The dimethyl ester was prepared by treatment with diazomethane, crystallization from methanol, and sublimation at 100° and 0.05 mm., m.p. 95–96° (lit.,[20] m.p. 94°).

Hemipinic Acid Anhydride.—A sample of hemipinic acid[23] was heated to 180–190° for 5 min. and was then sublimed at 100° and 0.05 mm. for 5 hr., m.p. 160–162°, ν_{max} 1775 cm.$^{-1}$ and 1845 cm.$^{-1}$.

Dimethylverticillatine (IV).—Verticillatine (II) (300 mg.) slowly dissolved in a mixture of 10 ml. methanol and 20 ml. of ethereal diazomethane over a 3-day period at 0°. The solution was filtered, concentrated to dryness, and crystallized from methanol to yield 195 mg., m.p. 245–246°. An analytical sample was prepared by recrystallization from methanol, m.p. 243–245°, [α] +159° (c, 1.59), λ_{max} 280 mμ (ϵ 14200), λ_{min} 258 mμ (ϵ 10700), ν_{max} 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{31}NO_5$: C, 72.14; H, 6.95; mol. wt., 449.5. Found (after drying to constant weight at 100° C.): C, 72.04; H, 6.86; mol. wt. (by titration), 452.

Dihydrodimethylverticillatine (VI).—A solution of 113 mg. of dimethylverticillatine (V) in 10 ml. of ethanol acidified with 2 drops of concentrated by hydrochloric acid and was hydrogenated using 67 mg. platinum oxide as catalyst. After 2 hr. 5.05 ml. of hydrogen was absorbed (theory 5.59 ml.). The solution was concentrated to dryness, taken up in water, made basic, and extracted into chloroform. The chloroform solution was dried over sodium sulfate and concentrated to dryness and the product was crystallized from ether to yield 81 mg., m.p. 180–182°. An analytical sample was prepared by crystallization from acetone–ether, m.p. 187–188°, [α] −99° (*c*, 1.13), λ_{max} 285 mμ (ϵ 4160), λ_{min} 258 mμ (ϵ 660), ν_{max} 1775 cm.$^{-1}$, pK_a' 8.3.

Anal. Calcd. for $C_{27}H_{33}NO_5$: C, 71.81, H, 7.20, mol. wt. 451.5. Found (after drying to constant weight at 100°): C, 71.38; H, 7.20; mol. wt. (by titration), 455.

Tetrahydrodimethylverticillatine (*VIII*).—To a partial solution of 182 mg. of dimethylverticillatine (V) in 40 ml. of ether was added 180 mg. of lithium aluminum hydride. The mixture was stirred for 18 hr. The excess hydride was then decomposed with water and the ether concentrated 194 mg. of a white froth which crystallized readily from benzene, m.p. 196–202°. An analytical sample was prepared by recrystallization from acetone m.p. 208–209°, [α] +7.5 (c, 1.20) λ_{max} 258 mμ (ϵ 15900), λ_{min} 248 mμ (ϵ 14850), $\lambda_{inflection}$ 280 mμ (ϵ 5260).

Anal. Calcd. for $C_{27}H_{35}O_5N$: C, 71.49; H, 7.78. Found (after drying to constant weight at 100° C.): C, 71.43; H, 7.56.

Diacetyltetrahydrodimethylverticillatine.—Tetrahydrodimethylverticillative (VIII) was dissolved in 1 ml. of pyridine. One milliliter of acetic anhydride was added and the mixture was allowed to stand at room temperature overnight. The solution was concentrated to near dryness, taken up in ether, and extracted into dilute hydrochloric acid. The acid solution was made basic with sodium carbonate and extracted into ether to yield 118 mg. of product. This was purified by elution from grade 3 alumina with benzene as an amorphous solid, λ_{max} 261 mμ (ϵ 12900), λ_{min} 247 mμ (ϵ 10900), $\lambda_{inflection}$ 281 mμ (ϵ 5650).

Anal. Calcd. for $C_{31}H_{39}NO_7$: C, 69.25; H, 7.31; 2-acetyl, 15.64. Found: C, 68.63; H, 7.40; acetyl, 15.53.

Hexahydrodesoxydimethylverticillatine (IX).—A solution of 51.2 mg. of tetrahydrodimethylverticillatine (VIII) was hydrogenated using 33 mg. of platinum oxide catalyst in acidified ethanol. Uptake of 4.08 ml. (theory for 1 mole 2.52 ml.) was complete in 15 min. The reaction mixture was filtered, concentrated, taken up in water, made basic, and extracted with ether. *The ether was concentrated and 12 mg. of hexahydro*dimethylverticillatine (VII) crystallized, m.p. 146–152°. The remainder of the material in the filtrate could not be obtained crystalline but could be converted to a methiodide on standing overnight in methyl iodide solution. A sample of hexahydrodesoxydimethylverticillatine methiodide (IX) recrystallized from methanol–ether melted at 197–201°, [α] −17° (*c*, 1.88 in CH_3OH), λ_{max} 285 mμ (ϵ 4956), λ_{max} 215 mμ (ϵ 57100), λ_{min} 260 mμ (ϵ 2830).

Anal. Calcd. for $C_{28}H_{40}NO_4I$: C, 57.83; H, 6.93; 1-C-CH_3, 2.59. Found: C, 57.61; H, 7.05; C-CH_3, 2.63.

Hexahydrodimethylverticillatine (VII).—To a solution of 325 mg. of dihydrodimethylverticillatine in ether was added 325 mg. of lithium aluminum hydride and the mixture was stirred at room temperature overnight. Water was added, the precipitate filtered and washed, and the filtrate concentrated to dryness and crystallized from acetone–methanol to yield 233 mg., m.p. 165–167°. An analytical sample was obtained from the same solvents, m.p. 167–169°, [α] −10° (c, 2.22), λ_{max} 281 mμ (ϵ 4770), λ_{min} 256 mμ (ϵ 1114).

Anal. Calcd. for $C_{27}H_{37}NO_5$: C, 71.18; H, 8.19. Found: C, 71.39; H, 8.39.

An amorphous diacetate was prepared in the usual manner and was purified by chromatography on alumina and elution with benzene.

Anal. Calcd. for $C_{31}H_{41}NO_7$: C, 68.99; H, 7.66; 2-acetyl, 15.95. Found (after drying to constant weight at 50°): C, 68.87; H, 7.55; acetyl, 16.14.

Acknowledgment.—The author wishes to thank Mr. Gerald Caple, Mrs. K. Osmond, and Mrs. D. DeTar for n.m.r. spectra and Dr. S. Rajappa for calling attention to reference 6.

---

(23) K and K Laboratories, Jamaica, N. Y.

A Novel Rearrangement of Epoxyalkyl Esters[1]

Wayne V. McConnell and William H. Moore

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

Received September 12, 1962

3,4-Epoxy-2,2,4-trimethylpentyl isobutyrate was found to undergo acid-catalyzed rearrangement predominantly to tetrahydro-2,2,4,4-tetramethyl-3-furyl isobutyrate. Such a rearrangement was indicated to be typical of 3,4-epoxyalkyl esters. Under similar conditions, a 4,5-epoxyalkyl ester underwent reactions typical of conventional epoxides. Mechanisms are proposed to explain the novel rearrangement.

In acidic media, epoxides generally undergo ring-opening reactions accompanied by addition of the acid or solvent molecules, or isomerization to a ketone or aldehyde. These typical reactions were observed in this investigation with 3,4-epoxyalkyl esters, but the predominant reactions with these epoxides were rearrangements to other types of compounds.

With the exception of 2,3-epoxypropyl esters, there is very little information on epoxyalkyl esters in the literature. Some assistance was forthcoming from the work of Gasson and associates, who reported the properties of epoxides with structures related to the epoxyalkyl groups which were the subject of this study.[2a,b,3] These workers found that 2,3-epoxy-2,4,4-trimethylpentane in the presence of sulfuric acid was converted mainly to 2,4,4-trimethyl-1-penten-3-ol, along with

---

[1] Presented at the American Chemical Society Southwest-Southeast Combined Regional Meeting, New Orleans, La., December, 1961.

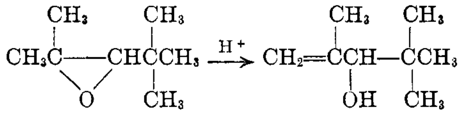
[2] (a) E. J. Gasson, A. F. Millidge, G. R. Primavesi, W. Webster, and D. P. Young, *J. Chem. Soc.*, 2161 (1954); (b) E. J. Gasson, A. R. Graham, A. F. Millidge, I. K. M. Robson, W. Webster, A. M. Wild, and D. P. Young, *ibid.*, 2170 (1954).

[3] A. R. Graham, A. F. Millidge, and D. P. Young, *ibid.*, 2180 (1954).

TABLE I

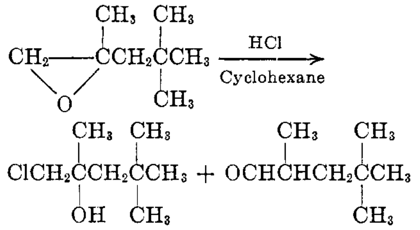
PHYSICAL CONSTANTS AND ANALYSIS OF 3,4-EPOXY-2,2,4-TRIMETHYLPENTYL ISOBUTYRATE AND ITS REARRANGEMENT PRODUCTS

Compound	B.p., °C. (0.8 mm.)	n^{20}_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sapon. equiv. Calcd.	Sapon. equiv. Found
I	70–71	1.4321	67.3	67.3	10.3	10.5	214	215
II	54–55	1.4307	67.3	67.2	10.3	10.6	214	216
III	68–69	—	—	—	—	—	—	—
Mixture of IV and V	88–89	1.4520	67.3	67.5	10.3	10.5	214	216



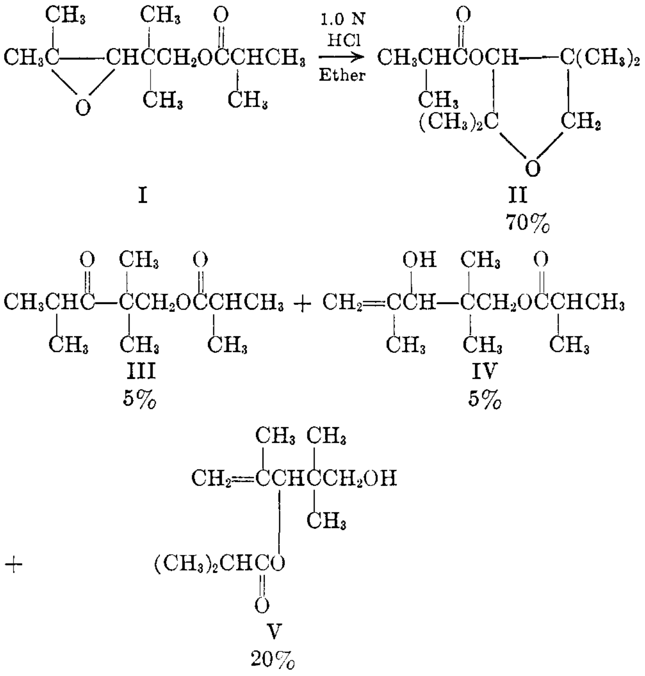
minor amounts of the hydrated compound and the ketone.

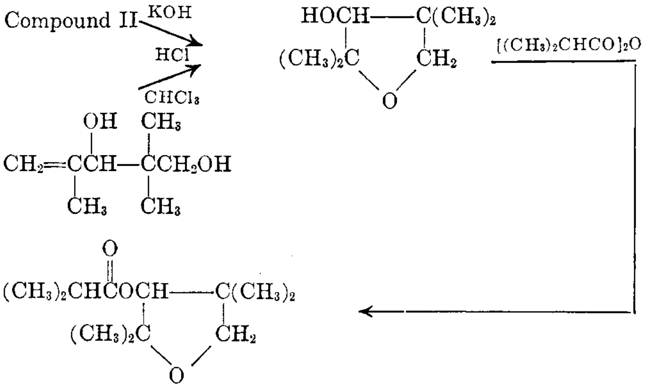
Only a small fraction of the theoretical amount of hydrogen chloride was found to add to this epoxide under conditions generally suitable for functional group (oxirane oxygen) analysis. The major reactions observed for an isomer of this compound, 1,2-epoxy-2,4,4-trimethylpentane, under acid catalysis were the usual addition reactions and isomerization to the aldehyde.



The unusual chemistry of 3,4-epoxy-2,2,4-trimethylpentyl isobutyrate became apparent from the low values obtained from oxirane oxygen determinations and from gas chromatograms of the products formed when the epoxy ester was treated with acids. Using a modification of the procedure described by King,[4] the oxirane oxygen content of 3,4-epoxy-2,2,4-trimethylpentyl isobutyrate was indicated to be 2.2%. This is only 29% of the theoretical value of 7.5% for this ester. Gas chromatograms obtained on solutions of the epoxy ester in 0.2 *N* solution of hydrogen chloride in dioxane (that is, the reagent used for the oxirane oxygen determination) showed four significant peaks. The epoxide was converted to the various products immediately after its addition to the acidic solution. The products were identified as tetrahydro-2,2,4,4-tetramethyl-3-furyl isobutyrate (II), 3-oxo-2,2,4-trimethylpentyl isobutyrate (III), 3-hydroxy-2,2,4-trimethyl-4-penten-1-yl isobutyrate (IV), and 1-hydroxy-2,2,4-trimethyl-4-penten-3-yl isobutyrate (V). With a chromatographic column containing silicone as the liquid phase under conditions described in the Experimental, the retention times observed for these peaks were 2.0, 3.0, 3.6, and 4.3 min., respectively. Using the 0.2 *N* solution of hydrogen chloride, the tailing of the dioxane peak was objectionable. To circumvent this, most of the chromatographic data was obtained using more concentrated solutions prepared from 0.5 g. of the epoxy ester in 3 ml. of a 1.0 *N* solution of hydrogen chloride in ethyl ether.

Physical constants and analyses of the products are shown in Table I. Compound II was isolated as described in the Experimental and its identity was established from the following evidence. Ring expansion was likely, in that this would account for the lower boiling point of compound II as compared to its isomer, the starting epoxy ester (I). Saponification of this ester gave an alcohol found by gas chromatography to be identical with tetrahydro-2,2,4,4-tetramethyl-3-furanol prepared by an alternate synthesis. In the latter preparation, 2,2,4-trimethyl-4-pentene-1,3-diol was cyclized by refluxing a chloroform solution of the diol in the presence of hydrogen chloride, using conditions similar to those described by Wasson and associates for the preparation of tetrahydrofurans.[5]





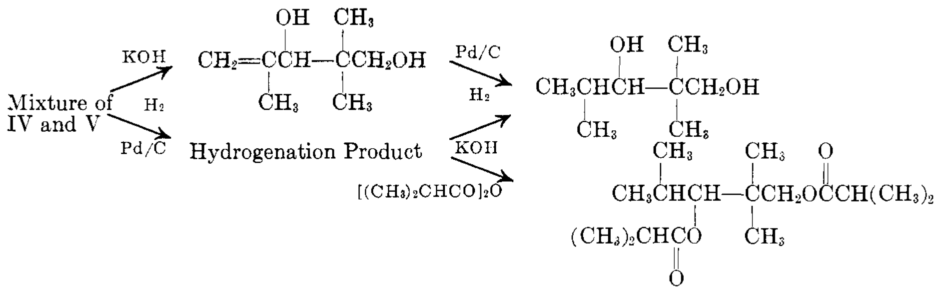
Compound II

Infrared and nuclear magnetic resonance spectra were consistent with the proposed tetrahydrofuranol structure and also with the isobutyric acid ester (compound II) of this alcohol.

---

[4] G. King, *Nature*, **164**, 706 (1949).

[5] B. K. Wasson, C. H. Gleason, I. Levi, J. M. Parker, L. M. Thompson, and C. H. Yates, *Can. J. Chem.*, **39**, 923 (1961).



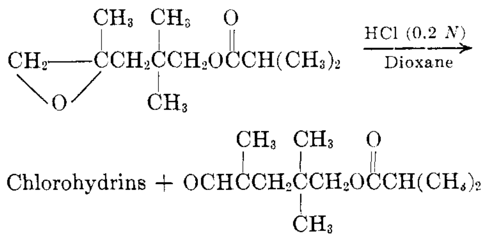
From the preparation of tetrahydro-2,2,4,4-tetramethyl-3-furyl isobutyrate, sufficient quantities of compounds III, IV, and V were available for identification. Compound III (3-oxo-2,2,4-trimethylpentyl isobutyrate) was identified in a distillation fraction rich in this component. Retention times for gas chromatographic peaks obtained for compound III on columns containing Carbowax, silicone, and Apiezon oil as liquid phases were identical with those observed for the authentic compound. The formation of this keto ester would be expected from the acid-catalyzed rearrangement of 3,4-epoxy-2,2,4-trimethylpentyl isobutyrate.

Compounds IV and V were not isolated individually, but redistillation of the higher boiling components provided a fraction which contained only these two compounds. The analyses shown in Table I indicated that IV and V were probably isomeric with the starting epoxy ester. The infrared spectrum of the mixture showed absorption bands characteristic of hydroxy, carbonyl, and terminal vinyl groups. Saponification of the mixture with alcoholic potassium hydroxide gave a single product which possessed hydroxy and terminal vinyl groups, but no carbonyl groups. These data indicated that compounds IV and V were unsaturated esters which were saponified to the same unsaturated alcohol. From these analyses and from the analogy of the starting epoxy ester to the previously mentioned 2,3-epoxy-2,4,4-trimethylpentane, the likely identities of these compounds were considered to be the two monoisobutyrates of 2,2,4-trimethyl-4-pentene-1,3-diol. These identifications were confirmed by hydrogenating the mixture of IV and V. The hydrogenated product was saponified to give a compound found to be identical with 2,2,4-trimethyl-1,3-pentanediol, and upon acylation with isobutyric anhydride it was converted to 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. These identities were established by comparing the derivatives with authentic compounds by infrared spectroscopy and gas chromatography. The unsaturated compound obtained from the saponification of the mixture of IV and V was 2,2,4-trimethyl-4-pentene-1,3-diol.

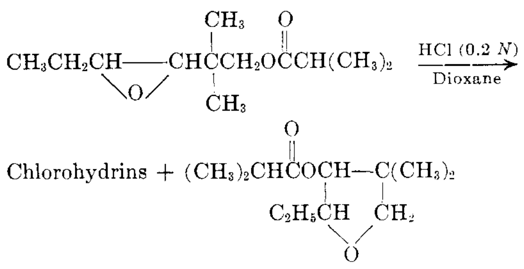
Similar rearrangements also occurred with other esters of 3,4-epoxy-2,2,4-trimethyl-1-pentanol. The determined oxirane oxygen values of these esters were about 30% of the theoretical value in each case as shown in Table II. Acetic acid esters analogous to compounds II, III, IV, and V were obtained from the epoxyalkyl acetate in about the same proportions as the corresponding isobutyric acid esters. The rearrangements were carried out in a 1.0 N solution of hydrogen chloride in ethyl ether and the isomerizations were followed by means of gas chromatography. 3,4-Epoxy-2,2,4-trimethylpentyl stearate was isomerized in a similar manner; the mixture of esters was saponified and steam distilled. Tetrahydro-2,2,4,4-tetramethyl-3-furanol was the major component found in the distillate.

The rearrangements of the 3,4-epoxy-2,2,4-trimethylpentyl esters also occurred in the presence of acid catalysts other than hydrogen chloride. Sulfuric acid, p-toluenesulfonic acid, and boron fluoride were among the catalysts used. When methanol and acetic acid were employed as solvents for the reaction, the same rearrangement products were obtained in about the same proportions. With methanol, the reaction products contained approximately 10% of the methyl ether derived from the addition of methanol to the epoxy ester.

Presumably, the formation of the tetrahydrofuran ring could arise from 3,4-epoxyalkyl or from 4,5-epoxyalkyl esters. To determine whether the latter esters do rearrange to form a tetrahydrofuran, 4,5-epoxy-2,2,4-trimethylpentyl isobutyrate was subjected to the conditions employed for the rearrangement of its isomer, the 3,4-epoxypentyl ester. Using the hydrogen chloride–dioxane reagent, an oxirane oxygen content of 6.6% was found. Since this represented 88% of the theoretical value for this functional group, the major reaction under these conditions was acid addition to give the chlorohydrins. The aldehyde which would be expected from this epoxy ester was the only other major reaction product. There was no evidence for the formation of a tetrahydrofuran derivative in this reaction

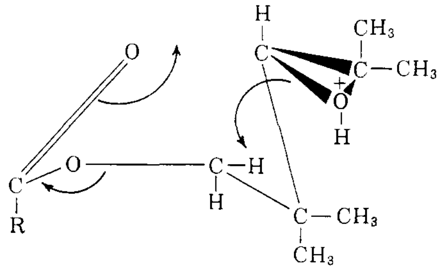


A similar investigation was carried out using 3,4-epoxy-2,2-dimethylhexyl isobutyrate, a compound in which the epoxy group in the 3,4-position is not sterically hindered. As shown in Table II, the oxirane oxygen value of 4.2% found for this ester shows that it undergoes addition of hydrogen chloride more readily than 3,4-epoxy-2,2,4-trimethylpentyl isobutyrate. On rearrangement, the corresponding tetrahydrofuryl ester

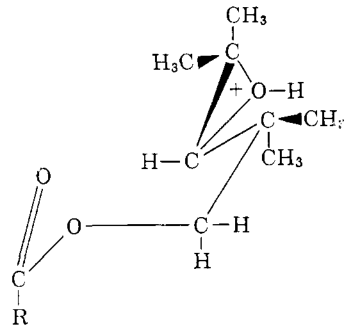


was virtually the only other product obtained. Thus, acid-catalyzed rearrangement to substituted tetrahydrofuryl esters appears to be a general reaction for 3,4-epoxyalkyl esters.

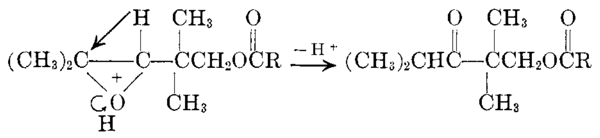
Although several logical explanations for the new rearrangement can be presented, the data at hand are not sufficient to establish which mechanism is the most probable. Examination of a molecular model (Fisher–Taylor–Hirshfelder) indicates that a concerted mechanism is plausible. This is considered to be initiated by a nucleophilic attack on the number 3 carbon atom of compound I by the carbonyl oxygen of the ester group. This is accompanied by the electron shifts shown in the structure below. The model shows that during this attack the oxirane oxygen atom can readily assume a position near the methylene group to enable bond formation between this carbon and oxygen atom.



In the chair form of the ester molecule, the oxirane oxygen atom is removed from the vicinity of the methylene group. This configuration favors the formation of the other products obtained in the reaction.



From the latter structure, the keto ester (III) can be derived *via* the conventional acid-catalyzed isomerization of an epoxide to a ketone.[6]



The 3-hydroxy-2,2,4-trimethyl-4-penten-1-yl ester (IV) results from a shift of electrons from a terminal carbon atom.

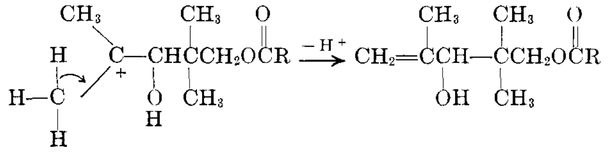
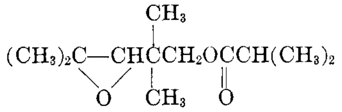
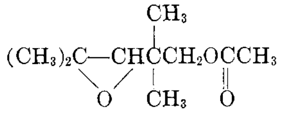
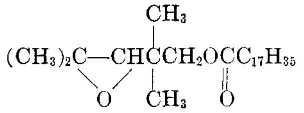
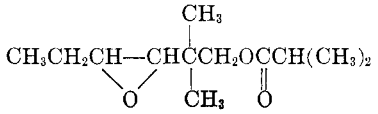
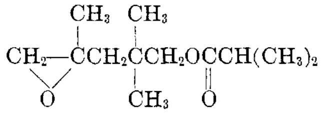
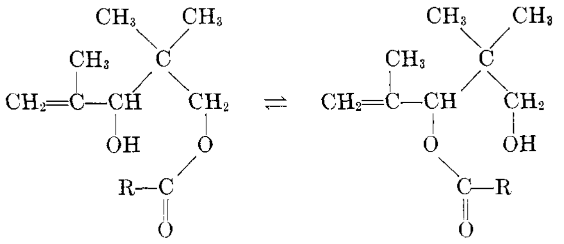


Table II

Oxirane Oxygen Analysis of Epoxy Esters

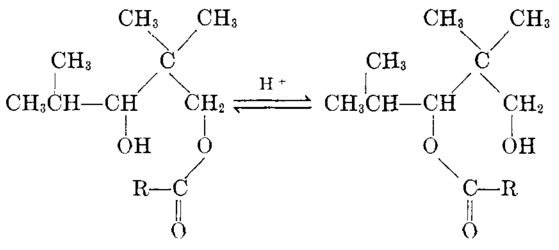
Epoxy ester	Oxirane oxygen, % Calcd. (C)	Oxirane oxygen, % Found (F)	F/C
	7.5	2.2	0.29
	8.6	2.6	.30
	3.9	1.1	.28
	7.5	4.2	.56
	7.5	6.6	.88

The formation of the 1-hydroxy-2,2,4-trimethyl-4-penten-3-yl ester (V) is thought to result from an intramolecular transesterification of IV, with the final composition containing an equilibrium mixture of these two compounds.



IV V

Dr. V. A. Hoyle of these laboratories has observed a rapid equilibration of this type between closely related glycol monoesters.[7]



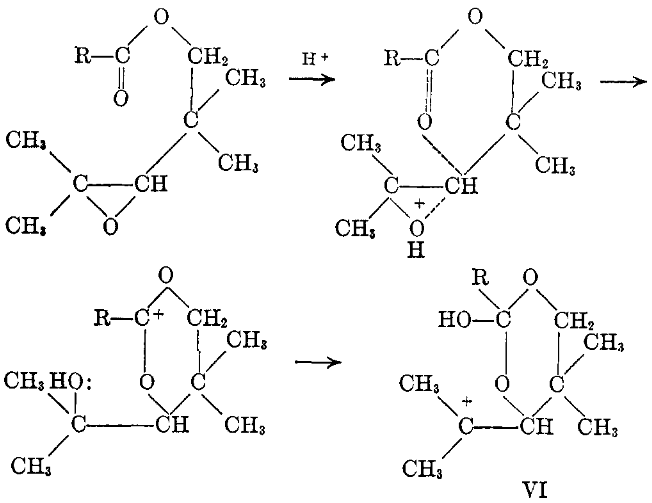
Dr. G. Maerker has suggested an interesting mechanism which is worthy of consideration.[8] According to his proposal the following sequence might take place:

---

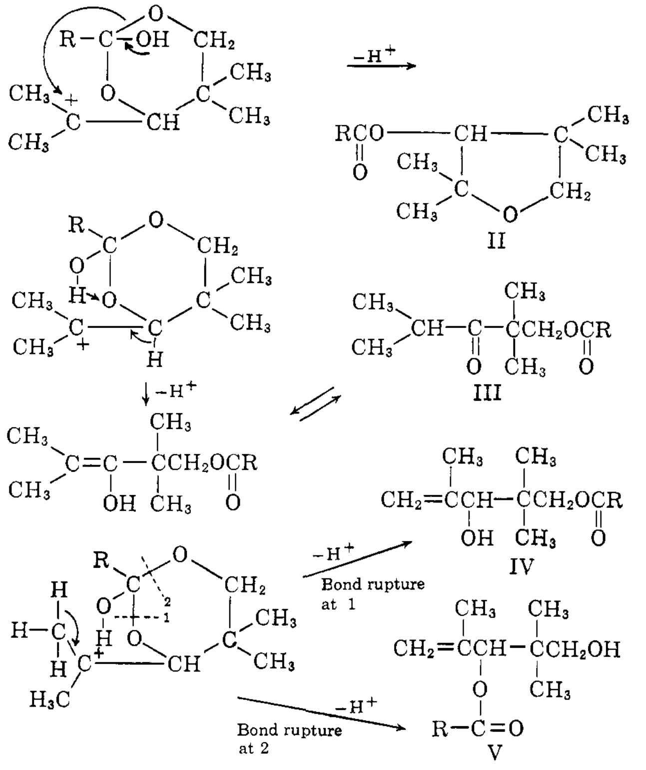
[6] R. E. Parker. *Chem. Rev.*, **59**, 737 (1959).

[7] V. A. Hoyle, Jr., unpublished results.

[8] G. Maerker, U. S. Department of Agriculture, Agricultural Research Service, Philadelphia, Pa., private communication.



Structure VI is then considered to serve as the intermediate for each of the four products:



Experimental[9]

Preparation of Intermediates.—2,2,4-Trimethyl-1,3-pentanediol diisobutyrate ("Texanol" isobutyrate) may be obtained from Eastman Chemical Products, Inc.

2,2,4-Trimethyl-3-penten-1-yl Isobutyrate.—This compound was prepared by thermally cracking 2,2,4-trimethyl-1,3-pentanediol diisobutyrate at 500°. The pyrolysis tube was constructed of Vycor glass 25 mm. in diameter and 70 cm. long and was packed with Vycor chips to a depth of 60 cm. The diisobutyrate (1144 g., 4 moles) was passed through the reactor at the rate of 240 ml./hr. Distillation of the pyrolysate yielded 660 g. (85%) of the unsaturated ester boiling at 211–213°, n^{20}_D 1.4376.

2,2,4-Trimethyl-3-penten-1-ol.—Saponification of 2,2,4-trimethyl-3-penten-1-yl isobutyrate (1188 g., 6 moles) with sodium hydroxide (320 g., 8 moles) in ethylene glycol (2 l.) at 120–130° gave a quantitative yield of good quality alcohol, which was isolated by steam distillation. If greater purity was required, distillation afforded a 90% yield of product boiling at 74–75° (15 mm.), n^{20}_D 1.4548.

2,2,4-Trimethyl-3-penten-1-yl Acetate.—This ester was obtained quantitatively by the esterification of 2,2,4-trimethyl-3-penten-1-ol (512 g., 4 moles) with acetic anhydride (450 g., 4.4 moles) in the presence of potassium carbonate (100 g.) at 90–95° for 18 hr. The boiling point of the product was 69–70° (9 mm.), n^{20}_D 1.4380.

2,2,4-Trimethyl-3-penten-1-yl Stearate.—2,2,4-Trimethyl-3-penten-1-ol (128 g., 1 mole), stearic acid (143 g., 0.5 mole), and butyl orthotitanate (3 drops) were stirred at 185–210°; water was removed by means of a Dean–Stark trap. After 3.5 hr., the theoretical amount of water had separated. The excess alcohol was removed by distillation under reduced pressure; the yield was 196 g. of crude ester which was not purified further.

2,2,4-Trimethyl-4-penten-1-ol.—This alcohol was prepared in 70% yield by the sodium borohydride reduction of 2,2,4-trimethyl-4-pentenal which obtained according to the procedure described by Brannock.[10] The aldehyde (50 g., 0.39 mole) was dissolved in a mixture of ethyl alcohol (100 ml.) and water (25 ml.). The solution was stirred at 10–20° while sodium borohydride (6.1 g., 0.16 mole) was added portionwise during a 1-hr. period. After stirring for an additional 0.5 hr. at 20°, the complex was hydrolyzed with 5% hydrochloric acid solution. Most of the ethyl alcohol was distilled and the aqueous residue was extracted with ether. The fraction boiling at 166–172° was collected as the desired unsaturated alcohol.

2,2,4-Trimethyl-4-penten-1-yl Isobutyrate.—The 4-penten-1-yl alcohol (37.5 g., 0.29 mole) was acylated with isobutyric anhydride (51 g., 0.32 mole) and potassium carbonate (20 g.) using the procedure described for 2,2,4-trimethyl-3-penten-1-yl acetate. The ester distilled at 212–215°, n^{20}_D 1.4329.

2,2-Dimethyl-3-hexen-1-yl Isobutyrate.—This ester was prepared in 85% yield from 2,2-dimethyl-3-hexen-1-ol (45 g., 0.35 mole), isobutyric anhydride (60 g., 0.38 mole), and potassium carbonate (4 g.), using the acylation procedure described for the preparation of 2,2,4-trimethyl-3-penten-1-yl acetate. The boiling point of the isobutyrate was 51–52° (1 mm.), n^{20}_D 1.4315. 2,2-Dimethyl-3-hexen-1-ol was prepared by the following sequence of reactions.

(1) **3-Hydroxy-2,2-dimethylhexanoic Acid, β-Lactone.**[11]—A solution of zinc chloride (2 g.) in methanol (3 ml.) was added to 500 ml. of ethyl ether in a 3-l., three-necked flask equipped with a mechanical stirrer, a condenser, an addition funnel, and a gas inlet tube. Dimethylketene[12] (280 g., 4 moles) and butyraldehyde (288 g., 4 moles) were added simultaneously to the stirred mixture while the temperature was maintained at 20–28°. The aldehyde was added at a rate of 3.2 ml./min. and the dimethylketene at 2.5 g./min. The latter was used immediately after its formation by the pyrolysis of isobutyric anhydride. The reaction mixture was stirred overnight at room temperature and was then washed successively with 5% sodium bicarbonate solution and with water. The reaction mixture was dried over sodium sulfate, and distilled to give the desired lactone (391 g., 69%) in the fraction boiling at 93–100° (14 mm.), n^{20}_D 1.4260.

(2) **3-Hydroxy-2,2-dimethylhexanoic Acid, Methyl Ester.**—The lactone (220 g., 1.6 moles) was added dropwise during 1 hr. at 20–30° to a stirred solution of sodium hydroxide (3 g.) in methanol (400 ml.). The resulting solution was stirred for an additional 1.5 hr. at 20–30°, then the methanol removed by distillation under reduced pressure. The residue (260 g.) was used without further purification for the next preparation.

(3) **3-Acetoxy-2,2-dimethylhexanoic Acid, Methyl Ester.**—The crude methyl ester of 3-hydroxy-2,2-dimethylhexanoic acid (260 g.) was stirred at steam bath temperature while acetic anhydride (194 g., 1.9 moles) was added dropwise during 1 hr. Heating and stirring was continued for 16 hr. The product was isolated by distillation under reduced pressure; the fraction boiling at 71–79° (0.6 mm.) weighed 245 g., n^{20}_D 1.4299.

(4) **Methyl 2,2-Dimethyl-3-hexenoate.**—The above described acetoxy compound (200 g.) was thermally cracked at 470° in the apparatus described for the preparation of 2,2,4-trimethyl-3-penten-1-yl isobutyrate, using a feed rate of 100 ml./hr. The pyrolysate (188 g.) was washed with 5% sodium bicarbonate solution to remove the acetic acid present, then washed with

---

(9) All boiling points are uncorrected.

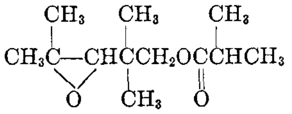
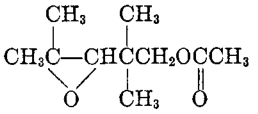
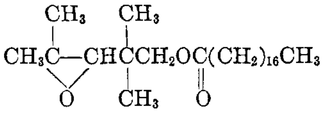
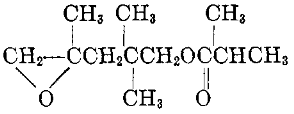
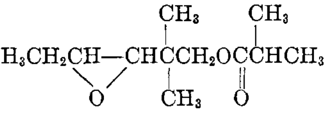
(10) K. C. Brannock, *J. Am. Chem. Soc.*, **81**, 3379 (1959).

(11) J. C. Martin, unpublished results.

(12) Attention is drawn to the formation of sensitive explosive peroxides if dimethylketene is contacted with air (H. Staudinger, "Die Ketene," F. Enke, Stuttgart, Germany, 1912, p. 141). All operations involving dimethylketene must be carried out under a nitrogen atmosphere.

TABLE III

PHYSICAL CONSTANTS AND ANALYSIS OF EPOXYALKYL ESTERS

Epoxy ester	Formula	B.p., °C.	Pressure, mm.	$n^{20}\mathrm{D}$	Yield, %	Calcd.	Found
3,4-Epoxy-2,2,4-trimethylpentyl isobutyrate	 $\mathrm{CH_3\overset{CH_3}{C}{-}\!\!\!\underset{O}{}CH\overset{CH_3}{\underset{CH_3}{C}}CH_2O\underset{O}{C}\overset{CH_3}{C}HCH_3}$	81–82	1.2	1.4321	82	C-67.3 H-10.3	C-67.3 H-10.5
3,4-Epoxy-2,2,4-trimethylpentyl acetate	 $\mathrm{CH_3\overset{CH_3}{C}{-}\!\!\!\underset{O}{}CH\overset{CH_3}{\underset{CH_3}{C}}CH_2O\underset{O}{C}CH_3}$	46–47	0.5	1.4315	81	C-64.5 H- 9.7	C-64.9 H-10.0
3,4-Epoxy-2,2,4-trimethylpentyl stearate	 $\mathrm{CH_3\overset{CH_3}{C}{-}\!\!\!\underset{O}{}CH\overset{CH_3}{\underset{CH_3}{C}}CH_2O\underset{O}{C}(CH_2)_{16}CH_3}$	—	—	—	90[a]	—	—
4,5-Epoxy-2,2,4-trimethylpentyl isobutyrate	 $\mathrm{CH_2{-}\!\!\!\underset{O}{}\overset{CH_3}{C}CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2O\underset{O}{C}\overset{CH_3}{C}HCH_3}$	79–81	.7	1.4369	65	C-67.3 H-10.3	C-67.0 H-10.3
3,4-Epoxy-2,2-dimethylhexyl isobutyrate	 $\mathrm{CH_3CH_2CH{-}\!\!\!\underset{O}{}CH\overset{CH_3}{\underset{CH_3}{C}}CH_2O\underset{O}{C}\overset{CH_3}{C}HCH_3}$	78–79	1.4	1.4305	84	C-67.3 H-10.3	C-67.3 H-10.6

[a] Yield of crude material.

water and dried over magnesium sulfate. Distillation yielded the unsaturated ester (111 g.), b.p. 91–99° (76 mm.), $n^{20}\mathrm{D}$ 1.4316.

(5) **2,2-Dimethyl-3-hexen-1-ol.**—Lithium aluminum hydride (16 g., 0.42 mole) and ethyl ether (700 ml.) were stirred at reflux for 1 hr.; external heating was discontinued and methyl 2,2-dimethyl-3-hexenoate (110 g., 0.71 mole) was added dropwise at such a rate as to maintain a gentle reflux. The addition required 2.5 hr., and the mixture was stirred at reflux for an additional 0.5 hr. Ethyl acetate (17 g.) was added to decompose the excess hydride. Water (50 ml.) was then added dropwise and stirring was continued for 0.5 hr. The mixture was filtered and the solid residue was washed with ether. The combined filtrate and ethereal wash was washed with water, dried over sodium sulfate, and the ether evaporated. The residue (80 g., 95% yield of crude material) was used without further purification for the preparation of the isobutyric acid ester.

Epoxidation of Unsaturated Esters. General Procedure.—The epoxy esters were synthesized by a general procedure using preformed peroxyacetic acid.[13] The reactions were run at 20–25°, and were generally complete within 3 hr. after the addition of the peroxyacetic acid. The course of the reactions was followed by means of gas chromatography or by iodometric titration of the unreacted peroxyacetic acid. The epoxy esters and their physical constants are listed in Table III.

Tetrahydro-2,2,4,4-tetramethyl-3-furyl Isobutyrate.—3,4-Epoxy-2,2,4-trimethylpentyl isobutyrate (107 g., 0.5 mole) and a 1.25 *N* solution of hydrogen chloride in ether (400 ml., 0.5 mole of hydrogen chloride) were added simultaneously with stirring to a flask maintained at 25–30° by immersion in a cooling bath. The rates of addition were adjusted to a ratio of one volume of the epoxy ester to four of the hydrogen chloride solution. When the addition was completed, the resulting solution was stirred for 15 min. at 25–30°, then washed with 5% sodium carbonate solution and water and dried over sodium sulfate. The furyl ester (72 g.) was obtained in 95% purity in a fraction boiling at 70–76° (2 mm.). Redistillation gave a product of 98% purity. The higher boiling components contained 3-oxo-2,2,4-trimethylpentyl isobutyrate (compound III) and the monoisobutyrates of 2,2,4-trimethyl-4-pentene-1,3-diol (compounds IV and V).

Tetrahydro-2,2,4,4-tetramethyl-3-furanol.—A. 2,2,4-Trimethyl-3-penten-1-ol (25.6 g., 0.2 mole) and anhydrous sodium acetate (2 g.) were stirred at 20–25° while 40% peroxyacetic acid solution (in acetic acid) (38 g., 0.2 mole) was added dropwise over a 1-hr. period. The reaction mixture was stirred at 25° for an additional 2 hr. At this time, gas chromatographic analysis of the mixture showed that no starting material remained. The reaction mixture was poured into two volumes of water, and the resulting clear solution was neutralized with solid sodium bicarbonate, which caused separation of an organic layer. The organic layer was separated and the aqueous layer was extracted with three 25-ml. portions of ether. The combined organic fractions were washed with water and dried over magnesium sulfate. After the ether was evaporated, the residue was distilled to yield 14.6 g. (47% yield) of the furanol, b.p. 53–55° (1 mm.), $n^{20}\mathrm{D}$ 1.4430.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.7; H, 11.1; mol. wt., 144. Found: C, 66.3; H, 11.7; mol. wt. (cryoscopic in ethyl alcohol), 145.

B. The furanol was obtained in 92% yield by saponification of tetrahydro-2,2,4,4-tetramethyl-3-furyl isobutyrate with 1.6 *N* methanolic potassium hydroxide solution.

Analysis for Oxirane Oxygen.—The epoxy compounds were analyzed for oxirane oxygen by a modification of the King[4] procedure as described by Jungnickel.[14] Phenolphthalein was used as the indicator for the titration of the hydrogen chloride solution.

Gas Chromatographic Columns.—The columns, 4 ft. in length, were constructed of 8-mm. o.d. glass tubing shaped in the form of elliptical spirals. The columns were packed with 40–50-mesh Chromosorb W, using the following liquid phases at a 10% level: Carbowax 20M, silicone GE-SF 96-40, and Apiezon oil. Hydrogen was employed as the carrier gas at a flow rate of 92 ml./min. The detector was a thermal conductivity cell, with the output being measured by a recording potentiometer.

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra were determined with a Varian Associates Model V-4300B, high-resolution n.m.r. instrument (40 Mc.) equipped with a flux stabilizer. The chemical shift positions were determined relative to tetramethylsilane as an internal standard.[15]

Infrared Spectra.—The infrared spectra were recorded on a Beckman IR-5 infrared spectrophotometer.

---

[13] T. W. Findley, D. Swern, and J. T. Scanlan, *J. Am. Chem. Soc.*, **67**, 412 (1945).

[14] J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, "Organic Analysis," Vol. 1, J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer, and A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 1953, p. 135.

[15] The n.m.r. spectra were recorded and interpreted by Dr. Wilson Goodlett of these laboratories.