ethanol, 10 ml. of 2 *N* sodium hydroxide was added. After 20 hr. at room temperature, the solution was chilled, diluted with an equal volume of water, and neutralized by the addition of 10 ml. of 2 *N* hydrochloric acid. The crystalline product was removed by filtration and dried to give 2.4 g. (83%) of *anti*-IX melting at 186–186.5°. Recrystallization from methylene chloride did not alter the melting point. The product was identical with material prepared by the reaction of 2-amino-5-chlorobenzophenone *anti*-oxime with acetyl chloride as described below for the *syn* form.

Anal. Calcd. for $C_{15}H_{13}ClN_2O_2$: C, 62.40; H, 4.54. Found: C, 62.56; H, 4.29.

2′-Benzoyl-4′-chloroacetanilide *syn*-Oxime (*syn*-IX) and 2′-Benzoyl-4′-chloroacetanilide *syn*-Oxime Acetate (XV).—A solution of 24.6 g. (0.1 mole) of 2-amino-5-chlorobenzophenone *syn*-oxime in 500 ml. of ether was stirred with 100 ml. of water and cooled to 0–5°. Acetyl chloride (14.2 g., 12.9 ml., 0.18 mole) was added dropwise over 40 min. while keeping the reaction slightly alkaline by the simultaneous addition of 10% sodium hydroxide. The ether layer was separated and washed with water. An insoluble crystalline material (XV) was separated by filtration of the ether layer. The crude product (5.4 g., m.p. 155–164°) was crystallized several times from chloroform to give colorless rods of XV, melting at 171–172.5°.

Anal. Calcd. for $C_{17}H_{15}ClN_2O_3$: C, 61.72; H, 4.57; N, 8.46. Found: C, 61.93; H, 4.61; N, 8.50.

The ether filtrate was dried over sodium sulfate and, on concentration, 16.8 g. of a mixture of *syn*-IX and XV melting at 152–176° crystallized. Recrystallization from chloroform gave mainly *syn*-IX (m.p. 179–182°, 6.9 g.). Further recrystallization from acetonitrile gave colorless plates of *syn*-IX melting at 182–184°. A mixture melting point with *anti*-IX showed a slight depression.

Anal. Calcd. for $C_{15}H_{13}ClN_2O_2$: C, 62.40; H, 4.54; N, 9.70. Found: C, 62.69; H, 4.47; N, 9.65.

Acknowledgment.—We are indebted to Mr. S. Traiman and Dr. F. Vane for the infrared and n.m.r. spectra, to Dr. V. Toome for his painstaking studies of the ultraviolet spectra, to Dr. Al Steyermark and his staff for the microanalyses, and to Mr. E. Stange for technical assistance.

Reaction of α-Pinene Oxide with Zinc Bromide and Rearrangement of 2,2,3-Trimethyl-3-cyclopentene Products Derived Therefrom[1]

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Studies of zinc bromide catalyzed isomerization of α-pinene oxide resulted in formation of principally 2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde in accordance with the report of Arbusow in 1935. Epoxides of esters of 2,2,3-trimethyl-3-cyclopentene-1-ethanol obtained from reduction of the aldehyde moiety were rearranged readily by acids to esters of 4-hydroxy-2,3,3-trimethyl-1-cyclopentene-1-ethanol.

In studies on isomerization of α-pinene epoxide (I) Arbusow[3] reported better than 90% yield of α-campholene aldehyde, 2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde (II) by action of zinc bromide on the oxide. King and Farber noted the presence of 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde in addition to the 2,2,3 isomer II when the epoxide I was treated in quinaldine solution with *p*-toluenesulfonic acid (see Chart I). Hartshorn and collaborators[5] have recently reported on the acid-catalyzed rearrangement of I using boron trifluoride, zinc bromide, and hydrogen fluoride. With each catalyst they report a substantial yield of the 2,2,4 isomer. In reactions of the aldehyde II, no one apparently has observed rearrangement of this aldehyde by methyl group migration from the C-2 to the C-3 positions although Tiemann[6] reported such a rearrangement in the synthesis of α-campholenic acid, 2,2,3-trimethyl-3-cyclopentene-1-acetic acid (VII) from camphoroxime or campholenonitrile. The 2,2,3-trimethyl analog is readily converted to 2,3,3-trimethyl-1-cyclopentene-1-acetic acid (VIII). In fact, in repeating this work, it was difficult to avoid transformation of this sort.

In the course of studies of terpenes in this laboratory, an investigation on reactions of aldehyde II was undertaken to find new uses for turpentine. In order to duplicate the results of Arbusow,[3] this research involved a study of the reaction of zinc bromide on α-pinene epoxide (I). An important phase was the characterization of the reaction product or products since the results of earlier workers suggested three possible isomeric cyclopentene derivatives represented by III, IX, and XII (see Chart II). The aldehyde function of the principal product, 2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde (II), was reduced to 2,2,3-trimethyl-3-cyclopentene-1-ethanol (III). For the purpose of characterization, alcohol III was compared with IX and XII. The alcohol III was considered an attractive intermediate since esters of mono- and polybasic acids might yield useful mono- and polyepoxides. In reactions of the epoxide XIII, formed by epoxidation of the acetate III, molecular rearrangements resulted in XIV and XVI.[7] The structural relationship of the cyclopentene compounds were confirmed by n.m.r. and infrared spectral analyses.

The reaction of α-pinene epoxide with freshly fused zinc bromide proceeded essentially in accordance with the results reported by Arbusow. Examination of the aldehyde by gas–liquid partition chromatography (g.l.p.c.) indicated it to be 96% pure. A second material was present to the extent of about 4%. Meerwein–Ponndorf and lithium aluminum hydride reductions of the aldehyde gave principally 2,2,3-trimethyl-3-cyclopentene-1-ethanol (III). G.l.p.c. analyses indicated the presence of two alcohols in a ratio of about

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[1] Presented at the Southeastern Regional Meeting of the American Chemical Society, Charleston, W. Va., Oct. 1964.

[2] One of the laboratories of Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] B. Arbusow, *Ber.*, **68**, 1430 (1935).

[4] L. C. King and H. J. Farber, *J. Org. Chem.*, **26**, 326 (1961).

[5] M. P. Hartshorn, D. N. Kirk, and A. F. A. Wallis, *J. Chem. Soc.*, 5494 (1965).

[6] F. Tiemann, *Ber.*, **30**, 243 (1897).

[7] While this paper was being reviewed for publication, an article appeared which described essentially the same rearrangement: see D. J. Goldsmith and C. J. Cheer, *J. Org. Chem.*, **30**, 2264 (1965).

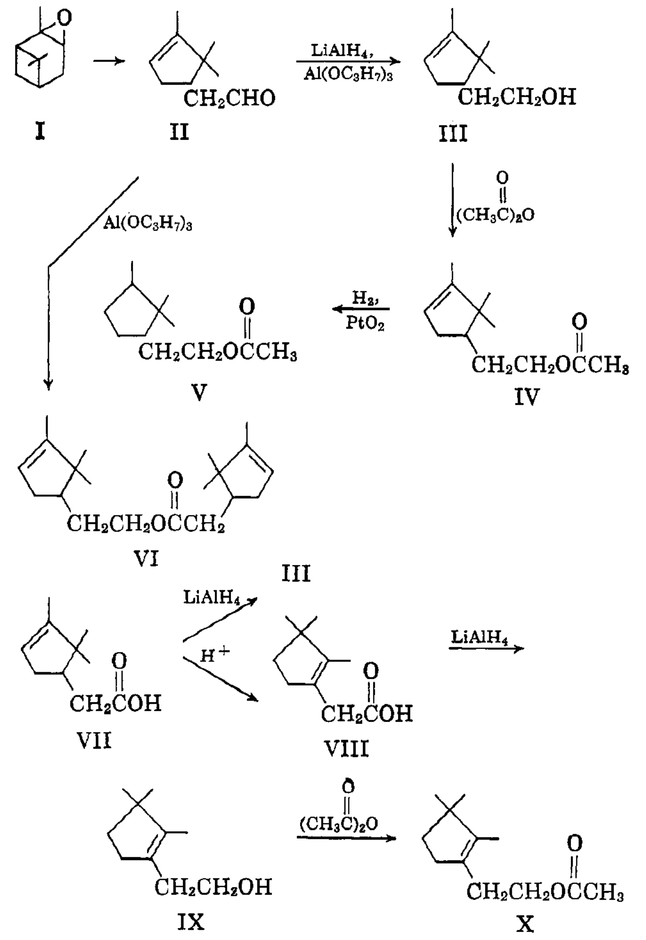

CHART I

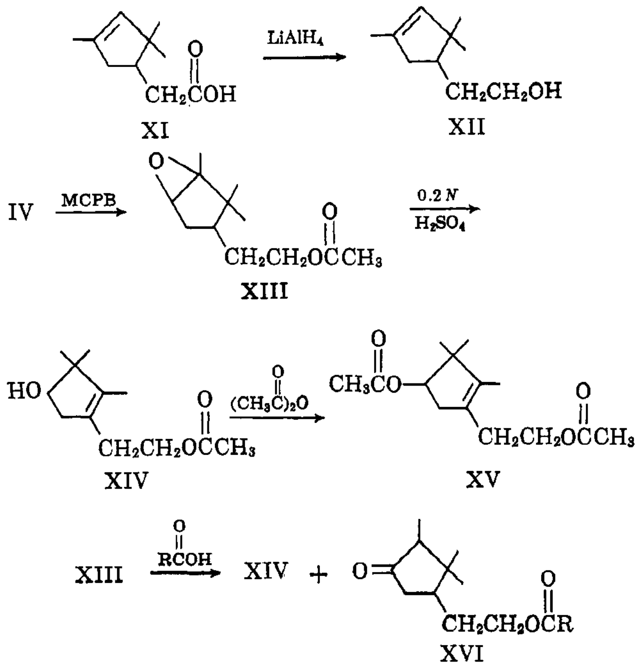

CHART II

96:4. When this mixture was compared by g.l.p.c. and infrared spectral analyses with the 2,2,4-trimethyl and the 2,3,3-trimethyl derivatives, differences in the alcohols III, IX and XII and the minor component were discernible. It was therefore concluded that the reaction of pinene epoxide with zinc bromide had not given any of the 2,2,4-trimethyl nor the 2,3,3-trimethyl materials, and that alcohol III and its esters had not rearranged to IX. The n.m.r. spectra of II, III, and IV confirm that these all have the 2,2,3-trimethyl structure. All spectra contained three three-proton singlet bands, two near $\delta = 0.95$ p.p.m., indicative of a geminal dimethyl group with a vicinal substituent, and the third in the allylic region at $\delta = 1.6$ p.p.m. In each case the olefinic proton appeared as an unresolved multiplet at $\delta = 5.2$ p.p.m. with the proper area. The chemical structure of the minor component has not been established. The two alcohols IX and XII were prepared by $LiAlH_4$ reduction of the corresponding acids XI[8] and VIII.[6]

Hartsborn, *et al.*,[5] state that the reaction of the oxide and zinc bromide was carried out by the method of Arbusow.[3] The discrepancy between the results of these authors and that reported here is believed due to catalyst preparation which was not well described by Arbusow.

The 2,2,3-trimethyl alcohol III was acetylated and the ester IV was epoxidized with *m*-chloroperbenzoic acid (MCPA) by the usual procedure. Some of the chemistry of the epoxide XIII has been delineated. The epoxide XIII was stable to refluxing alcoholic potassium hydroxide. With aqueous sulfuric acid the bulk of the crude reaction product was 4-hydroxy-2,3,3-trimethyl-1-cyclopentene-1-ethanol acetate (XIV).

The n.m.r. spectrum of XIV in CCl_4 confirms the assigned structure. As in the case of the 2,2,3-trimethyl isomers, three singlet bands of three-proton areas are observed, one in the allylic region, but no band attributable to an olefinic proton was present. The hydroxyl proton appeared as a band at $\delta = 3.76$ p.p.m. poorly resolved from the triplet centered at $\delta = 3.78$ p.p.m. owing to the C-4 methine proton split by the adjacent methylene group. The band at $\delta = 3.76$ p.p.m. disappeared on D_2O exchange or on acetylation to XV. The methine proton in XV showed the expected shift to lower field. Both XIV and XV have a four-proton band centered at $\delta = 2.3$ p.p.m. and consisted of a triplet superimposed on an unresolved multiplet in accord with the presence of two similar but nonidentical allylic methylene groups. The infrared spectrum of XIV confirmed the absence of olefinic protons and presence of both hydroxyl and ester groups. As expected from such a structure, XIV absorbed ozone readily but was resistant to hydrogenation. Products from the ozonization have not been characterized.

Infrared spectral analyses of the material obtained by saponification of XIV gave very little, if any, absorbance at 5.76 μ for ketonic materials and was principally XVIII. Organic acids with XIII produced varying amounts of what is believed to be esters of ketone 4-oxo-2,2,3-trimethylcyclopentane-1-ethanol acetate (XVI). The principal products obtainable by g.l.p.c. from reaction of XIII with glacial acetic acid–sulfuric acid or acetic acid–acetic anhydride were the esters XIV, XV, and XVI.

The epoxide XXI of the decanoic acid ester, 2,2,3-trimethyl-3-cyclopentene-1-ethanol decanoate (XX, Chart III), was treated with octanoic acid and saponified. The crude reaction products obtained from saponification, when examined by infrared spectral

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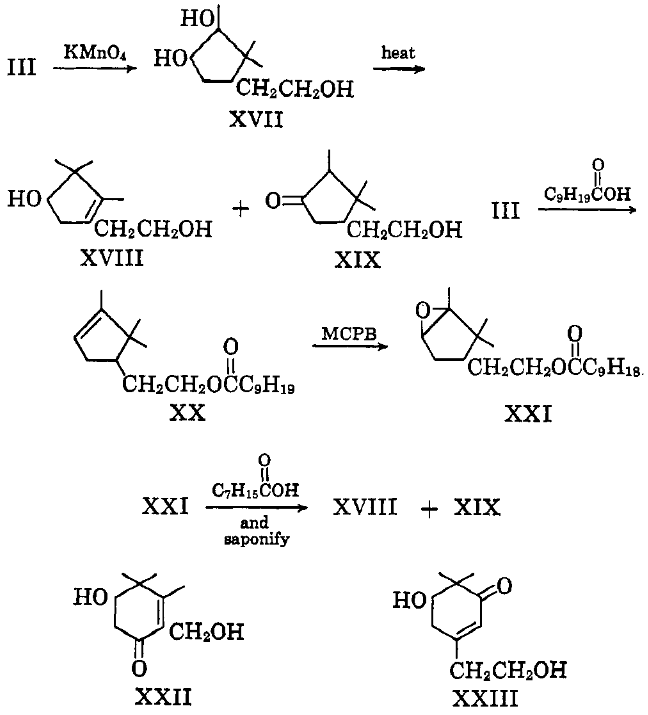
(8) J. D. Park, R. L. Settine, B. A. Parkin, Jr., and G. W. Hedrick, *J. Org. Chem.*, **27**, 898 (1962).

CHART III



analyses, contained both carbonyl and hydroxyl groups. Acetylation of the mixture gave, in addition to other materials, XV and what was believed to be the ketone XVI (R = acetyl).

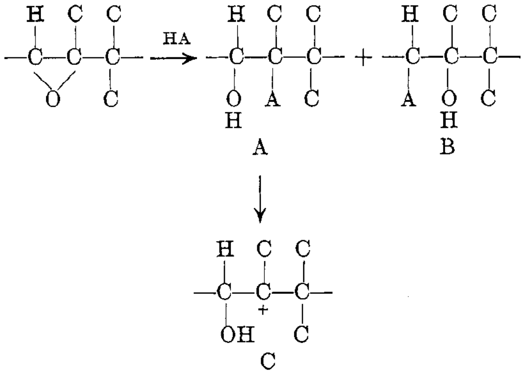
In reactions of VII with permanganate, Tiemann[9] isolated a ketonic material which was obtained from the glycol formed as a result of the oxidation. Komppa and Beckmann[10] reinvestigated the subject and isolated 4-oxo-2,2,3-trimethylcyclopentane-1-acetic acid from the distillation of the glycol obtained from permanganate oxidation of VII.

In a reaction similar to that of Komppa and Beckmann, III was oxidized with permanganate. Distillation of the resulting glycol XVII gave a mixture containing XVIII and an impure ketone which probably was XIX. The mixture containing the ketone had the same retention time by g.l.p.c. analyses and infrared absorption as the ketonic materials resulting from acid-catalyzed isomerization of the epoxide XIII.

From the products obtained from reactions of the epoxide with acid, rearrangement of the compound had occurred as a result of methyl-group migration in one case and isomerization or rearrangement of the epoxide to a ketone in the other.

There seems to be no record of an epoxy compound having a structure like XIII. The reactions of XIII with acids are believed to be normal and occur in two steps. The first step involves breaking the carbon-oxygen bond producing a carbonium ion at the C-3 position of the cyclopentane ring. With a carbonium ion in this position, methyl-group migration by the Whitmore mechanism[11] would be expected. Migration of hydrogen from the C-4 to the C-3 position would have resulted in a condition which could have produced the ketone XVI.

Parker and Isaacs[12] have arbitrarily assigned structures A and B in the following equation as normal and abnormal products.



In order to obtain compound XIV, the reaction could have proceeded by normal addition with ultimate elimination of A, producing the carbonium ion C which rearranged. The methyl group rearrangement is undoubtedly the same as that observed by Tiemann[6] when he treated VII with dilute acid. The migratory tendency of one of the methyl groups on the 2-carbon atom must be very great. This tendency exists when the acid function of VII is replaced by nitrile or acid amide.[6] This same rearrangement must have occurred when the XVII was distilled as evidenced by formation of XIV.

In the rearrangement of epoxides XIII and XXI and glycol XVII to ketones there appears to be nothing unusual. Winstein and Henderson[13] and Wheland[14] adequately explain rearrangement of glycols and epoxides to ketones as suggested here. The acid moiety in VII was obviously sufficiently strong to bring about the rearrangement observed by Tiemann[6] and later by Komppa and Beckmann.[10] The rearrangement of the glycol XVII without benefit of acid catalysis to give the ketone is a little strange.

Experimental Section

All temperature readings given are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer with NaCl optics; solids were run as mulls in mineral oil. N.m.r. spectra were determined with a Varian Associates A-60 spectrometer using 10–20% solutions in carbon tetrachloride with tetramethylsilane as an internal standard.

2,2,3-Trimethyl-3-cyclopentene-1-acetaldehyde (II).—α-Pinene oxide (I), commercial grade, $n^{20}\mathrm{D}$ 1.4697, b.p. 65° (10 mm.), $[\alpha]^{24.2}\mathrm{D}$ +42.37° (neat, 10 cm.), prepared from commercial α-pinene (82 g., 0.54 mole), and 200 ml. of benzene were heated to a reflux to remove traces of water in the system. The catalyst, approximately 1 g. of reagent grade zinc bromide, was heated to a boil in a small tube, boiled until distillate reached the top of the tube, and added rapidly while molten to the benzene solution at 60–65°. Freshly fused (melted) catalyst gave a sluggish reaction and poor yield of product. After a few seconds the reaction became very vigorous and lasted about 1 min. The batch was heated to a reflux for about 1 hr. and then cooled. A number of batches was combined and washed with water until free of zinc bromide, and the benzene was removed by distillation. Bulb-to-bulb distillation with water aspirator vacuum gave 1432 g. of crude product (87.6% yield) and 170 g. of pot

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[9] F. Tieman, *Ber.*, **27**, 3015 (1896).

[10] G. Komppa and S. Beckmann, *ibid.*, **B69**, 2783 (1936).

[11] F. C. Whitmore, *J. Am. Chem. Soc.*, **54**, 3274 (1932).

[12] R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 7373 (1959).

[13] S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 29.

[14] G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 465.

residue from a charge of 1638 g. (10.75 moles) of epoxide. Fractionation of the crude distillate using a 45-cm. column packed with protruded stainless steel helices gave a 100-g. forecut which contained 80% aldehyde and 1295 g. of product (79.2% yield): b.p. 85° (14 mm.); n^{20}_{D} 1.4645; $[\alpha]^{22.5}_{\mathrm{D}}$ −3.71° (neat, 10 cm.); $\delta^{\mathrm{CCl_4}}$ = 0.90 (3H, s), 1.00 (3H, s), 1.63 (3H, m), 5.22 (1H, m), 9.75 (1H, t) p.p.m. Gas–liquid partition chromatographic analysis of the large fraction using 30% Carbowax on Chromosorb W column gave two peaks in a ratio of about 96:4. The minor peak had a retention time about 1 min. longer than the major peak.

2,2,3-Trimethyl-3-cyclopentene-1-ethanol (III).—The aldehyde II (304 g., 1.95 mole), freshly distilled aluminum isopropoxide (70 g., 1.03 equiv.), and 2250 ml. of dry, peroxide-free isopropyl alcohol[15] were heated to a reflux and the reaction was carried out by the usual procedure, removing by-product acetone as it formed with an adequate distilling system. The alcoholate was decomposed with 150 ml. of 50% sodium hydroxide solution. After distilling the isopropyl alcohol, the residue was mixed with benzene and the product was isolated by washing to remove alkali, stripping of benzene, and finally by bulb-to-bulb distillation, b.p. 130° (25 mm.). The yield was 267 g. (87%). There was 8 g. of still residue which was subsequently identified as the Tischenko ester, 2,2,3-trimethyl-3-cyclopentene-1-ethanol 2,2,3-trimethyl-3-cyclopentene-1-acetate (VI).[16]

The crude alcohol was distilled through a 45-cm. column packed as above: b.p. 105° (8 mm.); n^{20}_{D} 1.4710; $\delta^{\mathrm{CCl_4}}$ = 0.86 (3H, s), 0.97 (3H, s), 1.60 (3H, m), 3.8 (1H, m), 5.19 (1H, m) p.p.m. Gas–liquid partition chromatographic analyses using a column described above gave two peaks. The minor peak, about 4%, appeared at 3 min. ahead of the major product peak.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.61; H, 11.78.

Lithium Aluminum Hydride Method.—The aldehyde (304 g., 1.95 moles) was dissolved in dry diethyl ether and treated with 22 g. (2.3 equiv.) of lithium aluminum hydride. The material was worked up by the usual procedure.[17] There was 290 g. of product (94%), n^{20}_{D} 1.4710, which was identical with the above alcohol.

2,2,3-Trimethyl-3-cyclopentene-1-ethanol Acetate (IV).—The alcohol III above was converted to its acetate by allowing it to react with excess acetic anhydride: n^{20}_{D} 1.4564; b.p. 104–106° (8.0 mm.); $\delta^{\mathrm{CCl_4}}$ = 0.88 (3H, s), 0.99 (3H, s), 1.62 (3H, m), 5.25 (1H, m) p.p.m.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27; sapon. equiv., 196.3. Found: C, 73.24; H, 10.16; sapon. equiv., 198.7.

2,2,3-Trimethylcyclopentane-1-ethanol Acetate (V).—The acetate IV (10 g., 0.05 mole) dissolved in absolute ethanol was reduced with 0.5 g. of Adams catalyst at room temperature. The reduction was quantitative. The product was distilled through a 12-cm. metal-packed column under water-aspirator vacuum: b.p. 115° (8.0 mm.), n^{20}_{D} 1.4496.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.83; H, 11.18.

3,4-Epoxy-2,2,3-trimethylcyclopentane-1-ethanol Acetate (XIII).—The acetate IV (98 g., 0.5 mole) in 500 ml. of diethyl ether was epoxidized[18] by addition of 101 g. (0.50 mole) of 85% metachloroperbenzoic acid (MCPB) dissolved in 500 ml. of diethyl ether at 15–20° with good agitation. Ureacted MCPB and by-product metachlorobenzoic acid were removed from the ether solution by washing with dilute aqueous alkali and water. A negative test for peracid was obtained when analyzed by the method described in the literature.[17] The usual caution was observed in removing and testing for peracid before continuing with the isolation of the epoxide. After drying over anhydrous sodium sulfate and stripping to remove ether, tests for acid and active oxygen (peracid) were negligible. The material was distilled through 12-cm. column packed with stainless steel helices: b.p. 136° (10 mm.), 94 g., 89% yield of crude epoxide, 95.5% epoxide (dioxane–hydrochloric acid method[19]). The oxirane group had strong absorbance in the infrared spectrum at 11.85 and 12.3 μ.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.92; H, 9.29.

Epoxide XIII (2 g., 0.0094 mole) was heated on a steam bath with 300 ml. of 0.1 *N* potassium hydroxide for a few hours. After standing a few days, the alcohol was removed and the product was extracted with ether. After stripping, 1.8 g. of residue was obtained. Infrared spectra had strong bands at 11.85 and 12.3 μ as a result of the epoxide group which obviously had not reacted to any extent.

4-Hydroxy-2,3,3-trimethyl-1-cyclopentene-1-ethanol Acetate (XIV).—Epoxide XIII (20 g., 0.094 mole) was mixed with 100 ml. of 0.2 *N* sulfuric acid and agitated for 8 hr. at room temperature. After standing overnight the acid was neutralized and the product was extracted with diethyl ether. The ether solution was washed and dried over anhydrous sodium sulfate, and the solvent was removed by stripping. The product was distilled through a 12-cm. column packed with protruded stainless steel helices: b.p. 154° (8.5 mm.), 100% yield. Analysis of the distillate by g.l.p.c. using a 15-ft., 30% Carbowax column (above) indicated the material was at least 96% pure: n^{20}_{D} 1.4759; $[\alpha]^{26}_{\mathrm{D}}$ −6° (*c* 10%, ethanol, 10 cm.); $\delta^{\mathrm{CCl_4}}$ = 0.86 (3H, s), 0.92 (3H, s), 1.54 (3H, m), 2.30 (4H, t, m), 3.76 (1H, s), 3.78 (1H, t) p.p.m. Infrared spectral analyses gave strong absorbance for hydroxyl group at 2.95 μ and no absorbance in the 12.5-μ region for a double bond.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.02; H, 9.69.

Epoxide XIII (23 g., 0.108 mole) was allowed to react with 65 g. (1.08 moles) of glacial acetic acid and 1 drop of concentrated sulfuric acid at 60° for 4 hr. Diluting with water, extracting with ether, and washing gave 27.6 g. of material, b.p. 130° (3.0 mm.). The distillate had strong infrared absorbance at 2.95 and 5.76 μ. Saponification of a portion of the ester and examination of the alkali-insoluble material by infrared spectral analyses gave strong absorbances at 2.95 and 5.75 μ attributable, respectively, to hydroxyl and carbonyl groups. The spectrum had absorbancies at the same wave lengths as the material obtained from the octanoate–decanoate ester and the distillate from the triol XVII below. Separation by g.l.p.c. established that the principal components of the material were XVIII and probably XIX. These, however, accounted for only about 60% of the total.

The use of acetic acid–acetic anhydride mixture without the sulfuric acid gave a mixture which contained XVIII and a ketonic substance much the same as the mixture from acetic acid–sulfuric acid reaction product.

The product XIV was ozonized using the procedure of Eschinasi[20] wherein the ozonide was subjected to reductive cleavage. For this, 10.6 g. of ester XIV (0.05 mole) was dissolved in 60 ml. of methanol and 30 ml. of water, cooled by an ice-water bath, and ozonized. After 4 hr., the ozone absorption ceased. Benzene (25 ml.), water (250 ml.), zinc dust (13 g.), and 32 g. of 62% sulfuric acid were added to reduce the ozonide. After boiling a few minutes, evaporation of benzene, and cooling, zinc sulfate was removed by addition of barium hydroxide to precipitate sulfate ion and oxalic acid to remove the zinc ion. The solvent and water were stripped under water-aspirator vacuum leaving a few grams of product which gave a negative test for methyl ketone and a positive test for olefin. In the infrared there was a strong absorbance at 2.95 μ as a result of the hydroxyl group and a strong carbonyl absorbance at 6.05 μ, probably an α,β-unsaturated ketone. The ester had undoubtedly hydrolyzed since there was no absorbance at 5.75 μ in the infrared. A hydrogenated sample had a carbonyl absorbance at 5.75 μ. In the ultraviolet spectrum, maximum absorbance was at 237.5 mμ (20 mg./l. of ethanol) (α 56). G.l.p.c. analyses of the hydrogenated and unreduced materials on a Craig polyester column gave two major peaks which accounted for 90% of the material in about equal amounts. The data indicated cyclization as a result of aldol condensations. Two possibilities for such condensations exist, XXII and XXIII.

Since degradation studies (ozonolysis) gave a mixture which appeared to be complex, a more direct method for proof of structure such as n.m.r. was examined.

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(15) A. L. Wilds, *Org. Reactions*, **2**, 178 (1944).

(16) V. E. Tischenko, *Chem. Zentr.*, **77**, 1309, 1552 (1906); W. C. Child and H. Adkins, *J. Am. Chem. Soc.*, **45**, 3013 (1923).

(17) W. G. Brown, *Org. Reactions*, **6**, 469 (1951).

(18) Technical Data Sheet, *m*-Chloroperbenzoic acid, FMC Corporation, Inorganic Division, Product Promotion Department, New York, N. Y., 1962.

(19) J. L. Junknickel, E. D. Peters, A. Polgar, and F. T. Weiss, "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 135.

(20) E. H. Eschinasi, U. S. Patent 3,023,244 (Feb. 27, 1962).

4-Acetoxy-2,3,3-trimethylcyclopentene-1-ethanol Acetate (XV).—A portion (10 g., 0.047 mole) of the distillation product from the 4-hydroxy compound XIV was acetylated by refluxing with a few milliliters of acetic anhydride. Acetic acid and excess anhydride were removed by distilling at atmospheric pressure. The product was taken up in ether, washed, and finally distilled bulb-to-bulb: b.p. 128° (2.0 mm.); $n^{20}D$ 1.4616; δ^{CCl_4} = 0.91 (3H, s), 1.00 (3H, s), 1.54 (3H, m), 2.34 (4H, t, m), 4.89 (1H, q) p.p.m.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.14; H, 8.90.

2,3,3-Trimethyl-1-cyclopentene-1-ethanol (IX).—2,3,3-Trimethyl-1-cyclopentene-1-acetic acid (VIII),[6] m.p. 50–52° from 1:1 methanol–water (48 g., 0.048 mole), was reduced with lithium aluminum anhydride (2.5 g.) in ether. After working up in the usual manner, 6.5 g. of alcohol was obtained, 88% yield. Analyses by g.l.p.c., using an alkaline Carbowax column, indicated the alcohol was pure. Furthermore, under the conditions employed, this alcohol could be distinguished for identification from 2,2,3-trimethyl-3-cyclopentene-1-ethanol and the minor component of III. There was no absorbance in the infrared spectrum in the 12.5-μ region because of the double bond.

2,3,3-Trimethyl-1-cyclopentene-1-ethanol Acetate (X).—Alcohol IX (6.5 g., 0.42 mole) was converted to the acetate by refluxing in 25 g. of acetic anhydride. After working up, 6.4 g. of ester was obtained in the middle fraction: b.p. 118° (20 mm.); $n^{20}D$ 1.4554; δ^{CCl_4} = 0.98 (6H, s), 1.51 (3H, m), 2.32 (2H, t) p.p.m.; sapon. equiv. 198.68 (calcd. 196.28).

2,2,4-Trimethyl-3-cyclopentene-1-ethanol (XII).—2,2,4-Trimethyl-3-cyclopentene-1-acetic acid[8] (XI) was reduced with lithium aluminum hydride by the same procedure as used in reduction of the 2,3,3-trimethyl derivative IX. The crude alcohol had strong absorbance in the infrared spectrum at 2.9 and 12.2 μ as the result of the hydroxyl and a trisubstituted double bond. G.l.p.c. analyses, Castorwax on Chromosorb W, established that the 2,2,3-trimethyl derivative III was not contaminated with the 2,2,4 isomer and that this isomer was different from the minor component of III.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.00; H, 11.85.

3,4-Dihydroxy-2,2,3-trimethylcyclopentane-1-ethanol (XVII).—The alcohol III (61.6 g., 0.4 mole), was added in 1 hr. at 2–4° to 500 ml. of 1.5% potassium permanganate (7.5 g., 0.19 mole) with agitation. After disappearance of color the manganese dioxide was removed by filtration and washed well with water. The filtrate and wash water were combined. The triol was extremely soluble in water and was not extractable by solvent. Water was removed by azeotropic distillation following the addition of chloroform. At the end, salts appeared which were removed by filtration. The chloroform was stripped *in vacuo*. The product crystallized, 75.3 g., 100% yield, m.p. 114–116° for analytical sample (from chloroform).

Anal. Calcd. for $C_{10}H_{19}O_3$: C, 63.79; H, 10.71. Found: C, 63.96; H, 10.74.

A small portion was distilled bulb-to-bulb at atmospheric pressure, b.p. 280–290°. Infrared spectral analysis of the crude distillate gave strong absorbances at 2.95 and 5.76 μ, thus establishing the presence of hydroxyl and carbonyl groups. Separation by g.l.p.c. using a Carbowax column gave three major peaks which accounted for 60% of the total. The third, the largest, was the only peak that showed an infrared spectrum having strong absorbance at 5.76 μ. The bulk of the material was acetylated and the crude acetates were separated by g.l.p.c. using again a Carbowax column. The first, which accounted for 10% of the crude pyrolysate, had an infrared spectrum identical with that of IV. The second peak, 10% of the crude product, had an infrared spectrum identical with that of XV. The third peak was believed to be a mixture containing the acetate of XIX.

2,2,3-Trimethyl-3-cyclopentene-1-ethanol Decanoate (XX).—The alcohol III (308 g., 2.0 moles), *n*-decanoic acid (688 g., 4.0 moles), and *p*-toluenesulfonic acid (2 g.) were dissolved in 1310 ml. of benzene and refluxed until no more water was trapped in a Dean–Stark decanter. After washing with dilute alkali to remove acid and with water, the ester was distilled bulb-to-bulb, b.p. 200° (8–9 mm.), 586 g., 95% yield. The material was distilled through a 30-cm. column packed with stainless steel packing, b.p. 132° (10 mm.), 553 g. (89.6%) yield, $n^{20}D$ 1.4575. Isolation and examination of the alcohol after saponification of the ester established that the alcohol was identical with alcohol III.

Anal. Calcd. for $C_{20}H_{36}O_2$: C, 77.86; H, 11.77; hydrogenation equiv., 308.49. Found: C, 78.02; H, 11.96; hydrogenation equiv., 305.

3,4-Epoxy-2,2,3-trimethylcyclopentane-1-ethanol Decanoate (XXI).—The decanoate ester XX (161 g., 0.5 mole) was epoxidized with 101 g. (0.5 mole) of MCPB by the procedure used above for X. After stripping ether (80° and 1 mm.) there was obtained 168 g. of residue, 93% yield. This was distilled bulb-to-bulb, b.p. 160° (1 mm.), 140 g., 82.5% yield, 91% epoxide,[18] $n^{20}D$ 1.4593.

The epoxide XXI (27 g., 0.09 mole) and *n*-octanoic acid (13.5 g., 0.09 mole) were heated at 230°. The disappearance of acid was followed by titration of aliquots with standard alkali. After 8 hr., about 50% of the acid had disappeared and the rate of decrease had diminished. The material was taken up in diethyl ether and washed free of acid with alkali and finally with water. After removing the ether, the residue was distilled through a 12-cm. column packed with glass helices, b.p. 170–210° (0.1 mm.). The fraction of material, 19.5 g., that boiled over 200° (0.1 mm.) was saponified with alcoholic sodium hydroxide. From this 5 g. of alkali-insoluble material (calcd. yield, 7 g. if the ester saponified was the octanoate–decanoate ester) was obtained which, by infrared analyses, contained hydroxyl and carbonyl groups as a result of absorbancies at 2.95 and 5.76 μ. Separation of crude alcoholic materials or the acetates therefrom, from saponified acetates by preparative-scale g.l.p.c. using a Carbowax column gave three peaks which accounted for 77% of the total. The first peak, 7% of the original, gave the same infrared spectrum as XVIII. The second peak, 20% of the original, had a very strong absorbancy in the infrared at 5.76 μ. The infrared spectrum had the same bands as peak 3 from pyrolysis of the triol XVII and was probably essentially XIX. This particular spectrum was identical with the spectrum of the material from the triol except for the intensity of absorbance at 11.5 μ. Further examination of peak 3 by g.l.p.c. showed that a second component was present which accounted for the 11.5-μ absorbance. Neither of the materials could be isolated in the pure state.

2,2,3-Trimethyl-3-cyclopentene-1-ethanol 2,2,3-Trimethyl-3-cyclopentene-1-acetate (VI).—2,2,3-Trimethyl-3-cyclopentene-1-acetaldehyde (II) (152 g., 1 mole) was added slowly to 30 g. of a dry solution of distilled aluminum isopropoxide (5.1 g.) in 40 ml. of benzene at 25°. The reaction was worked up by diluting with diethyl ether and washing with dilute hydrochloric acid and finally with water. After stripping the ether, the product was distilled through a 45-cm. column packed with protruded stainless steel packing, b.p. 172° (3.0 mm.). The total crude material recovered, 122.4 g., contained 100.2 g. of ester product, 67.5% yield, $n^{20}D$ 1.4821, and 22.2 g. of low-boiling material which was principally alcohol III. Saponification of a portion of the ester and examination by comparison of the resulting alcohol and acid with known materials by infrared spectral analyses established that the ester had the proposed composition.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.60; sapon. equiv., 304.46. Found: C, 79.03; H, 10.64; sapon. equiv., 308.9.

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