TABLE I

PRODUCTS OF ADDITION OF ISOTHIOCYANIC ACID TO OLEFINS

Olefin	Product	Yield, %	B.p., °C.	Mm.	n^{25}D	$d^{25}{}_{25}$	Nitrogen, % Calcd.	Found	Sulfur, % Calcd.	Found
$(CH_3)_2C=CHCH_3$	Mixture[a]	30	73–78	29	1.470– 1.474	0.928	10.9	10.7	24.8	24.6
$(CH_3)_3CCH=C(CH_3)_2$	$(CH_3)_3CCH_2C(CH_3)_2NCS$	66	83–85	12	1.4811	0.9045	8.2	8.0	18.8	18.6
$C_6H_5CH=CH_2$	$C_6H_5CH(CH_3)NCS$	52	135–137	23	1.5784	1.0754	8.6	8.4	19.6	19.7
$C_6H_5(CH_3)=CH_2$	$C_6H_5C(CH_3)_2NCS$	66	82–86	23	1.5678	1.0565	7.9	7.8	18.1	17.6
$CH_2=CHCOOCH_3$	$NCSCH_2CH_2COOCH_3$	20	78–80	0.5	1.4772	1.1839	9.7	9.5	22.1	22.3
$CH_2=CHCOOC_2H_5$	$NCSCH_2CH_2COOC_2H_5$	38	124	10	1.4699[b]	1.1381[b]	8.8	8.6	20.1	20.0

[a] Mixture of amyl thiocyanate and isothiocyanate; $[M]$D calcd. for $C_5H_{11}SCN$, 37.64; for $C_5H_{11}NCS$, 39.82; found, 38.09. [b] At 20°.

TABLE II

THIOCYANATES AND ISOTHIOCYANATES

Compound	B.p., °C.	Mm.	n^{25}D	$d^{25}{}_{25}$	Nitrogen, % Calcd.	Found	Sulfur, % Calcd.	Found
$C_2H_5C(CH_3)_2SCN$	57–60	10	1.4620[a]	0.9369[a]	10.9	10.7	..	..
$C_2H_5C(CH_3)_2NCS$	67–72	23	1.4820[a]	.9198[a]	10.9	10.4	..	..
$(CH_3)_3CCH_2C(CH_3)_2SCN$	88–92	10	1.4749[a]	.926[a]	8.2	8.3	..	..
$(CH_3)_3CCH_2C(CH_3)_2NCS^{9b}$	108–112	28	1.4811	0.9043	8.2	8.0	18.8	18.8
$C_6H_5CH(CH_3)NCS$	133–134	20	1.5780	1.0719	8.6	8.3	19.6	19.5
$C_6H_5C(CH_3)_2NCS$	83	0.7	1.5670	1.0537	7.9	7.9	18.1	17.9
$CH_3OOCCH_2CH_2SCN$	73–76	0.3	1.4770	1.1840	9.7	9.6	22.1	22.4
$C_2H_5OOCCH_2CH_2SCN$	101–105	3	1.4678	1.1281	8.8	8.7	20.1	20.0

[a] At 20°.

1,3-Bis-(α-phenylethyl)-2-thiourea.—α-Phenylethyl isothiocyanate (56 g., 0.34 mole) was heated under reflux with 20% aqueous sodium hydroxide solution (100 g., 0.5 mole) for 6 hours. Crystals gradually deposited on standing. They were collected (42 g., 87%) and recrystallized from ether, m.p. 158–159°.[13]

Anal. Calcd. for $C_{17}H_{20}N_2S$: N, 9.9; S, 11.3. Found: N, 9.6; S, 11.4.

(13) A. Michaelis and E. Linow, *Ber.*, **26**, 2168 (1893), reported m p. 163°.

1,3-Bis-(α,α-dimethylbenzyl)-2-thiourea, m.p. 150–152°, was obtained similarly but required 48 hours heating. The yield was low.

Anal. Calcd. for $C_{19}H_{24}N_2S$: N, 9.0. Found: N, 8.7.

Infrared absorption was measured with a Perkin–Elmer spectrophotometer, model 21, using sodium chloride prisms. Ethyl thiocyanate and *t*-butyl isothiocyanate[9b] were reference compounds.

PHILADELPHIA, PENNA.

The Mechanism of γ-Bromoester Pyrolysis

BY JOSEPH WEINSTOCK

It has been shown that the pyrolysis of a γ-bromoester to form lactone and alkyl bromide proceeds with inversion of configuration both in the formation of the new carbon–oxygen bond and in the formation of the new carbon–bromine bond. This has been interpreted as indicating an ionic two-stage mechanism for this reaction.

The pyrolysis of γ-bromoesters to form γ-lactones and alkyl bromides has been known for many years.[1] A more recent example was the observation of Linstead and Mead[2] that a sample of ethyl 2-bromocyclopentaneacetate was unstable at room temperature and that on heating it gave ethyl bromide, 2-hydroxycyclopentaneacetic acid lactone, hydrogen bromide and ethyl 1-cyclopentene-1-acetate. This reaction was investigated by Kharasch[3] during his classical work on the free radical addition of α-bromoesters to olefins to form γ-bromoesters. He found that pyrolysis of aliphatic γ-bromoesters proceeded smoothly at 160–180° to give good yields of the corresponding γ-lactones and the alkyl bromide derived from the alcohol portion of the ester. In connection with another problem it became necessary for us to learn the mechanism of this reaction.

The stereochemistry of the replacement of bromine by oxygen during the pyrolysis was studied using alicyclic bromoesters. The required ethyl *trans*-2-bromocyclopentaneacetate was prepared by treating *cis*-2-hydroxycyclopentaneacetic acid lactone with hydrogen bromide in ethanol.[2] Since the replacement of oxygen by bromine in this reaction is a nucleophilic displacement,[4] the product must be *trans*. The isomeric ethyl *cis*-2-bromocy-

(1) See C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 550, for a review of the older literature.

(2) R. P. Linstead and E. M. Mead, *J. Chem. Soc.*, 935 (1934).

(3) M. S. Kharasch, P. S. Skell and P. Fisher, THIS JOURNAL, **70**, 1055 (1948).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 393.

clopentaneacetate was prepared in a reaction modeled after the preparation of cis-1-bromo-2-methylcyclohexane.[5] The ultraviolet light catalyzed addition of hydrogen bromide to ethyl 1-cyclopentene-1-acetate gave an ethyl 2-bromocyclopentaneacetate whose physical properties were very similar to, but not identical with, those of the trans compound. The chemical behavior of the two isomers was quite different. Ethyl cis-2-bromocyclohexaneacetate was prepared in a manner similar to that of the cyclopentane analog.

Heating ethyl cis-2-bromocyclopentaneacetate without solvent at 180° for two hours caused the evolution of some hydrogen bromide; distillation of the reaction mixture gave back material which was identified by its infrared spectrum as starting material containing small amounts of ethyl 1-cyclopentene-1-acetate and 2-hydroxycyclopentaneacetic acid lactone. On the other hand, heating ethyl trans-2-bromocyclopentaneacetate at 180° gave a rapid evolution of ethyl bromide, and distillation of the residue after two hours gave a 95% yield of pure cis-2-hydroxycyclopentaneacetic acid lactone. In a similar manner pyrolysis of ethyl cis-2-bromocyclohexaneacetate under the same conditions gave a mixture containing almost no lactone and from which about 40% of the starting material and about a 40% yield of ethyl 1-cyclohexene-1-acetate were separated by distillation and identified by means of their infrared spectra.

These data and the good yields of lactone obtained by Kharasch[3] and others[1] from acyclic γ-bromoesters show that the pyrolysis to lactone proceeds well only when the oxygen of the ester can reach the rear of the carbon carrying the bromine atom.
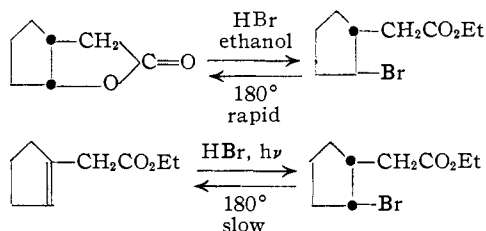
The stereochemistry of the replacement of oxygen by bromine during the pyrolysis was studied using an optically active bromoester derived from an optically active alcohol. 4-Bromodecanoic acid was prepared by refluxing ethyl 4-bromodecanoate[3] with 48% aqueous hydrogen bromide. This was converted into the γ-lactone by reaction with aqueous sodium bicarbonate and this treated with phosphorus pentabromide to give 4-bromodecanoyl bromide.[2] Reaction of this with (−)-2-butanol,[6] $[\alpha]^{25.5}D$ −4.68°, in dry ether gave a 92% yield of sec-butyl 4-bromodecanoate, $\alpha^{25}D$ −3.98° ($l = 1$ dm.).

Pyrolysis of this ester at 175–180° gave a 40% yield of (+)-2-bromobutane, $[\alpha]^{27}D$ +8.75°. Assuming a value of $[\alpha]^{20}D$ −13.83° for pure (−)-2-butanol,[7] this corresponds to a value of $[\alpha]^{25}D$ +25.8° for the bromide which would have been

obtained if optically pure (−)-2-butanol had been used in the preparation of the ester. The highest rotation reported for optically pure 2-bromobutane calculated on a similar basis is that of Letsinger[8] who obtained a value of $[\alpha]^{25}D$ −26.1° for (−)-2-bromobutane prepared from (+)-2-butanol by a careful reaction with hydrogen bromide. This result shows that the pyrolysis proceeds with exceedingly high retention of optical activity and with inversion of configuration at the carbon bearing the alkyl oxygen.

The stereochemical results cited above indicate that the pyrolysis probably is a two-stage ionic displacement reaction. The acyl oxygen has been indicated as the initial attacking atom rather than
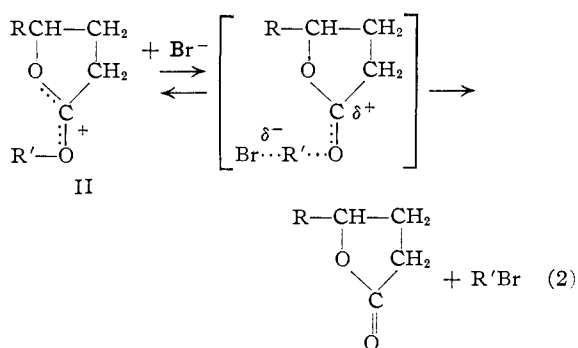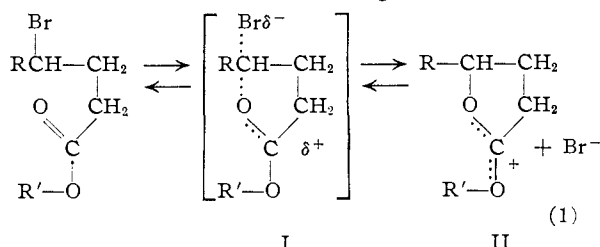
the alkyl oxygen because this gives a transition state I which can be better stabilized by resonance and which does not have two adjacent positive charges.
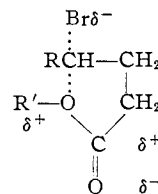
It is assumed that in the non-ionizing media present, the intermediate II exists as an ion pair.

A radical process involving free radicals as intermediates is excluded because of the high degree of stereospecificity at both reaction centers. In general radical reactions proceed with complete or almost complete racemization.[9] A "four-center" concerted type of reaction similar to the xanthate and ester pyrolysis[10] is also excluded because a study of molecular models shows that it is impossible in a transition state resembling the reactant

(5) H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, 74, 3588 (1952).

(6) We wish to thank Dr. R. L. Burwell of this Laboratory for this sample of (−)-2-butanol.

(7) J. Kenyon, H. Phillips and V. P. Pittman, J. Chem. Soc., 1072 (1935).

(8) R. L. Letsinger, THIS JOURNAL, 70, 406 (1948). However, it is possible that this is not the ultimate value that may be obtained.

(9) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 713.

(10) D. J. Cram, THIS JOURNAL, 71, 3882 (1949); E. R. Alexander and A. Mudrak, ibid., 72, 1810 (1950).

to simultaneously have all the necessary atoms properly arranged.

Experimental[11]

Ethyl cis-2-Bromocyclohexaneacetate.—A solution of 29.3 g. (0.174 mole) of ethyl 1-cyclohexene-1-acetate[12] in 100 ml. of n-pentane was irradiated in an apparatus consisting of a test-tube-shaped reaction flask into which was fitted a specially constructed quartz-jacketed water cooled Hanovia-type SC-2537 lamp. During the reaction dry hydrogen bromide gas was slowly bubbled in via a fritted disk sealed into the bottom of the reactor and the reaction kept at 15° by circulating cold tap water through the lamp jacket. At the end of the reaction the absorption of hydrogen bromide stopped quite sharply. The pentane solution was then washed with water, shaken for 5 min. with 20% aqueous sodium hydroxide to decompose any ethyl 1-bromocyclohexaneacetate, washed again, dried over magnesium sulfate and distilled. This gave 15.0 g. (34%) of a colorless liquid, b.p. 82–83° (0.7 mm.); redistillation gave 12.7 g., b.p. 80° (0.6 mm.), n^{25}D 1.4865.

Anal. Calcd. for $C_{10}H_{17}BrO_2$: C, 48.20; H, 6.88. Found: C, 48.94, 48.71; H, 6.71, 6.60.

Ethyl cis-2-Bromocyclopentaneacetate.—A solution of 12.0 g. (0.078 mole) of ethyl 1-cyclopentene-1-acetate[13] in 100 ml. of n-pentane was irradiated in the apparatus described in the preparation of ethyl cis-2-bromocyclohexaneacetate and dry hydrogen bromide gas bubbled in. The reaction mixture was washed with water, shaken for 5 min. with 30% aqueous potassium hydroxide solution, washed again, dried, and distilled. This gave 7.3 g. (40%) of a colorless liquid, b.p. 107–109° (6 mm.), n^{25}D 1.4808.

Anal. Calcd. for $C_9H_{15}BrO_2$: C, 45.97; H, 6.43. Found: C, 46.33; H, 6.18.

Ethyl trans-2-Bromocyclopentaneacetate.—This was prepared by the method of Linstead and Mead[2] using cis-2-hydroxycyclopentaneacetic acid lactone which had been purified as follows. Crude 2-hydroxycyclopentaneacetic acid lactone prepared by the method of Linstead and Mead[2] was dissolved in 20% aqueous sodium hydroxide by warming, extracted with ethylene chloride, and acidified. The acidified aqueous solution was warmed on a steam-bath for a few minutes and then extracted with ethylene chloride. The ethylene chloride extract was washed with aqueous sodium bicarbonate solution to remove non-lactonic material, with water, and then dried and distilled. This gave the pure cis-lactone, b.p. 102–104° (6 mm.).

A solution of 9.1 g. (0.072 mole) of cis-2-hydroxycyclopentaneacetic acid lactone in 30 g. of absolute ethanol was cooled to 0° and saturated with dry hydrogen bromide gas. This solution was stored at 5° overnight and then poured into water, extracted with ethylene chloride, and the ethylene chloride extract washed with 20% aqueous sodium hydroxide, saturated ammonium chloride, and water in turn. Drying over magnesium sulfate and distillation gave 14.4 g. (85%) of product, b.p. 108–110° (6 mm.), n^{25}D 1.4775; reported[1] b.p. 125° (15 mm.).

Pyrolysis of Ethyl cis-2-Bromocyclohexaneacetate. A.—A 5.0-g. sample of the cis-bromoester was heated at 180° for 2 hours. There was some evolution of hydrogen bromide which started shortly after the sample was heated. Distillation of the reaction mixture gave: (1) 1.4 g., b.p. 54–70° (0.7 mm.), identified by infrared spectra as mostly ethyl 1-cyclohexene-1-acetate (41% of theory); (2) 0.2 g., b.p. 70–81° (0.7 mm.); (3) 2.0 g., b.p. 81–85° (0.7 mm.), identified by infrared spectra as starting material containing a small amount of lactone (40% recovery).

B.—A 7.0-g. sample of bromoester was heated at 180° for two hours. Distillation of the reaction mixture gave: (1) 0.8 g., b.p. 68–76° (1.5 mm.), n^{25}D 1.4631, identified by infrared as essentially ethyl 1-cyclohexene-1-acetate; (2) 0.35 g., b.p. 76–99° (1.5 mm.); (3) 2.91 g., b.p. 99–103° (1.5 mm.), n^{25}D 1.4833, identified by infrared as starting material contaminated with a small amount of lactone; (4) 1.10 g., b.p. 103–107° (1.5 mm.), n^{25}D 1.4852, identified by infrared

as starting material. Fractions 3 and 4 represent a 56% recovery of starting material.

Pyrolysis of Ethyl cis-2-Bromocyclopentaneacetate.—Heating a 3.0-g. sample of ethyl cis-2-bromocyclopentaneacetate at 180° for 2 hours resulted in the evolution of some hydrogen bromide. Distillation of the residue gave 1.5 g. of material which by inspection of the infrared spectrum proved to be mostly starting material mixed with a very small amount of lactone and some ethyl 1-cyclopentene-1-acetate.

Pyrolysis of Ethyl trans-2-Bromocyclopentaneacetate.—Heating a sample of 4.0 g. (0.017 mole) of ethyl trans-2-bromocyclopentaneacetate at 180° caused an almost immediate commencement of reflux of ethyl bromide. After 2 hours the reaction mixture was cooled and distilled to give a forerun of ethyl bromide, b.p. 38° (760 mm.), followed by 2.05 g. (95%) of a colorless liquid, b.p. 104° (6 mm.), n^{25}D 1.4748. The infrared spectrum of this material was identical with that of the lactone whose preparation is described in the preparation of ethyl trans-2-bromocyclopentaneacetate.

sec-Butyl 4-Bromodecanoate.—A mixture of 58.0 g. of ethyl 4-bromodecanoate[3] and 75 ml. of 48% aqueous hydrogen bromide was refluxed overnight to convert it to the free acid. The layers were then separated, the water layer extracted with pentane, and the pentane extract combined with the organic layer and washed. In an attempt to purify the acid by extracting it with saturated aqueous sodium bicarbonate solution, an emulsion formed which could be broken only by reacidification. The product was then taken up in pentane and the pentane solution dried and the solvent removed under vacuum. An infrared spectrum of the residue showed the presence of much lactone. The residue was then added to phosphorus pentabromide prepared by slowly adding 11.7 ml. of bromine to 28.6 ml. of phosphorus tribromide. After the lactone was added it was warmed on a steam-bath for one hour and the reaction mixture distilled. A fraction of 31.9 g. (49% from the ethyl ester) was obtained, b.p. 147–157° (7 mm.), n^{25}D 1.4980, which was the desired 4-bromodecanoyl bromide. The identity of this product was established as follows.

A mixture of 6.28 g. (0.02 mole) of 4-bromodecanoyl bromide and 15 ml. of dry ether was cooled in an ice-bath and 0.90 g. (0.02 mole) of absolute ethanol added. After standing at room temperature for 10 min. it was heated on a steam-bath until the ether was evaporated. The reaction mixture was then poured into water, taken up in pentane, and the pentane washed successively with water, saturated aqueous sodium bicarbonate, and water. The pentane solution was dried and the solvent removed on a steam-bath. This left 5.5 g. (quant. yield) of a colorless liquid, n^{25}D 1.4592. The original ethyl 4-bromodecanoate had n^{25}D 1.4590, reported[3] n^{20}D 1.4599.

A mixture of 6.28 g. of 4-bromodecanoyl bromide in 15 ml. of dry ether was treated with 1.48 g. (0.02 mole) of 2-butanol. Treatment as described above gave after evaporation of the pentane 6.15 g. (100%) of product, n^{25}D 1.4598. Distillation during which time the pot temperature rose to 145° (and perhaps allowed some pyrolysis) gave: (1) 2.6 g., b.p. 93–98° (0.1 mm.), n^{25}D 1.4582; (2) 1.7 g., b.p. 98° (0.1 mm.), n^{25}D 1.4595.

Anal. Calcd. for $C_{14}H_{27}BrO_2$: C, 54.72; H, 8.86. Found: C, 54.82; H, 8.73.

(−)-sec-Butyl 4-Bromodecanoate.—A solution of 19.2 g. (0.061 mole) of 4-bromodecanoyl bromide in 50 ml. of dry ether was treated with 4.4 g. (0.0595 mole) of (−)-2-butanol, $[\alpha]^{25.5}$D −4.68°. Working up as described above without distillation gave 16.8 g. (92%) of (−)-sec-butyl 4-bromobutyrate, n^{25}D 1.4608, α^{25}D −3.98° (l = 1 dm.).

Pyrolysis of (−)-sec-Butyl 4-Bromodecanoate.—A sample of 12.15 g. (0.0396 mole) of (−)-sec-butyl 4-bromodecanoate was heated at 175–180° for 3.5 hours at 50 mm. while the volatile products were captured in a Dry Ice cooled trap. The contents of the trap were taken up in pentane and washed with saturated salt water, saturated aqueous sodium bicarbonate, and water in succession. Drying the pentane solution over magnesium sulfate and distilling gave 2.15 g. (40%) of 2-bromobutane, b.p. 89°, n^{25}D 1.4348, $[\alpha]^{27}$D +8.75°; reported[6] b.p. 89–91°, n^{26}D 1.4330.

Infrared Spectra.—Herewith are some of the characteristic bands used to identify the compounds mentioned above (wave lengths are in microns).

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(11) Microanalyses by Miss H. Beck. Boiling points are uncorrected. Infrared spectra were taken on a Baird Associates instrument.

(12) G. A. R. Kon and K. S. Nargung, *J. Chem. Soc.*, 2461 (1932).

(13) G. A. R. Kon, R. P. Linstead and G. W. G. Maclennan, *ibid.*, 2454 (1932).

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.

EVANSTON, ILLINOIS

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

BY W. F. SAGER[1]

RECEIVED DECEMBER 23, 1955

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-

(1) The George Washington University, Washington 6, D. C.
(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, **61**, 1486 (1929).
(4) C. Moureau and G. Barrett, Bull. soc. chim., [4] **29**, 1003 (1908).
(5) Tiffeneau and Dolencourt, Compt. rend., **143**, 127 (1906).

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