120 mg. of 2% palladium–calcium carbonate catalyst in 10 cc. of 2% ethanolic potassium hydroxide solution. Hydrogen consumption stopped after 3 hr., whereupon the catalyst was filtered, the filtrate neutralized with dilute hydrochloric acid and the product isolated with ether. The oily octalone XI did not contain any α,β-unsaturated ketone as demonstrated by its infrared ($\lambda_{max}^{CHCl_3}$ 5.88 μ) and ultraviolet (λ_{max}^{EtOH} 288 mμ, log ϵ 1.47) spectra. Gas phase and thin layer chromatography indicated the homogeneity of the material, but mass spectral analysis[29] demonstrated the presence of a small amount (less than 10%) of the completely saturated decalone (XII); R.D. (c 0.05 in dioxane): $[\alpha]_{589}$ −14°, $[\alpha]_{315}$ −1865°, $[\alpha]_{270}$ +2285°, $[\alpha]_{250}$ +1815°.

The yellow **2,4-dinitrophenylhydrazone** exhibited m.p. 125–127° (recrystallized from methanol); $\lambda_{max}^{CHCl_3}$ 367 mμ, log ϵ 4.45.

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.34; H, 6.32; N, 15.62.

(−)-3,9-Dimethyl-*trans*-1-decalone (XII).—Hydrogenation of the isolated double bond of 90 mg. of the octalone XI was effected in 1 hr. with 100 mg. of 5% palladized charcoal catalyst and 5 cc. of ethanol. The resulting oil was homogeneous as determined by gas phase and thin-layer chromatography as well as by mass spectral analysis.[29] The decalone exhibited the following spectral properties: infrared ($CHCl_3$) band at 5.88 μ, ultraviolet (EtOH) maximum at 285 mμ, log ϵ 1.52, and n.m.r. signals[27] ($CDCl_3$) at 1.08 (angular methyl group) and doublet at 0.90 and 1.07 due to the C-3 methyl function; no peaks corresponding to olefinic protons could be detected; R.D. (c 0.10 in methanol): $[\alpha]_{589}$ −108°, $[\alpha]_{309}$ −1767°, $[\alpha]_{271}$ +1108, $[\alpha]_{256}$ +745°.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.89; H, 11.14.

The yellow **2,4-dinitrophenylhydrazone** of **XII** melted at 133–135° after recrystallization from ethanol; $\lambda_{max}^{CHCl_3}$ 369 mμ, log ϵ 4.48.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 60.07; H, 6.49; N, 15.48.

(+)-3-*t*-Butyl-9-methyl-*trans*-$\Delta^{2,6}$-hexalone-1 (X).—To a solution of *t*-butylmagnesium chloride prepared from 2.5 g. of magnesium turnings and 13.5 cc. of *t*-butyl chloride in 10 cc. of ether was added 3.0 g. of the enol ether VIII and the mixture stirred at room temperature for 40 hr. After pouring into ice-water, extracting with ether, and removing the solvent, the residue was stirred overnight with 60 cc. of 50% aqueous dioxane containing 3 cc. of sulfuric acid. Sodium hydroxide was added until the mixture was slightly basic, the product was isolated with ether and chromatographed on 200 g. of neutral alumina. Elution was effected with hexane, hexane–benzene mixtures and benzene, the desired product (0.48 g.) being isolated from the benzene fractions. A small amount of impurity was separated by preparative gas phase chromatography at 180° with a Megachrom instrument using a SE-30 column (retention time 7.8 min.). Redistillation at 110–120° (0.1 mm.) provided 0.215 g. of colorless solid (m.p. 25–30°) of the hexalone X, λ_{max}^{EtOH} 233 mμ, log ϵ 4.02, $\lambda_{max}^{CHCl_3}$ 6.02 and 6.08 μ; n.m.r. signals[27] ($CDCl_3$) at 1.01 (angular methyl), 1.14 (*t*-butyl methyl groups), 5.80 (C-2 proton) and 5.67 p.p.m. (C-6 and C-7 protons); R.D. (c 0.12 in dioxane) reproduced in Fig. 1: $[\alpha]_{589}$ +45°, $[\alpha]_{378}$ −350°, $[\alpha]_{363}$ +123°, $[\alpha]_{357}$ −17°, $[\alpha]_{348}$ +750°, $[\alpha]_{341}$ +584°, $[\alpha]_{334}$ +967°, $[\alpha]_{328}$ +734°, $[\alpha]_{322}$ +867°, $[\alpha]_{314}$ +685°.

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.21; H, 10.06.

The dark orange **2,4-dinitrophenylhydrazone** was recrystallized from methanol; m.p. 156–158°, $\lambda_{max}^{CHCl_3}$ 386 mμ, log ϵ 4.43.

Anal. Calcd. for $C_{21}H_{26}N_4O_4$: C, 63.30; H, 6.58; N, 14.06. Found: C, 63.33; H, 6.46; N, 14.38.

(−)-3-*t*-Butyl-9-methyl-*trans*-1-decalone (XIII).—The catalytic hydrogenation of both double bonds of the hexalone X (100 mg.) was accomplished in 1 hr. in ethanol solution with 100 mg. of 5% palladized charcoal catalyst. The resulting oil exhibited a single, symmetrical peak in a gas phase chromatogram and showed $\lambda_{max}^{CHCl_3}$ 5.88 μ, λ_{max}^{EtOH} 287 mμ, log ϵ 1.60; n.m.r. signals[27] ($CDCl_3$) at 0.80 (*t*-butyl methyl groups), 0.98 (angular methyl group) and no signals corresponding to olefinic protons; R.D. (c 0.12 in methanol): $[\alpha]_{589}$ −76°, $[\alpha]_{310}$ −1685°, $[\alpha]_{273}$ +1270, $[\alpha]_{240}$ +730°.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.69; H, 11.66.

The yellow **2,4-dinitrophenylhydrazone** showed m.p. 208–209° after recrystallization from methanol; $\lambda_{max}^{CHCl_3}$ 368 mμ, log ϵ 4.36.

Anal. Calcd. for $C_{21}H_{30}N_4O_4$: C, 62.66; H, 7.51; N, 13.92. Found: C, 62.28; H, 7.71; N, 13.92.

1β-Methylandrostan-17β-ol-3-one (1β-methyldihydrotestosterone) acetate (II),[10] R.D. (c 0.10 in methanol): $[\alpha]_{589}$ +68°, $[\alpha]_{308}$ +1325°, $[\alpha]_{260}$ −760°, $[\alpha]_{255}$ −662°. In the presence of hydrochloric acid[30] the peak occurred at $[\alpha]_{308}$ +552°, while the trough was found at $[\alpha]_{265}$ −319°.

(29) We are indebted to Dr. Herbert Budzikiewicz for this determination.

(30) C. Djerassi, L. A. Mitscher and B. J. Mitscher, *J. Am. Chem. Soc.*, **81**, 947 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE, NEWARK, DEL.]

Mechanisms of Chromic Acid Oxidation. III.[2] The Oxidation of Diols

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The earlier interpretations[3,4] of the rates of chromic acid oxidation of diols are found to be misleading, in view of conformational and structural effects which are shown here to govern reactivity. The occurrence of cyclic chromate esters as intermediates in the oxidation of certain diol structures but not of others has been inferred from rate data obtained for a variety of bicyclic, alicyclic and acyclic 1,2- and 1,3-diols. In this fashion, also, the geometric requirements for such cyclic chromate ester formation have been found to be similar to those deduced earlier for boric acid complexing with diols. It is suggested that the formation of esters by interaction of chromic acid with alcohols is quite analogous to ester formation with boric rather than sulfuric acid, as claimed previously.[3]

This investigation was prompted by diverse observations in the literature concerning the oxidation of diols with chromic acid. Roček[3] has reported that ethylene glycol shows a reduced rate of oxidation compared to ethanol and has interpreted this as a failure of the chromate ester mechanism, reasoning that a cyclic chromate ester should have been formed in greater amounts at equilibrium than

(1) (a) Supported by the National Science Foundation under Grant NSF-G 6037. (b) Eastman Kodak Co., Rochester, N. Y. (c) Part of this work is abstracted from the Master's degree thesis of G. C. Corey presented to the University of Delaware, June, 1960.

(2) Previous papers in this series: (a) H. Kwart and P. F. Francis, *J. Am. Chem. Soc.*, **77**, 4907 (1955); (b) **81**, 2116 (1959); (c) H. Kwart, *Suomen. Kemi.*, **34A**, 173 (1961).

(3) J. Roček, *Coll. Czech. Chem. Comm.*, **25**, 1052 (1960).

the monoester of ethanol with a rate increase to be expected as a consequence. On the other hand, Favre and Richer[4] have utilized the relative rates of oxidation of substituted cyclohexane diols for structural assignment, assuming as a basis of choice the applicability of the chromate ester mechanism described by Westheimer and co-workers.[5]

The results we are reporting here on the oxidation rates of a wide variety of diol structures, under controlled and comparable conditions, have been gathered with the intention of testing the respective abilities of the proposed[2,3,5] alternative mechanisms of chromic acid oxidation of monoalcohols. We hope to show, in fact, that the relative rates observed could have been predicted by consideration of the three basic features which have been identified in the modified[2] Westheimer chromate ester mechanism as controlling the rate of oxidation of the carbinol group: (i) the polar substituent or inductive effect regulating the position of the chromate ester equilibrium; (ii) steric and geometric influences (entropy effects) that regulate the ease of attainment of the planar five-membered relationship for internal proton abstraction in the chromate ester; and (iii) the permissible formation of a *cyclic* chromate ester in the reaction of pinacols with chromic acid as established by Chang and Westheimer.[6] The hydride ion abstraction mechanism advanced by Roček as well as other alternatives, (see particularly footnote 16), are rejected as a basis for interpretation of our data because of many arguments discussed in our previous articles.[2]

Results and Discussion

Vicinal Diol Oxidation.—The rate constants we measured for the chromic acid oxidation of the various cyclic and acyclic *vic*-diols are listed in Table IA, along with an appropriate selection of reference monoalcohols. These values have been computed[3] on the stoichiometric assumption of only one carbinol group undergoing oxidation to the corresponding carbonyl. The basis for this assumption is established by the following lines of evidence; (i) the observation[7] of good pseudo-first-order kinetics in dilute solution using at least a tenfold excess of oxidizable (alcohol) function. (The bimolecular values listed in Tables IA and IB have been converted from the determined unimolecular constants in the usual fashion); (ii) the observation by Slack and Waters[8] as well as Chatterji and Mukherjee[7b] that *vic*-diols possessing other than tertiary alcohol functions show a deuterium isotope effect; and (iii) even under preparative conditions[7,8] (*i.e.*, in relatively concentrated solution where the alcohol component was not always in large excess) the incidence of cleavage products from chromic oxidation of primary and secondary *vic*-diols was quite small.

The first point we may try to decide is whether these data reveal anything concerning the tendency of chromate to form cyclic ester with *vic*-diols as has been suggested for other oxidants.[9] Roček[3] has assumed that a *vic*-diol must form a cyclic chromate ester and consequently the lack of rate exaltation by the second alcohol function in ethylene glycol (*vs.* ethanol) was construed as the failure of all mechanistic postulates involving a chromate ester intermediate on the path of oxidation of alcohols. However, this conclusion ignores earlier observations[10] concerning the ability of various oxy-ions and acids to form diol complexes. It has been shown,[10] for instance, that the formation of borate cyclic complexes with vicinal diols is strongly dependent on conformation and only the smallest projection angle between the two hydroxyl groups permits significant complexation. It seems quite clear, also, that conformational factors play a most important role in determining the ability of both cyclic and acyclic diols to complex cyclically with the copper in Schweitzer reagent.[11] In fact, evidence seems to be accumulating to indicate, in the latter case, a preference for polymolecular rather than cyclic complexing in certain concentration ranges.[12]

Additional grounds for the above suppositions can be immediately seen in comparisons of the oxidation rates of some of the diols in Table IA. Thus, although ethylene glycol is about one-fifth as oxidizable as ethanol, both the 2,3-*cis-endo*-(I) and *exo*-(II) norbornane diols are faster than the corresponding (mono)-*exo*-(β) and *endo*-(α) norborneols. Part of the explanation of why these rate differences are not even greater can be perceived in the analogous camphanediol oxidations. The *cis-endo*-(VII) and *cis-exo*-(VI) diols here oxidize much faster than both of the *trans*-diols V and VIII, which, in turn, show considerably smaller rates than either of the monofunctional alcohols, isoborneol and borneol. The *cis*-diols VI and VII, on the other hand, oxidize at rates which are at least comparable to the corresponding parent alcohols. Clearly, the second alcohol function, as in ethylene glycol, is rate retarding. The over-all rate increase that occurs in some diols (compared to their respective monoalcohols) is possible only where a cyclic diol chromate ester is structurally accommodated. That is to say, only where the hydrogen bonding distance (as reflected by the $\Delta\gamma$ value) and the projection angle between the –OH groups are sufficiently small to permit substantial borate complexing are we also able to realize the oxidation rate benefits of cyclic chromate ester formation, overcoming the unfavorable inductive effect of the second hydroxyl group. This conclusion is re-enforced and extended by comparison of the rates of 7-*syn*-(XXIII) and 7-*anti*-2-*exo* norbornane-diol (XXIV) listed in Table IB. Obviously cyclic chromate ester does not occur in either of these cases and the transannular inductive effect[15] of the *anti*-hydroxyl group has decreased the rate by a factor of three. The slightly greater rate of the *syn*-XXIII is thus indicative of the complexity of rate-regulating effects in

(4) H. Favre and J. C. Richer, *Can. J. Chem.*, **37**, 411 (1959).

(5) For a fuller discussion of these proposals see F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949), and references cited therein.

(6) Y. W. Chang and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 1401 (1960).

(7) (a) The work we are reporting here. (b) A. C. Chatterji and S. K. Mukherjee, *Z. physik. Chem.*, **208**, 281 (1958).

(8) R. Slack and W. A. Waters, *J. Chem. Soc.*, 594 (1949), and J. S. Littler and W. A. Waters, *ibid.*, 2767 (1960).

(9) For a discussion of this see J. S. Littler, A. I. Mallet, and W. A. Waters, *ibid.*, 2761 (1960), as well as ref. 7.

(10) H. Kwart and G. C. Gatos, *J. Am. Chem. Soc.*, **80**, 881 (1958).

(11) See, for instance, R. E. Reeves, *Adv. in Carbohydrate Chem.*, **6**, 109 (1951), as well as ref. 9.

(12) Private communication, R. E. Reeves, March, 1960.

this system[2d]: the *syn*-hydroxyl group inductive effect is presumably far more rate retarding than the *anti*, but the steric hindrance to free rotation in the 2-*exo*-monochromate ester created by the 7-*syn*-hydroxyl group results in a rate advantage[2b,16] to partly compensate the greater inductive retardation. The considerably smaller rate constant for 7-hydroxynorbornane oxidation suggests that in both the *syn*- and *anti*-2,7 diols XXIII and XXIV the 2-hydroxy group is undergoing preferential oxidation under our reaction conditions.

Entirely similar lines of argument can be very conveniently applied to explain the rate data for alicyclic *vic*-diols as well. Thus, in the case of cyclopentanediols X and XI the $\Delta\nu$-value of the *cis*-diol helps us to predict a smaller extent of cyclic chromate ester than in the bicyclic cases (I and II); but, again, the total rate increase from cyclopentanol is only about a factor of two because of the simultaneously opposing inductive effect of the second hydroxyl. The *trans-vic*-diol is slower than cyclopentanol by the same factor of *ca.* two because of the absence of the accommodation for cyclic chromate ester formation present in the *cis*, by which event the unfavorable inductive effect is compensated in X. The importance of steric hindrance to free rotation, which can also operate to favor cyclic chromate ester formation in a diol (as well as in the cyclic transition state for decomposition of a monochromate ester), may be seen in the instance of 5,5-dimethyl-1,2-*cis*-cyclopentanediol (IX), which is more than five times as readily oxidized as the unmethylated diol. The $\Delta\nu$-value (71 $cm.^{-1}$) is only very slightly larger than the unsubstituted and, consequently, we can conclude that the entropy factor favoring[2b,c] cyclic ester formation due to methyl substitution in the *cis*-cyclopentanediol (XII) is dominant. The importance of the $\Delta\nu$-value in determining cyclic chromate ester formation and, thereby, the over-all rate may be appreciated by comparing IX with the norbornanediols I and II between which it falls in the oxidation rate series. Thus, IX is faster than II because of greater steric hindrance (qualitatively estimated from atom models), but slower than I because of its smaller $\Delta\nu$-value.

Again, in the 1,2-cyclohexanediols, the *cis*-XII is almost six times faster than both the *trans*-XIII and cyclohexanol, presumably because cyclic ester formation has been experienced as an aid in overcoming the inductive retardation of the vicinal alcohol function. The *trans* has about the same rate as cyclohexanol and is not a great deal slower (as is usual for the diol which cannot structurally accommodate formation of the cyclic chromate ester), for a reason which is peculiar to the strainless six-membered ring. Thus, it is well known that a considerable population of diaxial structures exists in the conformational equilibrium for *trans-vis*-disubstituted cyclohexanes in which the substituent is a highly polar group.[13] Since the axial hydroxyl oxidizes almost three times faster than the equatorial (*i.e.*, compare *cis-t*-butylcyclohexanol *vs. trans* in Table IA), this rate advantage just about overcomes the rate decrease due to the inductive effect of the second hydroxyl in the diol, leaving, as a net residue, a diol rate equivalent to the parent monoalcohol.

Summarizing, then, *cis*-1,2-diols can be expected to oxidize much more readily when the possibility of cyclic chromate ester formation exists. However, the total magnitude of the rate difference between *cis*- and *trans*-diols must be weighted by consideration of the two other factors controlling the over-all rate enumerated earlier. It will be seen, for instance, that cyclic chromate ester formation with cyclic *vic*-diols might engender some difficulties in the succeeding proton abstraction step since this now involves a sort of bicyclic intramolecular process.

1,3-Diol Oxidation.—The rates of chromate oxidation of a number of cyclic and acyclic 1,3-diols which we have measured are listed in Table IB. The acyclic 1,3-diols constitute a self-consistent series which is calibrated by the values of neopentyl alcohol (XXV, Table IB), and ethanol (Table IA). The close similarity of these calibrating rates to that of the unsubstituted propanediol XIX suggests two conclusions: (i) the second hydroxyl group in XIX has very little if any retarding inductive effect as compared with the α-hydroxy in all the vicinal diols examined above; (ii) despite the relatively high $\Delta\nu$-values here, there is little or no rate evidence for a cyclic chromate ester, indicating that the chromate ester cannot form readily into a six-membered structure. The latter observation heightens the analogy to borate which not only is restricted to complex ring sizes of five members but also has an even more stringent requirement for minimum projected angle between the complexing hydroxyl functions.

The cyclic 1,3-diols are even more informative in this regard. The 1,3-*cis*-cyclohexanediol (XV) in solution normally has its two hydroxyl groups axial and intramolecularly bonded. Having formed chromate ester on one of the hydroxyl functions, however, changes the relation of the two carbon–oxygen bonds to the diequatorial. The loss of strong hydrogen-bonding energy in forming the predominantly equatorial monochromate ester accounts for part of the rate reduction compared to cyclohexanol itself (which is at least partially oxidized in the axial conformation[14]). One can also ascribe greater inductive retardation to the second hydroxy group here (as well as in XXIII and XXIV) than in the acyclic 1,3-diol relationship. It has been shown earlier that such inductive effects of polar groups are transmitted more readily across the intramolecular space of the cyclohexane and bicycloheptane rings.[15] The lower rate of the *trans*-1,3-diol *vs.* cyclohexanol, despite the fact that hydroxyl is here (entirely) axial, must indeed be attributed to the strong, transannular transmission of the inductive effect of the second hydroxyl.

The 5,5-dimethyl-*cis*-1,3-cyclohexanediol (XVIII must be compared to the unsubstituted case because the absence of hydrogen bonding ($\Delta\nu = 0$),

(13) See for examples S. Mizusbima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, p. 77 *et seq.*; and O. Hassel, *Quart. Revs.*, **7**, 221 (1953).

(14) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(15) See H. Kwart and L. J. Miller, *ibid.*, **83**, 4552 (1961), for a fuller discussion of these factors in rate processes.

TABLE I

TABLES OF RATES OF CHROMIC ACID OXIDATION IN 30% AQUEOUS ACETIC AT 30°. μ = 0.40; H^+ = 0.25 *M*

Compound	k_2 mole^{-1}/ min.$^{-1}$	Relative rate	$\Delta\nu$, cm.$^{-1}$	Pertinent references
A: Vicinal diols[d] and reference alcohols				
2,3-*cis-endo*-Norbornanediol (I)	11.1	32.6	102	16
2,3-*cis-exo*-Norbornanediol (II)	2.59	7.6	103	16
endo-exo-2,3-Camphanediol (V)	1.59	4.7	0	18
exo-exo-2,3-Camphanediol (VI)	6.50	19.1	90	18
endo-endo-2,3-Camphanediol (VII)	5.12	15.0	95	18
exo-endo-2,3-Camphanediol (VIII)	1.65	4.8	0	18
5,5-Dimethyl-1,2-*cis*-cyclopentanediol (IX)	4.95	1.46	71	..[c]
1,2-*cis*-Cyclopentanediol (X)	0.88	2.6	61	20
1,2-*trans*-Cyclopentanediol (XI)	0.17	0.5	0	21
1,2-*cis*-Cyclohexanediol (XII)	1.90	5.6	39	22
1,2-*trans*-Cyclohexanediol (XIII)	0.33	1.0	32	23
Ethylene glycol (XIV)	.078[a]	0.13[b]	32	17
Ethanol	.45[a]	.71[b]	..	..
2-Propanol	.31[a]	.49	..	2b
Cyclohexanol	.34	1.00	..	2b
Cyclopentanol	.48	1.4	..	2b
7-Hydroxynorbornane	.16	0.47	..	29
α-Norborneol (*endo*)	3.23	9.7	..	2b
β-Norborneol (*exo*)	1.30	3.9	..	2b
Isoborneol (*exo*)	16.6	49.1	..	2b
Borneol (*endo*)	8.46	25.0	..	2b
4-*cis-t*-Butylcyclohexanol	0.71	2.1	..	14
4-*trans-t*-Butylcyclohexanol	0.28	0.8	..	14
B: 1,3-Diols and reference alcohols[e]				
1,3-*cis*-Cyclohexanediol (XV)	0.15	0.44	75	24, 25, 17
1,3-*trans*-Cyclohexanediol (XVI)	0.24	0.71	0.0	24
5,5-Dimethyl-*trans*-1,3-cyclohexanediol (XVII)	1.90	5.6	0.0	26, 27, 4
5,5-Dimethyl-*cis*-1,3-cyclohexanediol (XVIII)	0.18	0.53	0.0	26, 27, 4
1,3-Propanediol (XIX)	.26	0.76	78–79	28
2,2-Dimethyl-1,3-propanediol (XX)	.54	1.6	88	28
2,2-Diethyl-1,3-propanediol (XXI)	1.49	4.4	90	28
2-Ethyl-2-*n*-butyl-1,3-propanediol (XXII)	1.58	4.6	89.8	28
7-*syn*-2-*exo*-Norbornanediol (XXIII)	0.70	2.1	76	16, 19
7-*anti*-2-*exo*-Norbornanediol (XXIV)	.50	1.5	0.0	19
Neopentyl alcohol (XXV)	.35	1.0	..	..

[a] Data taken in 1.0 *M* perchloric acid, entirely aqueous medium. [b] Determined in aqueous solution and transposed on the basis of assumptions discussed in reference. [c] Present work. [d] One mole of diol is reckoned as two equivalent of oxidizable alcohol function in computing k_2; this assumption was also made previously in ref. 3. [e] Rates relative to cyclohexanol = 1.0.

confirms the diequatorial relationship as well as (only) the monochromate ester formation. The same transannular inductive effects seem to be operative here, too, for the rates of substituted and unsubstituted are nearly equal (compare XVI and XVIII, Table IB) and about a factor of two less than cyclohexanol. Apparently, when we compare the *cis* and *trans* compounds, as above, we largely cancel out the inductive effect of the non-oxidizing hydroxyl.

The sudden rate increase (*ca.* 10×) experienced with 5,5-dimethyl substitution in the *trans* is just about what one observes for axial hydroxyl groups bearing a 1,3-relationship to the axial angular methyl group in certain steroids.[30] We have

(16) H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).
(17) L. P. Kuhn, *ibid.*, **74**, 2492 (1952).
(18) T. Takeshita and M. Kitajima, *Bull. Chem. Soc. Japan.*, **32**, No. 9, 985 (1959.)
(19) H. Krieger, *Suomen Kemi.*, **B31**, 320 (1958).
(20) J. Boeseken, *Rec. trav. chim.*, **47**, 685 (1928).
(21) L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4030 (1952).
(22) M. F. Clark and L. N. Owen, *ibid.*, 318 (1949).
(23) N. J. Rigby, *ibid.*, 1910 (1950).
(24) M. F. Clark and L. N. Owen, *ibid.*, 2105 (1950).
(25) J. Coops, J. W. Dienske, and A. Aten, *Rec. trav. chim.*, **57**, 304 (1938).
(26) H. Adkins and J. N. Sprague, *J. Am. Chem. Soc.*, **56**, 2669 (1934).
(27) A. S. Dreiding and J. A. Hartmann, *ibid.*, **75**, 3726 (1953).
(28) P. von R. Schleyer, *ibid.*, **83**, 1368 (1961).
(29) H. M. Walborsky and D. H. Loncrini, *J. Org. Chem.*, **22**, 1117 (1957).

(30) J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **38**, 1529 (1955). A referee has suggested that "Schreiber and Eschenmoser have supplied an alternative explanation for the phenomena which (we have) ascribed to steric hindrance of rotation." In response to this we wish to point out that the S. and E. proposal, involving relief of steric strain and consequent steric acceleration, requires the formation of considerable carbonyl character in the transition state. On the contrary, we have shown in earlier articles[2b,c] that this assertion is inconsistent with many of the facts that point to a rather small development of the product carbonyl structure in the transition state. One of the more obvious contradictions of the S. and E. contention (as can be seen from the data in Table A) is the fact that cyclopentanol, cyclohexanol and 7-hydroxynorborneol which are oxidized to carbonyls of such vastly different stabilities, nonetheless possess very similar oxidation rates.

earlier[2b] interpreted this effect as being due to the larger steric hindrance to free rotation in the chromate ester afforded by the bulky, axial methyl.

The effect of an α-substituent on the rate of oxidation in monoalcohols as well as 1,3-diols, where the hydroxyl groups obviously oxidize without cyclic chromate ester formation, can be seen in the three cases listed in Table IB, where the size of the alkyl substituent on the 2-position in 1,3-propanediols is successively increased. In going from neopentyl alcohol to the comparable diols XX, XXI and XXII, we encounter the incidence of steric effects on the oxidation rate which are predictable on the basis of the cyclic mechanism of proton abstraction in the monochromate ester[2b] and the operation of the "Rule of Six" proposed by Newman.[31] Effects of a similar magnitude in the homologous monoalcohol series (ethanol to hexanol) have been explained earlier[2c] in this fashion.

From the above correlations of reaction rate and diol structure we conclude that in *cyclic*-1,3-diols the *trans* oxidizes more rapidly because of the greater rate retarding inductive effect of the second hydroxyl group in the *cis* orientation. This is clearly the reverse of the situation in 1,2-diols where cyclic chromate esters can form in the *cis*-diol relationship, a factor affording rate enhancement. However, again, the exact magnitude of the rate difference between *trans*- and *cis*-1,3-diols must be weighted by consideration of the other two rate-regulating factors discussed previously.

The Course of Chromate Ester Formation.—It has been claimed[3] that the mechanism of ester formation of chromic and sulfuric acids are very similar. However, while it is clear that both chromate and sulfate ester formation and reversal involve, respectively, the chromium–oxygen and sulfur–oxygen bonding, the great disparity in the rates of these two processes has not been pointed out. Thus, sulfate esters form and sulfate ion exchanges its sulfur bond to oxygen only extremely slowly.[32] On the other hand, our experience teaches us that chromate is esterified with all alcohols (primary, secondary and tertiary) very rapidly[33] and in a manner reminiscent of the $A_{AC}1$ mechanism.[34]

The central atom in the chromic acid is obviously much more unsaturated and subject to coördination by nucleophiles than the sulfur atom in sulfuric, approaching in this respect the boron in boric acid. The rapid exchange of ligands in the coördination sphere of boron and chromium in their respective oxyacids is well established.[34b] When considered in conjunction with the conclusion we have drawn earlier that cyclic chromate ester formation is governed by the same factors as cyclic borate ester formation, we deduce that boric acid affords a much more fruitful analogy for chromic acid behavior than sulfuric acid.

The $A_{AC}1$ mechanism of chromic acid esterification and the consequent lack of sensitivity of the esterification rate to alkyl substitution in the alcohol is in sharp contrast to what has been observed for lead tetraacetate[22a] and periodic acid.[35b] It would appear in the latter cases that the rate-controlling step of the oxidation is involved with the establishment of esterification equilibrium rather than the ester decomposition step, as it is in chromic acid oxidation.

Experimental

Kinetics Runs.—The technique and practices employed here are identical with those described in earlier publications from these laboratories.

Preparation and Properties of Alcohols.—The method of preparation followed in each case is described in the pertinent reference in Tables IA and IB, with the exception of 5,5-dimethyl-*cis*-1,2-cyclopentanediol (IX), which was made first the first time in the course of this work (as follows): Oxidation of 20.0 g. of 5,5-dimethylcyclopentene[36] in 75 ml. of chloroform and 2250 ml. of ethanol with a solution of 40.5 g. of potassium permanganate and 96 g. of magnesium sulfate heptahydrate in 960 ml. of water was effected by the familiar procedure. This gave 15.7 g. (59%) of colorless liquid, b.p. 68–71° (0.3 mm.). Redistillation gave 4 g., b.p. 69–71° (0.3 mm.), and 9 g., b.p. 73–73° (0.3 mm.). The second fraction was used for the hydrogen bond and conductivity measurements.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.57; H, 10.83. Found: C, 64.00; H, 10.66.

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(33) (a) Only in base and neutral solution is the rate of chromate reaction with water sufficiently slow to be measured; V. K. LaMer and C. L. Read, *J. Am. Chem. Soc.*, **52**, 3098 (1930), estimate a half life = 0.0785 sec. for the reaction $Cr_2O_7^- + H_2O \rightleftarrows 2HCrO_4^-$ in basic solution. (b) See also E. R. S. Winter, M. Carlton and H. U. A. Briscoe, *J. Chem. Soc.*, 131 (1940).

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