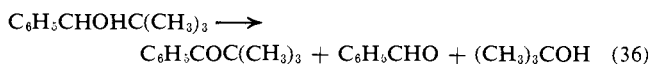
In this and similar cases, the carbon–carbon bond cleavage (reaction 37) is facilitated by the relative stability

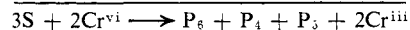$$C_6H_5CHOHC(CH_3)_3 + Cr^{iv} \longrightarrow$$
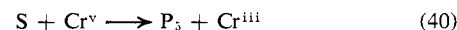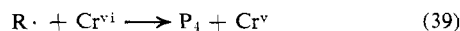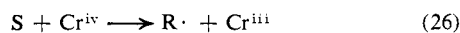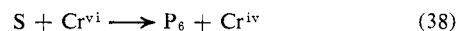$$C_6H_5CHO + (CH_3)_3C\cdot + Cr^{iii} \quad (37)$$
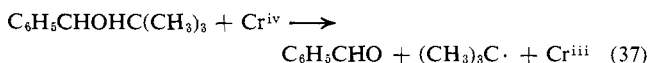
of the cleavage products, the aromatic aldehyde and tertiary radical.

It is interesting to speculate why carbon–carbon bond cleavage, which is obviously favored by the relief of strain in the oxidative cleavage of cyclobutanol, does not take place in the chromium(VI) oxidation. The oxidation of cyclobutanol to cyclobutanone by chromium(VI) (the "normal" oxidation) may be due to the particular ease by which this transformation can be accomplished via the ester intermediate (reactions 24–27), and it may therefore be intimately tied to the ester mechanism. Another possibility is that it would require much more energy to produce the carbonium ion, $^+CH_2CH_2CH_2CHO$, instead of the radical, and that the carbon–hydrogen bond breaking reaction therefore will be typical for all two-electron oxidations.

Chromium(V) Oxidation Step. Chromium(V) which is produced in reaction 32 could in principle react either analogously to chromium(VI) to yield cyclobutanone or similarly to chromium(IV) to give a cleavage product. The reaction sequence in containing the reactions of all oxidation states of chromium is represented in Scheme IV, in which P_6, P_4, and P_5 represent the products re-

Scheme IV

$$S + Cr^{vi} \longrightarrow P_6 + Cr^{iv} \qquad (38)$$
$$S + Cr^{iv} \longrightarrow R\cdot + Cr^{iii} \qquad (26)$$
$$R\cdot + Cr^{vi} \longrightarrow P_4 + Cr^{v} \qquad (39)$$
$$\underline{S + Cr^{v} \longrightarrow P_5 + Cr^{iii}} \qquad (40)$$
$$3S + 2Cr^{vi} \longrightarrow P_6 + P_4 + P_5 + 2Cr^{iii}$$

sulting from the initial reaction of the substance with chromium(VI), chromium(IV), and chromium(V), respectively. If P_5, the product of the oxidation of cyclobutanol with chromium(V), is cyclobutanone, $P_5 \equiv P_6$, then a 67% yield of cyclobutanone would be expected. If, on the other hand, chromium(V) reacted with cyclobutanol under cleavage to give 4-hydroxybutyraldehyde ($P_5 \equiv P_4$), the yield of cyclobutanone should be only 33%.

The actual yields of cyclobutanone (Table II) are usually around 50% and it is thus obvious that Scheme IV alone does not adequately predict the experimental results.
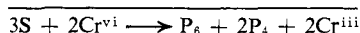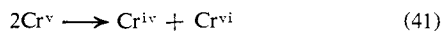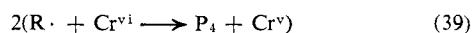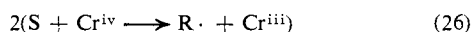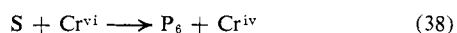
We believe that the most plausible explanation is that

chromium(V) does indeed oxidize cyclobutanol to cyclobutanone in a mechanism closely resembling the chromium(VI) oxidation. However, we suspect that this reaction is sufficiently slow to permit the accumulation of chromium(V) in high enough concentrations to permit its bimolecular disproportionation according to reaction 41. In this way, additional amounts of

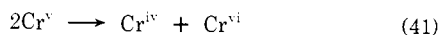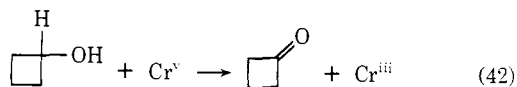$$2Cr^v \longrightarrow Cr^{vi} + Cr^{iv} \qquad (41)$$
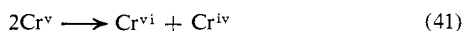
chromium(IV) can be produced which are then responsible for higher yields of the cleavage reaction than would be predicted from Scheme IV on the assumption that P_5, the oxidation product formed in the chromium(V) oxidation, is cyclobutanone. It should be noted that the reaction 41 is the reverse of the previously discussed reaction 28 and is therefore thermodynamically highly favored. If all chromium(V) reacted by disproportionation, then the overall reaction would correspond to Scheme V and the yield of cyclobutanone would be reduced to 33%.

Scheme V

$$S + Cr^{vi} \longrightarrow P_6 + Cr^{iv} \qquad (38)$$

$$2(S + Cr^{iv} \longrightarrow R\cdot + Cr^{iii}) \qquad (26)$$

$$2(R\cdot + Cr^{vi} \longrightarrow P_4 + Cr^v) \qquad (39)$$

$$2Cr^v \longrightarrow Cr^{iv} + Cr^{vi} \qquad (41)$$

$$\overline{3S + 2Cr^{vi} \longrightarrow P_6 + 2P_4 + 2Cr^{iii}}$$

The actual product composition should thus be determined by the relative rates of the two reactions involving chromium(V), reactions 42 and 41, so that the

$$\text{H} \atop \square\!-\!\text{OH} + Cr^v \longrightarrow \square\!\!=\!\!O + Cr^{iii} \qquad (42)$$

$$2Cr^v \longrightarrow Cr^{iv} + Cr^{vi} \qquad (41)$$

actual yield of cyclobutanone should vary between 67 and 33%. As reaction 42 involves the breaking of a carbon–hydrogen bond and is therefore expected to be subject to a deuterium isotope effect, the yield of cyclobutanone in the oxidation of 1-deuteriocyclobutanol should be lower than the yield obtained in the oxidation of cyclobutanol. The results given in Tables I and II are in agreement with this expectation. It is significant that the results summarized in Table II, which were determined by glpc, all seem to lie around the value of 33%. This suggests that 1-deuteriocyclobutanol reacts slowly enough to make reaction 42 relatively unimportant, so that the limiting yield predicted by Scheme V is obtained. The yield of cyclobutanone (20%) given in Table I seems too low. However, ring cleavage yield still accounts for only 47% of the oxidant, since the remaining oxidant was consumed in the formation of higher oxidation products. The low ratio of 2:1 of the substrate to the oxidant would be responsible for this.

The oxidation of cyclobutanol by chromium(V) (reaction 42) is probably acid catalyzed.[26] If one assumes that the disproportionation of chromium(V) (reaction 41) is not dependent on acidity, then the chromium(V) oxidation of cyclobutanol to cyclobutanone should become more important as the acidity of the medium increases. This conclusion is supported

(26) K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, **91**, 933 (1969).

by the data summarized in Table II, which show that the yields of cyclobutanone increase with increasing acidity from about 33% in 0.1 *M* acid to yields actually exceeding the expected 67% at very high acidities.

Effect of Ring Strain. An unexpected feature of the chromium(VI) oxidation of cyclobutanol to cyclobutanone is the ease of the reaction characterized by a rate which is of the same order and which is actually somewhat higher than that for similar strain-free alcohols. It was expected that conversion of the sp^3-hybridized >CHOH group to the sp^2-hybridized >C=O should lead to an increase in the already considerable strain of the four-numbered ring;[27] hence the oxidation of cyclobutanol to cyclobutanone should be considerably more difficult and slower than the oxidation of a strain-free secondary alcohol. This expectation was so strong that it led Kuivila and Becker to propose a completely different course for the oxidation, involving a rearrangement of cyclobutanol under the reaction conditions, when they found that cyclobutanol is not less, but in fact slightly more reactive toward chromic acid oxidation than cyclohexanol and even cyclopentanol.[18]

Our work has confirmed Kuivila and Becker's findings concerning the relatively rapid oxidation of cyclobutanol, but has also clearly demonstrated that cyclobutanone is indeed the product formed by chromium(VI) oxidation in the rate-limiting step.

A relatively rapid rate of formation of cyclobutanone from cyclobutanol seems incompatible with its assumed highly strained nature. A similar finding, namely, the relatively rapid oxidation of 7-norbornanol by chromium(VI) to yield probably 7-norbornanone led Kwart to postulate earlier that the transition state, the chromium(VI) oxidation state, does not resemble a ketone.[28] We therefore felt compelled to question the basic assumption, namely, that the conversion of an sp^3-hybridized hydroxymethylene group into an sp^2-hybridized carbonyl group within a strained compound should lead to a dramatic increase in strain.

In order to examine the assumption that cyclobutanone with an sp^2 carbon atom should be considerably more strained than cyclobutanol in which the same carbon atom is present as an sp^3 hybrid, it was necessary to determine the strain energies of the two compounds. The enthalpies of formation obtained from the experimentally determined enthalpies of combustion are given in Table XI, together with the values calculated for the strain-free molecules[29] and with the data for cyclobutane.[30] The heats of vaporization were estimated using Klage's method[31] and the following equations: ΔH_v (25°) = 6.8 + 0.045t kcal/mol for cyclobutanol and ΔH_v (25°) = 5.4 + 0.036t kcal/mol for cyclobutanone, where t is the boiling point.

The results show that cyclobutanone is not more strained than cyclobutane or cyclobutanol, but that, in fact, the strain energy is slightly lower. This is con-

(27) *Cf*, *e.g.* (a) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *ibid.*, **73**, 212 (1951); (b) H. C. Brown, *J. Chem. Soc.*, 1248 (1958); (c) H. C. Brown and V. Ichikawa, *Tetrahedron*, 1, 226 (1957).

(28) H. Kwart, *Chem. Ind.* (*London*), 610 (1962).

(29) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(30) S. Kaarsemaker and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **71**, 261 (1952).

(31) G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955, pp 88, 90–91.

trary to the assumption that a compound like cyclo-
butanone, in which the bond angle is deformed by 30°
(from the usual 120 to 90°), should be much more
strained than a compound like cyclobutane or cyclo-
butanol, in which the deformation of the bond angle
is only 19° (from 109 to 90°). The result is in agreement
with the finding that the CCC bond angle of the car-
bonyl group in cyclobutanone is very close to 90° (90°
38'),[32] with the results of Wiberg and Fenoglio[33] that
cyclobutene with two sp^2 carbon atoms in the ring is
only moderately more strained than cyclobutane, and
with the finding of Turner and coworkers that the heat
of hydrogenation of methylenecyclobutane[34] (ΔH =
−29.4 kcal/mol) is only moderately higher than for
methylenecyclopentene[35] (ΔH = −26.8 kcal/mol). It
is, however, noteworthy that while the introduction
into the cyclobutene ring system of an sp^2 carbon atom
which is part of a carbon–carbon double bond does
result in a measurable increase in the total strain

Table XI. Enthalpies of Formation and Strain Energies
(kcal/mol) per Cyclobutane, Cyclobutanol, and
Cyclobutanone at 25°

| Compd | $-\Delta H_f°_g$ | | Total strain energy |
	Exptl	Calcd[a]	
Cyclobutane	−6.30[b]	19.8	26.1
Cyclobutanol	34.6[c]	59.7	25.1
Cyclobutanone	21.9[d]	46.4	24.5

[a] For strain-free compounds.[29] [b] Reference 28. [c] From heat of
combustion $-\Delta H_c°_1 = 601.87 \pm 0.16$ kcal/mol and heat of vapor-
ization $\Delta H_v = 13.0$ kcal/mol. [d] From $-\Delta H_c°_1 = 549.89 \pm 0.15$
kcal/mol and $\Delta H_v = 9.4$ kcal/mol.

energy, the effect of the carbonyl sp^2 carbon is in the
opposite direction.

The finding that the ring strain in cyclobutanol and
in cyclobutanone are about equal thus makes the oxida-
tion rates obtained in this study and earlier by Kuivila
and Becker[18a] readily understood: as the reaction does
not lead to an increase in ring strain, there is no reason
to expect cyclobutanol to be less reactive than related
strain-free alcohols.

(32) A. Bauder, F. Tank, and H. H. Günthard, *Helv. Chim. Acta,*
46, 1453 (1963). If considerably more energy were required to deform
the carbon–carbon bonds of a carbonyl carbon than of a methylene
carbon, then the bond angle at the carbonyl group should have been
considerably greater, which would at the same time reduce the bond
angle at the two neighboring methylene groups.
(33) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.,* **90,**
3395 (1968). Using the same method[29] for the calculation of the
enthalpy of formation for the strain-free compound employed in Table
XI, a value of 29.8 kcal/mol for the strain energy of cyclobutene is ob-
tained. This value is somewhat greater than the value of 28.5 kcal/mol
estimated by the authors.
(34) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F.
Coburn, Jr., and M. Pomerantz, *ibid.,* **90,** 4315 (1968).
(35) R. B. Turner and R. H. Garner, *ibid.,* **80,** 1424 (1958).

Anodic Oxidation of Methoxybibenzyls. Products and Mechanism of the Intramolecular Cyclization

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Abstract: The intramolecular cyclization of a number of methoxy-substituted bibenzyls and bis(3-methoxy-
phenyl)methane was shown to take place upon anodic oxidation in acetonitrile or in media containing trifluoro-
acetic acid (TFA). Yields are low in the former solvent due to the fact that the cyclized products are more easily
oxidized than their precursors and the oxidation products are not stable. In the presence of TFA, the cation radi-
cals derived from the oxidation of the cyclized products are stable and, thus, after reduction the dihydrophenan-
threnes or fluorene may be isolated in high yield. Potential step cyclic voltammetry was used to provide evidence
that the reactions occur by oxidation to the dication diradicals which couple and eliminate protons. In acetonitrile,
voltammetry was used to show that the coupling reaction is markedly sensitive to the conditions and appears to be
catalyzed by H_3O^+, in the absence of which no coupling was observed.

Coupling reactions are perhaps the area in which
electrochemical synthesis can be of the most
practical importance. The coupling of aromatic
nuclei by anodic oxidation has recently been the sub-
ject of several investigations. In a preliminary com-
munication of this work, the intramolecular coupling
reaction of 3,3',4,4'-tetramethoxybibenzyl (**2**) in ace-

tonitrile to the corresponding dihydrophenanthrene
was reported.[2] More recently, coupling of compounds
structurally similar to **2** has been described by two
groups of workers.[3] Anodic intramolecular phenol
coupling has been shown to be useful in the alkaloid

(2) A. Ronlán and V. D. Parker, *Chem. Commun.,* 1567 (1970).
(3) (a) M. Sainsbury and R. F. Schinazi, *J. Chem. Soc., Chem. Com-
mun.,* 718 (1972); (b) L. L. Miller, F. R. Stermitz, and J. R. Falck,
J. Amer. Chem. Soc., **93,** 5941 (1971).

(1) (a) Lund Institute of Technology; (b) University of Copenhagen.