Ethyl *cis*-2-bromocyclohexaneacetate: intense peak at 5.80.
cis-2-Hydroxycyclohexaneacetic acid lactone: intense peaks at 5.65 and 10.55, medium peak at 7.01.
Ethyl 1-cyclohexane-1-acetate: intense peak at 5.80, medium peak at 6.08.
Ethyl *cis*-2-bromocyclohexaneacetate: intense peak at 5.80.

cis-2-Hydroxycyclopentaneacetic acid lactone: intense peak at 5.65 and 10.10, medium peak at 10.97.
Ethyl 1-cyclopentene-1-acetate: intense peak at 5.80, medium peaks at 6.04 and 8.87.

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The Chromic Acid Oxidation of 3-Ethyl-3-pentanol

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The oxidation of triethylcarbinol by chromic acid in acidified aqueous acetic acid has been found to proceed by prior dehydration to the olefin. Subsequent steps consist of rapid conversion to the epoxide in accord with the findings of others and the direct oxidation of the epoxide which takes precedence over acid-catalyzed ring opening.

Introduction

The oxidation of organic molecules by chromic acid encountered most frequently involves a carbon–hydrogen bond. Smooth reaction occurs if this bond is activated by its situation at a tertiary carbon, by adjacent oxygen, as in primary or secondary alcohols and in aldehydes, or by anchimeric assistance, as observed in the oxidation of camphane. The oxygen of tertiary alcohols renders the adjacent carbon–carbon bond liable to oxidative cleavage, and it was to discover the basis for this sensitivity that this study was undertaken. Therefore the dependence of the oxidation rate on oxidant and substrate was measured and pertinent facts concerning the oxidation of various intermediates were secured.

Experimental

Materials.—The acetic acid was freed of oxidizable impurities by two distillations from chromic oxide.

Triethylcarbinol was prepared by a Grignard reaction between pentanone-3 and ethylmagnesium bromide. The fraction boiling between 135° and 141° was refractionated in order to obtain a center cut boiling from 141 to 142°.[2]

3-Ethylpentene-2 was prepared by catalytic dehydration of triethylcarbinol with iodine.[3] Refractionation of the crude product gave a center cut boiling from 96–97°.

3-Ethyl-2,3-epoxypentane was made by oxidation of 3-ethylpentene-2 with monoperphthalic acid in ether solution at room temperature. Two distillations yielded a fraction boiling between 125–125°.[4]

3-Ethyl-2,3-pentanediol was prepared by hydrolysis of the corresponding epoxide by 2% sulfuric acid solution at room temperature over a period of 48 hours. The product, isolated by ether extraction and two distillations, boiled from 195–196°.[5]

Analysis for Dichromate.—The reactions were quenched by diluting with 3 volumes of water. This solution was quantitatively transferred to a 250-ml. erlenmeyer flask. About 0.5 g. of sodium iodide was added, the solution was further acidified with 5 ml. of 50% sulfuric acid and then titrated with 0.01 N sodium thiosulfate with the aid of starch indicator. To ensure that no oxidation of the organic substances occurred during this analytical procedure, the method was checked by a precipitation technique. The reaction mixture was poured into 500 ml. of water and the flask carefully rinsed. The trivalent chromium was coprecipitated with aluminum hydroxide by addition of aluminum chloride solution and dilute ammonia. After repre-

cipitation the chromic hydroxide was dissolved in dilute sulfuric acid and oxidized by potassium permanganate. Excess potassium permanganate was reduced to manganese dioxide with manganous sulfate. Filtration of the manganese dioxide and iodometric titration of the filtrate gave results in excellent agreement with the shorter procedure in most occasions. A few low results which were obtained were found to result from incomplete precipitation of the mixed hydroxides.

Oxidation of 3-Ethylpentanol-3.—The oxidations were carried out by pipetting aliquots of stock solutions of the alcohol and sodium dichromate dihydrate in acetic acid into a 50-ml. erlenmeyer flask. A vial containing the appropriate amount of aqueous sulfuric acid was then introduced. This solution had sufficient water to adjust for the amount added as hydration water of the sodium dichromate. Final concentrations of all components are listed in the tables. When the reactants had been brought to 15° in a thermostat controlled to within 0.1°, the vial was overturned and the mixture swirled vigorously for 10 to 15 seconds. At the appropriate time the reaction was quenched and analyzed by the procedure described. Blank determinations were carried out for all runs.

Oxidations of 3-Ethylpentene-2, 3-Ethyl-2,3-epoxypentane and 3-Ethyl-2,3-pentanediol.—The method of mixing the reactants was that employed in the oxidation of triethylcarbinol. Although the procedure for mixing was the same, the behavior of these three substances during the first five to ten seconds of the reaction differed sharply from triethylcarbinol. In contrast to experiments with the alcohol, an immediate color change to an intense greenish-blue occurred on mixing which faded after about 10 seconds to a fairly constant dirty orange color characteristic of mixtures of dichromate and chromic ions. This behavior was also noted with other rapidly oxidized substances, namely, ethanol and acetaldehyde. To ensure that no reaction had occurred prior to addition of the sulfuric acid solution, one experiment in each series was checked by use of a weighed sample of the organic substance in a thin ampule which was crushed and mixed five seconds before the acid was added. In no case was any significant difference noted. It should be mentioned that none of the stock solutions of the organic component stood for more than four hours before use.

For the oxidations of olefin and epoxide, which employed a large excess of oxidant, weighed aliquots were used. This was necessary to obtain the greater accuracy necessitated by the small concentration change in these runs. In order to limit the volume during titration, pipetted quantities of 0.5 N sodium thiosulfate were used to consume most of the iodine.

Oxidations in which ketonic products were investigated were carried out in the same fashion. The quenched reaction mixtures were diluted with 300 cc. of water, neutralized, and 200 cc. of distillate was collected; 0.25 g. of dinitrophenylhydrazine in 30 cc. of 85% phosphoric acid was added and the reaction was allowed five hours at room temperature for completion. Complete removal of ketone by the distillation procedure was shown by a negative dinitrophenylhydrazone test of the distillate collected after the 200-cc. sample had

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(2) T. E. Davis and F. S. Kipping. *J. Chem. Soc.*, **99**, 298 (1911).

(3) G. Edgar, G. Calingaert and R. E. Marker, This Journal. **51**, 1486 (1929).

(4) C. Moureau and G. Barrett. *Bull. soc. chim.*. [4] **29**, 1003 (1908).

(5) Tiffeneau and Dolencourt, *Compt. rend.*, **143**, 127 (1906).

distilled. The precipitates were filtered, dissolved in chloroform, and the small amount of dinitrophenylhydrazine removed by chromatographic separation on a short alumina column. The solvent was evaporated and the residue weighed. This procedure gave 102% yield when applied to a sample of pentanone-3. Slightly lower yields of slightly lower melting product were obtained if the ketonic products were removed from the neutralized reaction mixture by ether extraction instead of distillation.

From most runs, especially those of short duration, a small amount of yellow derivative was noted. Removal and purification of these crystals by recrystallization from alcohol gave a product, m.p. 166–167°, which showed no depression on mixing with a sample of acetaldehyde dinitrophenylhydrazone. The main constituent of the crude dinitrophenylhydrazone mixture was the pentanone-3 derivative. This substance was readily obtained in pure condition from all but the lowest melting products by recrystallization from ethanol. Its identity was shown by mixed melting point determinations with an authentic sample. The experimental results are summarized in the tables which follow.

TABLE I
RATE OF 3-ETHYLPENTANOL-3 OXIDATION[a]

$Cr_2O_7^-$	3-Ethyl-pentanol-3, moles/l. $\times 10^2$	H_2SO_4, moles/l.	H_2O, moles/l.	Time, sec.	Init. slope equiv. oxidant/ moles alc. $\times$ liters $\times$ sec. $\times 10^4$
5.04	13.6	0.655	3.49	600	5.81
5.47	12.4	.655	3.49	600	5.84
2.46	13.6	.655	3.49	600	5.88
2.29	12.4	.655	3.49	600	5.80
0.982	13.6	.655	3.49	600	5.93[b]
1.14	12.4	.655	3.49	600	5.82
1.14	12.4	.655	3.49	300	5.78
1.14	6.13	.655	3.49	600	5.80
1.14	3.09	.655	3.49	600	5.79
1.14	1.55	.655	3.49	600	5.84
1.45	12.1	.328	3.49	600	1.49
1.45	12.1	.164	3.49	600	0.388
1.45	12.1	.328	1.57	600	4.33
1.45	12.1	.164	0.873	600	3.31

[a] All runs at 15° in acetic acid. [b] 71% of the oxidant was consumed in this run.

TABLE II
EFFECT OF CONCENTRATION AND TIME ON CONSUMPTION OF DICHROMATE[a]

Reactant	$Cr_2O_7^-$, moles/l. $\times 10^2$	Reactant, moles/l. $\times 10^2$	Time, sec.	Equiv. oxidant consumed/ mole of reactant
Olefin[b]	0.613	0.472	10	3.70
Olefin	.613	.472	10	3.74
Olefin	.671	.570	10	3.29
Olefin	6.76	.570	10	4.09
Olefin	0.613	.472	60	4.35
Olefin	.613	.472	[c]	4.18
Olefin	.671	.570	60	3.87
Epoxide[b]	.596	.812	10	2.00
Epoxide	18.2	1.065	10	2.09
Epoxide	0.596	0.812	60	2.36
Epoxide	.596	.812	660	2.61
Glycol[b]	.671	.550	10	2.58
Glycol	6.76	.550	10	2.94

[a] All runs at 15° in acetic acid solution containing 0.655 M H_2SO_4 and 3.49 M H_2O. [b] Olefin = 3-ethylpentene-2; epoxide = 3-ethyl-2,3-epoxypentane; glycol = 3-ethyl-2,3-pentanediol. [c] Olefin–acetic acid solution added over 40-sec. interval. Reaction quenched after 1 minute.
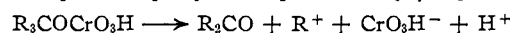
TABLE III
EFFECT OF CONCENTRATION AND TIME ON KETONIC PRODUCTS[a]

Reactant	$Cr_2O_7^-$, moles/l. $\times 10^2$	Reactant, moles/l. $\times 10^2$	Time, sec.	Yield of DNP,[c] %	M.p. of DNP, °C.
Olefin[b]	18.2	1.39	15	44	131–138
Olefin	18.2	1.44	15	49	129–136
Olefin	6.22	0.502	15	53	100–130
Olefin	18.2	1.31	60	55	136–141
Epoxide[b]	18.2	1.36	15	43	136–142
Epoxide	18.2	1.28	60	52	141–148
Epoxide	18.2	1.50	600	73	135–142
Epoxide	7.92	24.4	15	67	101–117
Glycol[b]	18.2	1.06	60	26	106–120
Glycol	18.2	1.23	15	30	108–124

[a] All runs at 15° in acetic acid solution containing 0.655 M H_2SO_4 and 3.49 M H_2O. [b] Olefin = 3-ethylpentene-2; epoxide = 3-ethyl-2,3-epoxypentane; glycol = 3-ethyl-2,3-pentanediol. [c] Yield of crude dinitrophenylhydrazone calculated as the dinitrophenylhydrazone of pentanone-3 and on the assumption that that ketone is the only ketonic product.

Discussion

Three alternatives for the rate-determining step for the degradation of tertiary alcohols were considered.

$$R_2COHCH_2CH_3 \longrightarrow R_2C{=}CHCH_3 + H_2O$$
$$R_3COCrO_3H \longrightarrow R_2CO + R^+ + CrO_3H^- + H^+$$
$$H^+ + R_2COHCH_2CH_3 \longrightarrow R_3C^+ + H_2O$$

The third process, which would involve some kind of rapid oxidation of a carbonium ion, is ruled out by the observation that triethylcarbinol is the first product from oxidation of triethylmethane.[6] This shows that hydration of the carbonium ion is faster than its oxidation provided the evidence for a carbonium ion intermediate in the hydrocarbon oxidation is valid. A decision between the first and second processes may be made from a determination of the rate dependence on oxidant concentration. Westheimer showed that the rate of secondary alcohol oxidation was proportional to the concentration of acid chromate ion.[7] Thus, the second mechanism, which resembles that proposed for secondary alcohol oxidation, predicts first-power dependence on acid chromate ion. This dependence would also hold if the chromate ester were formed in a rate-determining process rather than reversibly, as in the system referred to. The observed independence of rate on oxidant concentration in Table I is consistent only with the first mechanism. Variations of rate with changes in acidity and water concentration are in qualitative accord with this mechanism. A quantitative correlation of these factors would require additional information on the acid-catalyzed dehydration reaction and on the acidity of the solutions.

In order to use the rate of oxidant disappearance as a measure of the rate of this first step an important assumption was necessary, namely, that the oxidation of intermediate products also proceeded at a rate independent of the oxidant. This requires that all intermediates be oxidized rapidly

(6) W. F. Sager and A. Bradley, THIS JOURNAL, 78, 1187 (1956).
(7) F. H. Westheimer and A. J. Novick, J. Chem. Phys., 11, 506 (1943).

or at a rate proportional to that of the dehydration step. The latter condition would require some sort of induced oxidation employing tetra- or pentavalent chromium produced from reaction of olefin and dichromate, or some process independent of oxidant concentration.

An interpretation of the behavior of these intermediates is complicated by the difficulty in reproducing conditions akin to those of the alcohol oxidation. In the short duration experiments listed in Table II the reactants were mixed rapidly to furnish solutions with far higher concentrations of olefin or epoxide, as well as unstable states of chromium, than could be generated by the slow oxidation of the alcohol. That an intermediate valence of chromium, probably 5, is formed and persists for a few seconds seems likely in view of the intense color change noticed whenever a rapidly oxidizable substance was introduced. Evidence for pentavalent chromium has been reported before.[8] It is felt that this behavior of chromium is responsible for the weird stoichiometry of some of the olefin oxidations. Oxidations of ten seconds duration regularly showed consumption of something less than four equivalents of oxidant per mole of olefin. In the one experiment in which a large excess of oxidant was used the figure was very close to four equivalents of oxidant. Just such a value would be expected if the first product of the olefin oxidation is the epoxide, for this substance was found to consume exactly two equivalents of oxidant with extreme rapidity. This is the expected intermediate in view of the extensive evidence for this course of reaction published by Hickinbottom.[9]

An explanation for incomplete oxidation on grounds of a competing olefin hydration would seem to conflict with the rate measurements on the tertiary alcohol oxidation. However a hydration too slow to rival a fast oxidation by dichromate might still prove important in cases where olefin remained after all the hexavalent chromium had been consumed. Should pentavalent chromium oxidize the olefin more slowly than it reacts with water, temporary storage of two-thirds of the oxidizing capacity in this form would permit the

(8) C. Wagner, Z. anorg. Chem., 168, 279 (1928); C. Wagner and W. Preiss, ibid., 168, 265 (1928).

(9) W. J. Hickinbottom, et al., J. Chem. Soc., 1334 (1948); 1600 (1951); 1906 (1953); 1360 (1955).

hydration reaction to occur unless the mole ratio of chromate to olefin was two or greater. If the color changes in the first few seconds can be attributed to formation of pentavalent chromium and its subsequent disproportionation to dichromate and chromic ions, the conditions for such a hydration prevail in many of the runs. In all cases but the one which gave the expected stoichiometry, the amount of oxidant was insufficient to consume all the olefin if pentavalent chromium were the end result of the first rapid reaction. Additional support is given to this idea by comparison of runs 1 and 3 in Table II, which shows that the proportion of oxidant consumed is decreased by an increase of the olefin–oxidant ratio even though the oxidant concentration was increased at the same time. If the hydration of the olefin competes with oxidation by hexavalent chromium, an increase in the olefin–oxidant ratio would have the opposite effect. Of course, these arguments have no bearing on the question of which chromium valence is formed at the instant of reaction with the olefin. In addition to the evidence from the stoichiometric result for the premise that oxidation of the olefin gives the epoxide, the similarity of the ketonic products illustrated in Table III gives support to the same conclusion.

Oxidation of the epoxide is clean and fast to give a product, as yet unidentified, which results from the uptake of two equivalents of oxidant. That the oxidation of the epoxide was faster than its ring opening is shown by the difference in stoichiometry and in the nature of ketonic products between the epoxide and glycol oxidations.

Up to this point the reaction pattern appears to be remarkably straightforward. Yields at each step are virtually quantitative up to the production of the unidentified product from oxidation of the epoxide. In order to locate the factors which limit the yield of pentanone-3, attention should be focused on events subsequent to this stage.