prepared from CF₂CFClCCl₂CF₃ by dechlorination followed by bromination of the product.

Addition of CF₃CFClCFBrCF₃ to Ethylene.—CF₃CFBrCCl-BrCF₄ (2.42 g, 0.64 mol), ethylene (7 g, 0.25 mol) and benzoyl peroxide (3 g, 0.012 mol) were heated in an autoclave at 100° for 4 hr with constant rocking. On venting the autoclave 50 g of low-boiling material was condensed. This consisted of CF₃-CF=CclCF₃ with small amount of ethylene. Gas chromatography showed the presence of only one new chief product in the residual mixture. It was identified as CH₂BrCH₂Br. Glpc analysis indicated quantitative yields of the two products.

| Registry | No.— | 1, 18621-12-0 |); 2, | 18621-13-1; | З, |
|-------------|------|---------------|-------|-------------|----|
| 18621-14-2; | 4, | 18599-02-5; | 5, | 18599-03-6; | б, |
| 18599-05-8; | 7. | 18599-04-7: | 8, | 18599-06-9; | 9. |

| 18621-15-3; | 10, | 18599-07-0; | 11, | 18599-08-1; | 12, |
|-------------|-----|-------------|-----|-------------|-----|
| 18599-09-2; | 13, | 18599-10-5; | 15, | 18599-11-6; | 16, |
| 18599-12-7; | 17, | 18599-13-8; | 18, | 812-31-7; | 19, |
| 18599-15-0; | 20, | 18599-16-1; | 21, | 18599-17-2; | 22, |
| 18621-16-4; | 23, | 18599-18-3; | 24, | 18599-19-4; | 26, |
| 18599-20-7; | 27, | 18599-21-8; | 28, | 18599-22-9; | 29, |
| 18599-23-0; | 30, | 18599-24-1; | 31, | 3871-35-0; | 32, |
| 2546-54-5. | | | | | |

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Oxidation of Organic Compounds by Cerium(IV). VI. Oxidative Cleavage of Glycols by Cerium(IV) and Lead(IV). The Question of One- and Two-Electron Oxidative Cleavages¹

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The yields of cyclohexanone obtained from the oxidation of bicyclohexyl-1,1'-diol in 75% aqueous acetic acid by cerium(IV) or lead(IV) in the absence of any addend and in the presence of acrylamide and acetamide have been measured. It is found that the yields of cyclohexanone are ca. 90% in all cases except for the cerium(IV) oxidation in the presence of acrylamide which gives a yield of 48%. These results clearly indicate that an intermediate radical can be trapped in the oxidation by cerium(IV) but no radicals are trapped by acrylamide in the oxidation of glycols by lead(IV). Mechanistic implications of these results are discussed.

The initial step of metal ion oxidative cleavage of glycols can be, in principle, either a one- or two-electron oxidation. These two pathways are outlined below for a tetrapositive metal ion. For simplicity monodentate glycol-metal complexes are drawn, but similar mechanisms could be drawn which involve bidentate glycol-metal complexes.² Since an intermediate radical is formed in the one-electron pathway, the presence of an effective radical trap should reduce the yield of ketone by a factor of 2.

one-electron oxidative cleavage



two-electron oxidative cleavage

$$\begin{array}{c} - \overset{}{} C - \overset{}{} \overset{}{} C - \overset{}{} \overset{}}{ \overset{}}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{}} \overset{}{} \overset{}}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}{} \overset{}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}}{} \overset{}}{} \overset{}{} \overset{}}{} \overset{}{} \overset{}}{} \overset{}}{} \overset{}{} \overset{}}{} \overset{}}{}$$

Mino, Kaizerman, and Rasmussen³ studied the oxidation of pinacol (2,3-dimethylbutanediol-2,3) by ceric sulfate in water at 25° in the presence and absence of acrylamide and concluded that the yield of acetone was decreased by a factor of 2 in the presence of acrylamide. They argued that the acrylamide was an effective trap for an intermediate radical which means that their results indicate that the first step of a cerium(IV) oxidation of a glycol is a one-electron oxidation. However, these workers quantitatively analyzed for acetone by an involved spectrophotometric method and carried out no control experiments to ascertain whether or not the high concentration of an amide affected the reaction. For these reasons, we felt that it was worthwhile to repeat this study using a glycol that produced a ketone that could be accurately analyzed directly by glpc methods that are now available and running a control run in the presence of a high concentration of some nonradical-trapping amide such as acetamide. Moreover, we wanted to carry out a similar set of experiments under identical conditions with a lead(IV) instead of cerium(IV) oxidizing agent. Since no evidence for cerium(II) or cerium(I)in aqueous solutions exists, it is reasonable that the cerium(IV) glycol cleavage goes by a one-electron oxidation. However, lead(IV) oxidations are known to go by both one- and two-electron pathways⁴ and

^{(1) (}a) Part V: P. M. Nave and W. S. Trahanovsky, J. Amer. Chem. Soc., 90, 4755 (1968). (b) This work was partially supported by Public Health Service Grant GM 13799 from the National Institutes of General Medical Sciences. (c) National Science Foundation Undergraduate Research Participant, Summer 1966.

^{(2) (}a) H. L. Hintz and D. C. Johnson, J. Org. Chem., **32**, 556 (1967); (b) L. B. Young and W. S. Trahanovsky, unpublished results.

⁽³⁾ G. Mino, S. Kaizerman, and E. Rasmussen, J. Amer. Chem. Soc., 81, 1494 (1959).

^{(4) (}a) R. Criegee in "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter V; (b) W. H. Starnes, Jr., J. Amer. Chem. Soc., 90, 1807 (1968), and references cited therein.

therefore the initial step of glycol cleavage could be either a one- or two-electron oxidation.

Results

In Table I are presented the yields of cyclohexanone obtained from the oxidation of bicyclohexyl-1,1'-diol

TABLE I

Oxidation of Bicyclohexyl-1,1'-diol in 75% Aqueous Acetic Acid at 25° °

| Addend | Yield of cyclohexanone, % ^b |
|--|--|
| | 94 ± 2 |
| 10% CH2=CHCONH2 | $48\pm2^{c,d}$ |
| $10\% \mathrm{CH_{3}CONH_{2}}$ | 89 ± 2 |
| | 94 ± 3 |
| $10\% \mathrm{CH}_{2}$ = CHCONH ₂ | 93 ± 3 |
| 10% CH2CONH2 | 95 ± 3 |
| | Addend 10% CH2=CHCONH2 10% CH3CONH2 10% CH2=CHCONH2 10% CH2CONH2 |

^a The concentration of glycol was 0.25 M and the concentration of oxidant was 0.025 M. ^b All measurements were made on two to six runs and standard deviations of the averages are given. ^c Under these conditions the reaction mixture was very viscous which indicates the formation of a polymer. ^d Cerium(IV) (2 equiv) was still used in this case since the termination of the free radical polymerization must involve the oxidation of the polymer radical by cerium(IV).

in 75% aqueous acetic acid by cerium(IV) or lead(IV) in the absence of any addend and in the presence of a radical trap, acrylamide, and a typical nonradical-



trapping amide, acetamide. Our trapping experiments with cerium(IV) are in agreement with those reported by Mino, Kaizerman, and Rasmussen³ and our results clearly indicate that an intermediate radical can be trapped in the oxidation of glycols by cerium(IV) but no radicals are trapped by acrylamide in the oxidation of glycols by lead(IV). The identical conditions used for the two oxidants make these findings particularly meaningful.

Discussion

The simplest interpretation of our results is that the first step of glycol cleavage is a one-electron oxidation with cerium(IV) but a two-electron oxidation with lead(IV). Although it is attractive to think of the lead(IV) glycol cleavage as a two-electron oxidation, there are two other ways to interpret our results which must be considered. A radical could be involved in the lead(IV) oxidation but complexation with lead could make it too stable to react with acrylamide. Another possibility is that oxidation of an intermediate radical might be faster by lead(IV) or lead(III) than cerium(IV). If this is so, the acrylamide might be able to compete for the radical with cerium(IV) but not with lead(IV) or lead(III). Since there is no evidence that the radical formed by cleavage is complexed with the metal and the oxidation of a radical should be very fast with $\operatorname{cerium}(IV)$ as well as $\operatorname{lead}(IV)$, we feel that the best interpretation of our results is that glycol cleavages by cerium(IV) are one-electron oxidations

but are two-electron oxidations by lead(IV). Nevertheless, the other two explanations for the failure to trap a radical during the lead(IV) oxidation must be considered.

Experimental Section

Materials and Methods.—Ceric ammonium nitrate, acrylamide, acetamide, cyclopentanone, and cyclohexanone were obtained from commercial sources and used without further purification. Pinacol hydrate was obtained from Aldrich and recrystallized from water. Lead tetracetate was prepared by the method of Vogel.⁵ Bicyclohexyl-1,1'-diol was prepared by the method of Nayarov and Torgov⁶ and recrystallized from benzeneligroin, mp 126-136.5° (lit. mp 123-124°).

Equipment has been previously described.⁷ Use was made of 6 ft \times 0.25 in. columns of 20% Carbowax 20M on Chromosorb P.

Procedure for the Cerium(IV) Oxidations.—To 6 ml of 0.34 Mbicyclohexyl-1,1'-diol in acetic acid was added 2.0 ml of freshly prepared 0.10 M ceric ammonium nitrate solution. The yellow color of the cerium(IV) disappeared within 2 min. After 2 hr, ca. 30 μ of cyclopentanone was weighed and added as a standard. A quantity of 25 ml of saturated sodium chloride solution was added and the mixture was extracted with 5 ml of 50% methylene chloride-pentane. The organic layer was washed with 10 ml of saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and filtered. The precipitate was washed with 1 ml of 50% methylene chloride-pentane and the combined filtrate and washings were analyzed by glpc. Yields were calculated as described below. For the runs that contained acrylamide or acetamide, a quantity of 0.800 g (11.3 mmol) of acrylamide or 0.800 g (13.6 mmol) of acetamide was dissolved in the glycol solution prior to the addition of the cerium(IV) solution. The work-up for these runs was the same.

The relative thermal conductivity and distribution ratio of product to standard in the absence of added amides were determined as follows. The cerium(IV) was reduced with a minimum amount of pinacol hydrate before it was added to the bicyclohexyl-1,1'-diol solution. To this solution was added weighed amounts of cyclohexanone and the standard, cyclopentanone, and the solution was worked up and analyzed by glpc as described above.

In order to determine the relative thermal conductivity and distribution ratios in the presence of amides, the following method was used. A miniumum amount of pinacol hydrate and 0.800 g of the appropriate amide were dissolved in 6 ml of glacial acetic acid. A quantity of 2.0 ml of the 0.10 M ceric ammonium nitrate solution was added. After 2 hr, 0.423 g (1.90 mmol) of bicyclohexyl-1,1'-diol and weighed amounts of cyclohexanone and standard were added and the solution was worked up and analyzed as described above.

The yield of product was calculated using eq 1, where A is the weight of the cyclohexanone peak divided by the weight of

$$\% \text{ yield } = \frac{[A(B/B')](\text{millimoles of added standard})(100)}{(\text{equivalents of oxidant})}$$
(1)

the cyclopentanone peak, B is the ratio of millmoles of cyclohexanone to millimoles of standard added in the artificial run, and B' is the ratio of the weight of the cyclohexanone peak to the weight of the cyclopenanone peak in the artificial run. The B/B' ratios were based on at least two independent runs and were found to be 0.720 ± 0.014 , 0.464 ± 0.072 and $0.790 \pm$ 0.004, with no addend, in the presence of acrylamide and in the presence of acetamide, respectively. Yields are reported in Table I.

Procedure for the Lead(IV) Oxidations.—A quantity of 2.0 ml of 0.10 M lead tetraacetate in glacial acetic acid was added to 4 ml of 0.5 M bicyclohexyl-1,1'-diol and 2 ml of water. After 2 hr, a weighed amount of cyclopentanone and 10 ml of water were added to the reaction mixture which then was extracted

⁽⁵⁾ A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1957, p 199.

⁽⁶⁾ I. Nayarov and I. Torgov, Zh. Obshch. Khim., 22, 228 (1952); Chem. Abstr., 46, 11122 (1952).

⁽⁷⁾ W. S. Trahanovsky and M. P. Doyle, J. Org. Chem., 32, 146 (1967).

with 5 ml of methylene chloride. The organic layer was separated, washed with 10 ml of saturated sodium bicarbonate solution, dried over magnesium sulfate, and filtered. The precipitate was washed with 1 ml of methylene chloride and the combined filtrate and washings were analyzed by glpc. For the runs that contained amides, 0.800 g of acrylamide or acetamide was dissolved in the water-glycol mixture before the addition of the lead(IV).

Relative thermal conductivity and extraction ratios for the product to standard for the three types of lead(IV) reactions

were determined in a fashion similar to that used for the cerium (IV) reactions.

The yields of cyclohexanone were calculated by the method used for the cerium(IV) runs and are reported in Table I. The B/B' ratios were based on at least two runs and were found to be 0.777 \pm 001, 0.774 \pm 0.033, and 0.765 \pm 0.002 with no addend, in the presence of acrylamide and in the presence of acetamide, respectively.

Registry No.-Bicyclohexyl-1,1'-diol, 2888-11-1.

Factors Influencing Episulfonium Ion Formation. The Reactivity of Unsaturated Aliphatic Hydrocarbons toward Methanesulfenyl Chloride

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The reaction of methanesulfenyl chloride with a series of unsaturated hydrocarbons has been utilized to measure relative rates of episulfonium ion formation. The structure-reactivity correlation obtained in this fashion contrasts with other electrophilic additions such as chlorination in that the methanesulfenyl chloride additions appear to be significantly less sensitive to the nucleophilicity of the unsaturated hydrocarbon and quite sensitive to steric factors. The data have been interpreted in terms of transition states in which the positive charge resides essentially on sulfur, and consequently alkyl substituents about the double bond contribute relatively little toward delocalization of the positive charge. The observed reactivities reflect the opposing steric and electronic factors.

Early studies pertaining to the mechanism of electrophilic sulfenyl halide reactions with olefins utilized 2,4dinitrobenzenesulfenyl chloride¹ as a convenient model reagent due to its unusual stability. More recent discoveries of novel aspects of the mechanism of sulfenyl chloride addtions² indicate that only limited generalizations can be drawn from this model. The addition of sulfenyl halides to olefins evidently proceeds *via* episulfonium ion intermediates, the substituents both



on carbon and sulfur exerting profound directive influences controlling the structure of the β -chloro thioether products. Recent studies^{3.4} correlating episulfonium ion structure with product geometry have provided considerable insight into the nature of episulfonium ions and have demonstrated that simple alkyl- (and aryl-) sulfenyl chlorides frequently behave quite differently from 2,4-dinitrobenzenesulfenyl chloride. Although examination of product structures has provided data concerning episulfonium ring opening in the second reaction step, there is a paucity of information on the formation of these species during the first reaction step, especially in systems involving unsaturated aliphatic hydrocarbons and simple alkylsulfenyl halides. The object of the present investigation is a correlation between structure and reactivity for episulfonium ion formation from unsaturated aliphatic hydrocarbons and alkanesulfenyl halides.

Results

The relative rates of reaction of pairs of unsaturated hydrocarbons with methanesulfenyl chloride in dilute paraffin solution at -70° was measured by means of vapor phase chromatography. Initial experiments utilizing dropwise addition of CH₃SCl and analysis at frequent intervals demonstrated that relative reactivities were independent of conversion. The relative rates reported in Table I are the mean values of dupli-

| TABLE I |
|---------------------------------|
| Competition of Olefin Pairs for |
| METHODIA DENNI CHIODIA |

| MI | ETHANESULFENYL | CHLORIDE | |
|-----------------------|-------------------|-------------------|-------------------------|
| Olefin A | Olefin B | Solvent | Mean ka/kB |
| Cyclopentene | cis-Pentene-2 | <i>n</i> -Heptane | $1.76^{a} \pm 0.05^{b}$ |
| Pentene-1 | 3-Methyl-1-butene | <i>n</i> -Heptane | 1.17 ± 0.04 |
| ris-Pentene-2 | Pentene-1 | n-Heptane | 7.94 ± 0.28 |
| Cyclopentene | 2-Methyl-2-butene | n-Heptane | 5.06 ± 0.52 |
| 2-Methyl-2-butene | 3-Methyl-1-butene | n-Heptane | 4.22 ± 0.49 |
| B-Methyl-1-butene | trans-2-Pentene | n-Heptane | 1.18 ± 0.02 |
| B-Methyl-1-butene | Isobutylene | Cyclopentane | 2.62 ± 0.18 |
| Butene-1 | trans-2-Butene | n-Pentane | 1.40 ± 0.03 |
| ris-2-Butene | Butene-1 | n-Pentane | 13.04 ± 1.40 |
| Isobutylene | 1,3-Butadiene | n-Pentane | 4.86 ± 0.31 |
| rans-2-Butene | Isobutylene | n-Pentane | 0.96 ± 0.04 |
| 1,3-Butadiene | 1-Butyne | Cyclopentane | 6.11 ± 0.68 |
| Isobutylene | 2-Butyne | Cyclopentane | 4.63 ± 0.13 |
| 2,3-Dimethyl-2-butene | 2-Methyl-2-butene | n-Heptane | 1.56 ± 0.02 |
| Vinylcyclohexane | Styrene | n-Pentane | 1.17 ± 0.09 |
| | | 1 | |

^a Mean value of four runs. ^b Mean deviation.

⁽¹⁾ N. Kharasch, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, 1961, pp 375-396.

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(1966). (b) W. H. Mueller and P. E. Butler, Chem. Commun., 646 (1966).
(3) W. A. Thaler, W. H. Mueller, and P. E. Butler, J. Amer. Chem. Soc.,

^{90, 2069 (1968).}

⁽⁴⁾ W. H. Mueller and P. E. Butler, ibid., 90, 2075 (1968).