carbonyl region, bands at 5.57, 5.63 and 5.72 μ (CCl_4) were present. Evaporative distillation at 1 mm. and −50° failed to achieve a good separation of the formic acetic anhydride from methyl acetate.

Acetic Trichloroacetic Anhydride.—A solution of 1.114 g. (6.82 mmoles) of freshly sublimed trichloroacetic acid (purity determined as 99.8% by titration) in 1 ml. of dry ether was treated dropwise over 20 minutes at 0° with 811 mg. (6.98 mmoles) of 1-methoxyvinyl acetate; yield, after leaving overnight at −20° and 1 mm., 1.387 g. (99%), m.p. mainly[16] −6 to −4°, 5.42 and 5.63 μ (CCl_4). In the absence of solvent, polymerization of the 1-methoxyvinyl acetate was found to occur to an appreciable extent.

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[16] A very small amount of liquid was present even at −20°. A. R. Emery and V. Gold, *J. Chem. Soc.*, 1456 (1950), report a m.p. of *ca.* −5°.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS & SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

Synthesis and Characterization of the Geometric and Structural Isomers of 3,7-Dimethyl-2,4,6-octatrienoic Acid. I

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The *trans–trans* structure of dehydrogeranic acid (VI), m.p. 187°, prepared by a Reformatsky reaction with 6-methylhepta-3,5-dien-2-one (I) and the structure of its 2-*cis* isomer VIII, m.p. 161°, prepared by decarboxylation of the 4-carboxy-octatrienoic acid (VII), have been established and their infrared and ultraviolet absorption characteristics have been determined. The carboxy acid VII has absorption characteristics establishing that it has the 2-*cis*:4-*cis* configuration. The Reformatsky reaction between senecialdehyde and methyl γ-bromosenecioate gives rearranged products (IX,X) whose structures also have been established by absorption characteristics.

There are four geometrical isomers and five isomeric cyclized structures of 3,7-dimethyl-2,4,6-octatrienoic acid. Two of the former—m.p.'s. 187°[1-3] and 137°[1]—and four of the latter—m.p.s. 63°,[4] 111°,[5] 117°,[6] and 130°[4]—have been reported. With the possible exception of the 187° acid, which has been assigned[1] the *trans–trans* structure on the basis of its identity with a natural occurring[3] dehydrogeranic acid, the evidence for the structural assignments for these compounds is somewhat incomplete. A recent study[7] of the nuclear magnetic resonance properties of isomeric systems similar to the acyclic types has provided a new basis for structural assignments in such systems. The syntheses of the 3,7-dimethyl-2,4,6-octatrienoic acids, by Reformatsky and decarboxylation reactions, have been examined and the nuclear magnetic resonance characteristics of the isomeric products have been evaluated. These studies will be described in this and a subsequent paper with reference to a recent clarification[8] of the stereochemistry of the analogous 3-methyl-5-phenylpentadienoic acid system. The effect of these compounds on the enzymatic biosynthesis of cholesterol will be reported elsewhere.

3,7-Dimethyl-2-*trans*:4-*trans*-6-octatrienoic Acid (VI).—An acid having this structure has been isolated from the oil of the wood of *Callitropsis arancarioides* where it is found as the geranyl ester.[3] The acid is reported to have a m.p of 185–186° and a maximum in the ultraviolet at 311 mμ (log ϵ 4.55). The carbon skeleton was established by hydrogenation to DL-tetrahydrogeranic acid and by synthesis.[1,2] The synthesis involved a Reformatsky reaction with 6-methylhepta-3,5-dien-2-one (I) and bromoacetate followed by dehydration and saponification of the hydroxy ester II. This acid was assigned the 2-*trans*:4-*trans* structure and an isomeric acid, m.p. 137°, which was also obtained,[1] was assigned the 2-*cis*:4-*trans* structure. This assignment is in question since it is known[8,9] that Reformatsky syntheses of similar structures often give mixtures of isomers crystallizing as low melting complexes. We have confirmed this synthesis of the acid which we have observed to melt at 187°, but have not obtained the 137° acid. The heptadienone was prepared by condensation of senecialdehyde with acetone or, somewhat more conveniently, by decarboxylation of the acetoacetic ester obtained from diketene and 2-methylbut-3-yn-2-ol.[10] The Reformatsky reaction gives an excellent yield of the hydroxy ester II which on dehydration gives different products under different conditions. Dehydration in ether with *p*-toluenesulfonic acid gives a readily polymerizable ester which has maxima in the infrared at 1727 (saturated ester carbonyl stretching), 1706 (unsaturated ester carbonyl stretching), 966 (C–H out of plane deformation of *trans* —CH=CH—) and 885 cm.$^{-1}$ (C–H out of plane deformation of terminal methylene). Although undoubtedly a mixture of isomers this material probably contains some of the ester III or IV. An abnormal dehydration of a Reformatsky product to give a non-conjugated unsaturated ester has been reported previously.[11] If the dehydration is run in benzene, an ester, m.p. 17–23°, is obtained in 86% yield which on saponification gives 55% yield of the 187° acid. Esterification of the acid with diazomethane gives the pure methyl ester, m.p. 38–39°. The acid absorbs in the ultraviolet at 308 mμ (log ϵ 4.56); the ester at 311 mμ (log ϵ 4.50). The acid absorbs in the

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[1] R. Kuhn and M. Hoffer, *Ber.*, **65**, 651 (1932).

[2] F. G. Fischer and K. Löwenburg, *Ann.*, **494**, 263 (1932).

[3] R. S. Cahn, A. R. Penfold and J. L. Simonsen, *J. Chem. Soc.*, 3134 (1931).

[4] G. Wendt, *Ber.*, **74**, 1242 (1941).

[5] O. Jeger and G. Büchi, *Helv. Chim. Acta*, **31**, 134 (1948).

[6] G. Merling and R. Welde, *Ann.*, **366**, 215 (1909).

[7] L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

[8] R. H. Wiley, *J. Chem. Soc.*, 3831 (1958).

[9] R. Stoermer, F. Grimm and E. Laage, *Ber.*, **50**, 959 (1917).

[10] R. N. Lacey, *J. Chem. Soc.*, 827 (1954).

[11] L. Crombie, S. H. Harper and K. C. Sleep, *ibid.*, 2743 (1957); *cf. Chemistry & Industry*, 1538 (1954).

infrared at 1672 (unsaturated acid carbonyl stretching), 1597 (carbon–carbon double bond stretching) and 952 cm.$^{-1}$ (C–H out of plane deformation of *trans* —CH=CH—); the ester at 1700 (unsaturated ester carbonyl stretching), 1634 and 1602 (carbon–carbon double bond stretching), and 950 cm.$^{-1}$ (C–H out of plane deformation of *trans* —CH=CH—). These properties are consistent with the 3,7-dimethyl-2-*trans*:4-*trans*:6-octatrienoic acid structure. The nuclear magnetic resonance characterization of the ester confirms this assignment.[12]

3,7-Dimethyl-2-*cis*:4-*trans*:6-octatrienoic Acid (VIII).—The decarboxylation of 4-carboxy-3,7-dimethyl-2-*cis*:4-*cis*:6-octatrienoic acid (VII) provides a reasonable route to the 2-*cis*:4-*trans* isomer of 3,7-dimethyl-2,4,6-octatrienoic acid. Condensation of benzaldehyde with dimethyl β-methylglutaconate is known to give the 2-*cis*:4-*cis*-4-benzylidene-3-methylglutaconic acid which decarboxylates with inversion to 3-methyl-5-phenyl-2-*cis*:4-*trans*-pentadienoic acid.[3] If similar stereochemistry applies to the analogous reaction with senecialdehyde, the 2-*cis*:4-*trans*-acid VIII would result. The condensation gives 29.5% yield of the dibasic acid VII, m.p. 185–186°, if run at −10°. The ultraviolet absorption maximum at 274 mμ ($\log \epsilon$ 4.31) corresponds to that of a conjugated dienoic acid such as 2,5-dimethylsorbic acid[13] ($\lambda_{\max}$ 273 mμ, $\log \epsilon$ 4.35) and is at a significantly lower wave length than that of the 3,7-dimethyl-2,4,6-octatrienoic acids ($\lambda_{\max}$ 308 mμ, $\log \epsilon$ 4.56; $\lambda_{\max}$ 300 mμ, $\log \epsilon$ 4.49) described herein. This is similar to the ultraviolet absorption correlation established in the phenyl series for which the 2-*cis*:4-*cis* structure of the dioic acid is reasonably certain.[13] Apparently, and this is confirmed on examination of models, in this aliphatic analog the hindered *cis* structure prevents conjugation of the 2,3-double bond with the remainder of the molecule. As a result, only a dienoic acid is present as the effective chromophore. Decarboxylation in lutidine with cupric acetate gives a monobasic acid, m.p. 161°, $\lambda_{\max}$ 300 mμ ($\log \epsilon$ 4.49). Its infrared absorption spectrum shows a maximum at 966 cm.$^{-1}$ required for the 4-*trans* structure formed on inversion during decarboxylation. The methyl ester, m.p. 34–35°, formed with diazomethane also shows the absorption at 963 cm.$^{-1}$ required for the C–H out of plane deformation of the *trans* —CH=CH— grouping. Nuclear magnetic resonance characteristics confirm the 2-*cis*:4-*trans* structure.[12]

The Reformatsky Reaction with Senecialdehyde and Methyl γ-Bromosenecioate.—There is a possibility that this Reformatsky reaction will lead to additional geometrical isomers of 3,7-dimethyl-2,4,6-octatrienoic acid. If the dehydration of the intermediate hydroxy ester gave both the 4-*cis* and 4-*trans* isomers and the bromosenecioate is a *cis–trans* mixture, then all four of the possible isomers could be formed. Small amounts of the 2-*trans*:4-*trans* isomer have been obtained in the present and previous[14] studies, but the principal products obtained in our study have properties establishing that they cannot have the 3,7-dimethyl-2,4,6-octatrienoic acid structure. Fractionation of the dehydrated esters formed in the Reformatsky reaction gives two products: a lower boiling fraction, 76–80° (4 mm.), $n^{25}\text{D}$ 1.4840–1.4870, and a higher boiling fraction, 85–130° (4 mm.), $n^{25}\text{D}$ 1.4925–1.5085. The lower boiling fraction on refractionation through a spinning band column gives an ester, b.p. 49–50° (0.65 mm.), $n^{25}\text{D}$ 1.4820, $\lambda_{\max}$ 230 mμ ($\log \epsilon$ 4.34), as the main component. The infrared spectrum shows maxima at 1733 (saturated ester carbonyl stretching), 1645 and 1613 (carbon–carbon double bond stretching of an unconjugated 1,3-diene), 966 (C–H out of plane deformation of *trans* —CH=CH—) and 898 and 890 cm.$^{-1}$ (C–H out of plane deformation of two terminal methylene groups, one conjugated). These data can be correlated consistently with the methyl 2-isopropenyl-5-methyl-3-*trans*:5-hexadienoate structure (IX).[15] Alternative structures formed by a normal Reformatsky reaction require either a conjugated unsaturated ester, such as V, or a conjugated triene structure both of which are eliminated by the absorption data.

Saponification of this ester (IX) is accompanied by a prototropic rearrangement to give an acid, m.p. 131°, which although isomeric with the 3,7-dimethyl-2,4,6-octatrienoic acids, would be expected to have the same carbon skeleton as the ester IX. Furthermore, esterification of this acid with diazomethane gives an ester, $n^{25}\text{D}$ 1.5215, identical with a component of the higher boiling fraction obtained from the Reformatsky reaction, which is different from that (IX) from which the acid was formed. This acid, and the ester, absorb in the ultraviolet at 275 mμ ($\log \epsilon$ 4.37) and 280 mμ ($\log \epsilon$ 4.39) respectively, indicating a conjugated dienoic acid as the effective chromophore.[11] Absorption maxima for the ester occur in the infrared at 1701 (unsaturated ester carbonyl stretching) 1629 and 1587 (conjugated 1,3-diene carbon–carbon double bond stretching) and 901 cm.$^{-1}$ (out of plane deformation of terminal methylene carbon–hydrogen bond). The acid shows similar absorption at 1667, 1621, 1585 and 898 cm.$^{-1}$. These data are consistent with the structure 2-isopropenyl-5-methyl-2-*trans*:4-hexadienoic acid[15] and its methyl ester (X, R = H, CH_3). Nuclear magnetic resonance data confirm both the structures (IX, X).[12]

Although methyl γ-bromocrotonate is known to give rearranged products in Reformatsky[16,17] reactions, previous studies with methyl γ-bromo-

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[12] R. H. Wiley, J. L. Jackman and R. P. Houghton, unpublished observations.

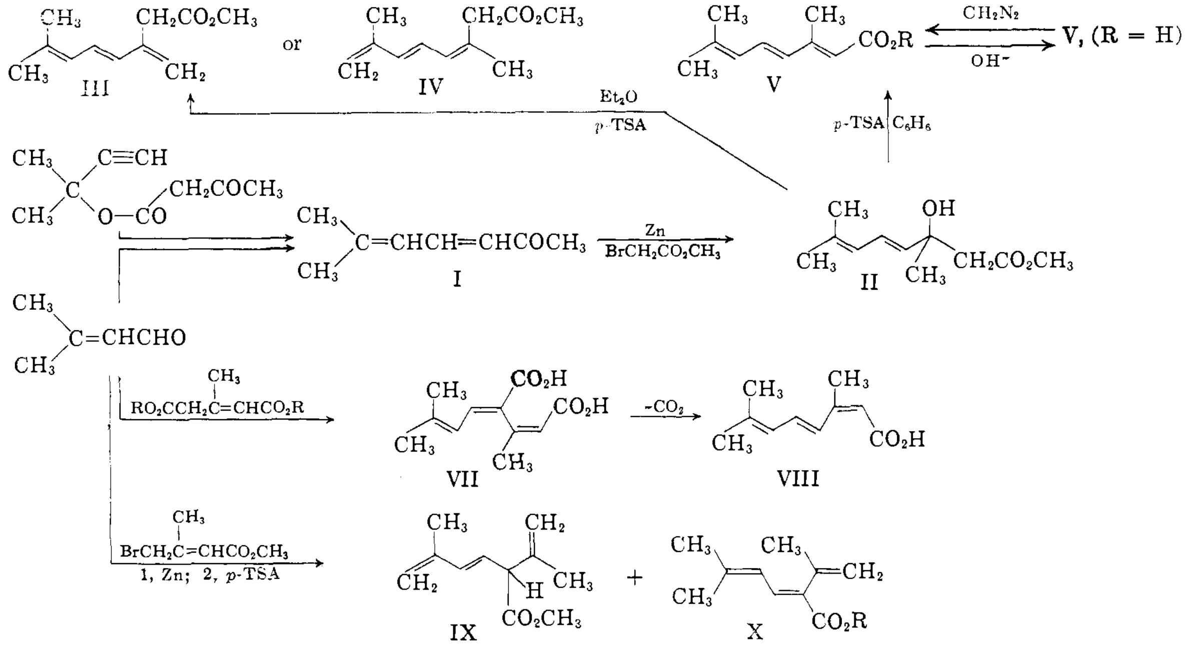
[13] J. D. Cawley and D. R. Nelan, This Journal, **77**, 4130 (1955).

[14] H. H. Inhoffen and H. Eysenbach, German Patent 873,547, April 16, 1953; *C. A.*, **50**, 8711 (1956).

[15] Rule 29 of the definitive report of the commission on reform of the nomenclature of organic chemistry (This Journal, **55**, 3905 (1933)) suggests that this compound (IX) is preferably named methyl 2,6-dimethyl-1,4-*trans*:6-heptatriene-3-carboxylate and that X should be named methyl 2,6-dimethyl-1,3-*cis*:5-heptatriene-3-carboxylate. Since having these acids and the octatrienoic acids named by the same nomenclature principle provides an element of consistency in this paper, the hexadienoic names have been used.

[16] E. R. H. Jones, D. G. O'Sullivan and M. C. Whiting, *J. Chem. Soc.*, 1415 (1949).

[17] J. English, J. D. Gregory and J. R. Trowbridge, This Journal, **73**, 615 (1951).



senecioate[14,18,19] have given no indication that the bromo ester reacts *via* an allylic rearrangement

$$\mathrm{BrZn^+[:CH_2C(CH_3){=}CHCO_2R]^- \longleftrightarrow BrZn^+[CH_2{=}C(CH_3)\ddot{C}HCO_2R]^-}$$

The results presented here establish that such reactions are involved, with these reactants at least, and indicate that further search may disclose additional examples.

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Experimental[20]

Ultraviolet absorption measurements were made with a Beckman DK-2 recording spectrophotometer using 1.00-cm. silica cells and a hydrogen discharge light source. The infrared spectral measurements were made with a Baird double beam recording spectrometer using potassium bromide pellets or the solvent as stated. The infrared absorption frequencies assigned to the various groups are those given by Bellamy.[21]

Senecialdehyde.—3-Hydroxy-3-methylbutyraldehyde dimethyl acetal[11] (45 g.) was added dropwise during 45 min. to 1 l. of boiling dilute sulfuric acid (2.5% by vol.) through which steam and nitrogen were passed. The distillate (500 ml.) was extracted with ether (6 × 50 ml.) and the extracts were combined, dried over magnesium sulfate, and fractionated to give 13.7 g. (54%) of the aldehyde, b.p. 62–65° (50 mm.), n^{27}D 1.4580; reported[11] b.p. 40–46° (13 mm.), n^{20}D 1.4550. The procedure described here gives substantially higher yields than the method described previously.[11] In our hands the synthesis of the aldehyde from 1-bromo-3-methylbut-2-ene is less convenient and gives slightly lower yields.[22] The material was stored over hydroquinone at 0° and distilled immediately before use.

6-Methylhepta-3,5-dien-2-one (I).—Condensation of senecialdehyde with acetone in the presence of aqueous sodium hydroxide as described previously[1] gave the ketone (42%), b.p. 46–48° (1 mm.), n^{24}D 1.5300; reported b.p. 86–87° (15 mm.). Pyrolysis of the acetoacetate of 2-methylbut-3-yn-2-ol gave the same product in 25% yield.[10]

Methyl 3-Hydroxy-3,7-dimethylocta-4,6-dienoate (II).—A solution of 10.8 g. of the dienone I and 16.0 g. of methyl bromoacetate in 70 ml. of dry benzene was added dropwise during 15 min. to a stirred refluxing suspension of 4.5 g. of zinc in 25 ml. of dry ether under nitrogen. The mixture was stirred and refluxed for a further 30 min., cooled, and added to a solution of 6.0 ml. of acetic acid in 150 ml. of water at 0°. The organic layer was washed with water (2 × 250 ml.), dried over magnesium sulfate and fractionated to give 15.5 g. (90%) of the hydroxy ester II, b.p. 69–71° (0.2 mm.), n^{26}D 1.4905, λ_{max} 237 mμ (log ϵ 4.43).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.76; H, 9.08.

Methyl 7-Methyl-3-methyleneocta-4,6-dienoate (III) and Methyl 3,7-Dimethylocta-3,5,7-trienoate (IV).—A solution of 6.0 g. of the hydroxy ester II and 0.5 g. of p-toluenesulfonic acid in 100 ml. of ether was refluxed under nitrogen for 3 hr. The mixture was cooled, washed twice with 100 ml. of saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and fractionated to give 4.6 g. (85%) of an oil, b.p. 96–104° (3 mm.), n^{26}D 1.5415–1.5605; λ_{max} 270, 281 and 310 mμ (ϵ 4.43, 4.38 and 4.07, respectively). The infrared spectrum in chloroform showed maxima at 1727, 1709, 966 and 885 cm.$^{-1}$. The ester polymerized rapidly and was not analyzed. Saponification gave the acid, m.p. 187°, identified by its infrared absorption, in low yields.

Methyl 3,7-Dimethylocta-2-*trans*:4-*trans*:6-trienoate (V) and 3,7-Dimethyl-2-*trans*:4-*trans*-6-octatrienoic Acid (VI).—A solution of 5.5 g. of the hydroxyester II and 0.15 g. of p-toluenesulfonic acid in 70 ml. of dry benzene was refluxed under nitrogen for 45 min. The mixture was cooled and the product was isolated as described above to give 4.3 g. (86%) of the crude ester V, b.p. 67–69° (0.2 mm.), n^{26}D 1.5778. This fraction solidified when kept at 0°, m.p. 17–23°. A solution of the ester (1.0 g.) and 0.4 g. of potassium hydroxide in 20 ml. of 80% aqueous ethanol was refluxed under nitrogen for 1 hr. Most of the ethanol was removed under reduced pressure and the residual solution was diluted with 20 ml. of water. The mixture was extracted with ether (2 × 10 ml.) and the aqueous portion acidified with dil. hydrochloric acid at 0°. The acidified solution was extracted with ether (2 × 10 ml.), the extract

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(18) S. H. Harper and J. F. Oughton, *Chemistry & Chemistry*, 574 (1950).

(19) R. C. Fuson and P. L. Southwick, THIS JOURNAL, **66**, 679 (1944).

(20) Analyses by Micro Tech Laboratories, Skokie, Ill. Melting points are uncorrected.

(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1958.

(22) W. G. Young and S. L. Linden, THIS JOURNAL, **69**, 2912 (1947).

dried over magnesium sulfate, and the ether removed under reduced pressure. The residue was recrystallized from aqueous methanol to give 0.51 g. (55%) of the acid VI, m.p. 186-187°, λ_{max} 308 mμ (log ϵ 4.56); reported[13] m.p. 185-186°, λ_{max} 311 mμ (log ϵ 4.55). The infrared spectrum in potassium bromide showed maxima at 1672, 1597 and 952 cm.$^{-1}$.

The acid formed a *p*-bromophenacyl ester, m.p. 133–134°, from ethanol.

Anal. Calcd. for $C_{18}H_{19}BrO_3$: C, 59.50; H, 5.27. Found: C, 59.42; H, 5.25.

A solution of 541 mg. of the acid VI in 70 ml. of ether was treated with a slight excess of ethereal diazomethane at 0°. The mixture was fractionated to give 436 mg. (74%) of the 2-*trans*:4-*trans* ester V, b.p. 90–100° (bath) (0.05 mm.), n^{25}D 1.5860. This fraction solidified when cooled to 0°, m.p. 38–39°; λ_{max} 311 mμ (log ϵ 4.50). Infrared absorption maxima in chloroform: 1700s, 1634m, 1602s and 950m.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.00; H, 8.91.

4-Carboxy-3,7-dimethyl-2-*cis*:4-*cis*:6-octatrienoic Acid (VI).—Diethyl β-methylglutaconate (19.4 g.) was added to a stirred solution of 21.7 g. of potassium hydroxide in 130 ml. of methanol at −10° under nitrogen. The mixture was stirred for 1 hour at −10°. Senecialdehyde (6.3 g.) was added and the mixture was kept at −10° for 30 min. and room temperature for one week. The precipitated potassium salt was collected, washed with methanol, and dissolved in water. Acidification precipitated a solid which was recrystallized twice from methanol to give 4.71 g. (29.5%) of the diacid, m.p. 185–186° dec., λ_{max} 274 mμ (log ϵ 4.31); infrared absorption maxima in potassium bromide: 1672s and 1634s cm.$^{-1}$. If heated to 184° and cooled, the acid shows no change in infrared absorption characteristics. This indicates that the acid does not decarboxylate to give the *trans–trans*-acid (m.p. 187°) prior to melting.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71; neut. equiv., 105. Found: C, 62.55; H, 6.71; neut. equiv., 106.

The acid formed a dibenzylethylenediamine salt, m.p. 108–110° from diethyl ether.

Anal. Calcd. for $C_{27}H_{34}N_2O_4$: N, 6.22. Found: N, 6.40.

3,7-Dimethyl-2-*cis*:4-*trans*:6-octatrienoic Acid (VIII).—A solution of 2.74 g. of the diacid and 70 mg. of cupric acetate in 20 ml. of freshly distilled lutidine was heated under nitrogen for 1 hr. at 125–130°. Approximately half the lutidine was removed under reduced pressure and the residue added to 65 ml. of 2.5 *N* hydrochloric acid at 0°. The precipitate was collected and recrystallized twice from methanol (Norite) to give 1.02 g. (47%) of the acid, m.p. 160–161°, λ_{max} 300 mμ (log ϵ 4.49); infrared absorption maxima in potassium bromide: 1661s, 1603, 1575s and 966m.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.76; H, 8.28.

The acid formed a *p*-bromophenacyl ester, m.p. 128–129° from aqueous methanol.

Anal. Calcd. for $C_{18}H_{19}BrO_3$: C, 59.50; H, 5.27. Found: C, 59.40; H, 5.40.

A solution of 205 mg. of the acid in 20 ml. of ether was treated with ethereal diazomethane at 0°. The ether was removed under reduced pressure to give 218 mg. (98%) of the 2-*cis*:4-*trans* methyl ester, m.p. 34–35°, λ_{max} 312 mμ (log ϵ 4.50); infrared absorption maxima in chloroform: 1700s, 1634m, 1605s, 1582m and 963m cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.15; H, 8.80.

Reformatsky Reaction with Senecialdehyde and Methyl γ-Bromosenecioate.—A solution of 19.2 g. of senecialdehyde and 44.3 g. of γ-bromosenecioate in 75 ml. of ether was added dropwise to a stirred, refluxing suspension of 15.0 g. of zinc in 50 ml. of benzene. The mixture was refluxed for 30 min., cooled, and added to 300 ml. of water. The organic layer was separated, washed with water and with 5% aqueous sodium bicarbonate, and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue dissolved in 100 ml. of dry benzene. *p*-Toluenesulfonic acid (0.3 g.) was added, the mixture was refluxed under nitrogen for one hour, and the water which was formed was removed by azeotropic distillation. The reaction mixture was cooled, washed with saturated aqueous sodium bicarbonate, dried over sodium sulfate, and fractionated to give 17.0 g. of an oil, b.p. 76–80° (4 mm.), n^{25}D 1.4840–1.4870, and 8.7 g. of a higher boiling fraction, b.p. 85–130° (4 mm.), n^{25}D 1.4925–1.5085. The lower boiling material was refractionated twice through a spinning band column to give 9.8 g. of methyl 2-isopropenyl-5-methyl-3-*trans*:5-hexadienoate (IX), b.p. 49–50° (0.65 mm.), n^{25}D 1.4820, λ_{max} 230 mμ (log ϵ 4.34); infrared absorption maxima in carbon tetrachloride: 1733s, 1645m, 1613m, 966s, 898s and 890s cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.23; H, 9.15.

A mixture of 5.0 g. of the ester IX, n^{25}D 1.4820, and 60 ml. of 1 *N* sodium hydroxide was stirred at 95° for 40 minutes, cooled and extracted with ether. Acidification of the aqueous layer precipitated a solid which was recrystallized twice from aqueous methanol to give 2.1 g. (46%) of 2-isopropenyl-5-methyl-2-*trans*:4-hexadienoic acid (X, R = H), m.p. 130–131°, λ_{max} 275 mμ (log ϵ 4.37); infrared absorption maxima in potassium bromide: 1667s, 1621s, 1585s and 898m cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; neut. equiv., 166.2. Found: C, 72.48; H, 8.70; neut. equiv., 166.2.

The acid formed a *p*-bromophenacyl ester, m.p. 110–111° from aqueous methanol.

Anal. Calcd. for $C_{18}H_{19}BrO_3$: C, 59.50; H, 5.27. Found: C, 59.72; H, 5.36.

The acid (1.0 g.) was esterified with ethereal diazomethane to give 0.90 g. (83%) of the ester (X, R = CH_3), n^{22}D 1.5251, λ_{max} 280 mμ (log ϵ 4.39); infrared absorption maxima at 1701, 1629s, 1587m and 901s cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.05; H, 9.01.

Refractionation of the crude higher boiling fraction gave seven fractions, b.p. 43-82° (0.6 mm.). The fifth fraction, b.p. 61–69° (0.6 mm.), n^{25}D 1.5205, had infrared and ultraviolet absorption characteristics equivalent to those of the pure ester X. The last fraction, b.p. 70–82° (0.6 mm.), n^{25}D 1.4965, on saponification gave a mixture of acids from which an identifiable amount of the 187° acid VI was separated.

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