Preparation and Pyrolysis of Methyl 12-Methylricinoleate[1]

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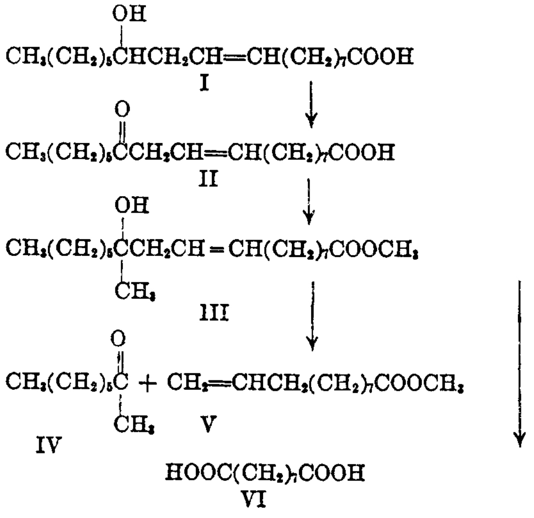
Methyl ricinoleate (the methyl ester of I) pyrolyzes to give heptaldehyde and methyl undecylenate.[2] We have now found that methyl 12-methylricinoleate (III) pyrolyzes analogously to give 2-octanone (IV) and methyl undecylenate (V). Accordingly, in agreement with the cyclic mechanism supported by Arnold and Smolinsky,[3] the hydrogen atom at the 12-position plays no essential role in the pyrolysis of methyl ricinoleate.



$CH_3(CH_2)_5\overset{OH}{C}HCH_2CH{=}CH(CH_2)_7COOH$ I

$CH_3(CH_2)_5\overset{O}{\overset{\|}{C}}CH_2CH{=}CH(CH_2)_7COOH$ II

$CH_3(CH_2)_5\underset{CH_3}{\overset{OH}{C}}CH_2CH{=}CH(CH_2)_7COOCH_3$ III

$CH_3(CH_2)_5\underset{CH_3}{\overset{O}{\overset{\|}{C}}} + CH_2{=}CHCH_2(CH_2)_7COOCH_3$ IV V

$HOOC(CH_2)_7COOH$ VI

Methyl 12-methylricinoleate (III) was prepared from castor oil ricinoleic acid (I). Short exposure of ricinoleic acid to acid dichromate[4] gave 12-oxo-*cis*-9-octadecenoic acid (II), which after esterification with diazomethane, and reaction with methylmagnesium bromide furnished the desired product III. To show that no double bond migration occurred during the Grignard reaction, the methyl 12-methylricinoleate (III) was oxidatively cleaved. Since azelaic acid (VI) was the only dibasic acid isolated, the $\Delta^{9,10}$ formulation as in III was established.

EXPERIMENTAL[5]

12-Oxo-cis-9-octadecenoic acid (II). Crude castor oil fatty acids (100 g.) supplied by Baker Castor Oil Co. was oxidized essentially according to published directions.[4] The keto acid II obtained (54 g.; m.p. 39–40°) was more conveniently recrystallized from petroleum ether (b.p. 30–60°) than from 80% ethanol. The purified 12-oxo-*cis*-9-octadecenoic acid (II), m.p. 40–41°, weighed 51 g. The reported melting point is 40–40.5°.[4]

Methyl ester of 12-oxo-cis-9-octadecenoic acid (II). A distilled ethereal solution of diazomethane, prepared from 0.20 mole of *N*-methyl-*N*-nitrosourea,[6] was slowly added to a solution of 21.0 g. (0.071 mole) of freshly prepared keto acid II[7] in 30 ml. of ether. After standing overnight at room temperature, the yellow solution was distilled on the steam bath. The last traces of volatile material were removed under reduced pressure. The methyl ester of keto acid II, remaining as a brown oil, was used without further treatment.

Methyl 12-methylricinoleate (III). The keto methyl ester was transferred with 75 ml. of absolute ether to a 3-necked flask fitted with a dropping funnel, mechanical stirrer, and condenser. The reaction mixture was blanketed with pure nitrogen during the entire preparation. An ethereal solution of methylmagnesium bromide (25.5 ml. of a 4*M* solution, or 0.10 mole) was added by drops over a period of 1 hr. to the stirred keto ester solution at ice-salt temperatures. The reaction mixture, in which a dark red insoluble resin had appeared, was allowed to warm to room temperature, and was stirred for 15 hr.

Acetic acid (20 ml.) in cold water (100 ml.) was added slowly to the vigorously stirred, ice cold ether mixture. After the upper ether layer was separated, the aqueous layer was extracted with four 25-ml. portions of ether. The combined ether solutions were washed with water until the washings were neutral to litmus, and were then dried with sodium sulfate. Removal of all volatile material by distillation under reduced pressure on the steam bath left a yellow oil (16.1 g.; 70%).

Purified adduct III was obtained by placing 1.0 g. of this oil in 10 ml. of petroleum ether (b.p. 30–60°) on a 1.7 cm. chromatography column containing 25 g. of alumina (Merck, acid washed). Elution with 50 ml. portions of mixtures of petroleum ether–benzene in the volume proportions 4:1, 3:2, and 1:4 failed to remove nonvolatile material. Passage of 200 ml. of benzene did remove product, which was obtained solvent-free by distillation on the steam bath under a jet of pure nitrogen directed at the surface of the liquid. The residual, faintly yellow methyl 12-methylricinoleate (0.71 g.) was further purified by distillation in a 2 ml. short-path still. The distillate (0.56 g.) collected at b.p. 137–140° (0.02 mm.), was taken as pure product III, n_D^{25}1.4670.

Anal. Calcd. for $C_{20}H_{38}O_3$: C, 73.57; H, 11.73. Found: C, 73.6; H, 11.5.

Methyl 12-methylricinoleate (III), as neat liquid, showed strong infrared absorption peaks at 2.89 and 5.74 μ, but only negligible absorption in the 10.3 μ region.

In another preparation, 72 g. (0.24 mole) of 12-oxo-*cis*-9-octadecenoic acid (II) was esterified and treated with methylmagnesium bromide in a manner analogous to that described above. The crude adduct III (53.5 g.) was chromatographed on a 4 cm. column containing 500 g. of alumina to give 44.6 g. (57%) of faintly yellow methyl 12-methylricinoleate (III), n_D^{25} 1.4674, which was used without further purification.

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[1] Abstracted from a portion of the dissertation submitted by Carolyn B. Abrahams to the Graduate School of Boston University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1957.

[2] *Cf.* A. Barbot, *Ann. chim. (Paris)*, [11] 11, 519 (1939).

[3] R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc.*, **81**, 6443 (1959); *J. Org. Chem.*, **25**, 129 (1960). Also S. Isikawa, T. Tosimitu, A. Miyata, Z. Araki, and R. Someno, *Chem. Abstr.*, **34**, 3240 (1940) [*Science Repts. Tokyo Bunrika Daigaku*, A3, 273 (1939)].

[4] J. Nichols and E. Schipper, *J. Am. Chem. Soc.*, **80**, 5705 (1958).

[5] Temperatures are uncorrected. Elementary analyses were performed by Carol K. Fitz, 115 Lexington Ave., Needham Heights, Mass.

[6] F. Arndt, *Org. Syntheses*, Coll. Vol. II, 165 (1943).

[7] 12-Oxo-*cis*-9-octadecenoic acid (II) autoxidizes readily at room temperature. *Cf.* G. W. Ellis, *J. Chem. Soc.*, 9 (1950).

Treating 12-oxo-*cis*-9-octadecenoic acid (II) first with methylmagnesium bromide (3 molar proportions) and then with diazomethane gave the same product III, b.p. 139–144° (0.1 mm.), n^{25}_{D} 1.4667, but in only 20% yield.

Oxidative cleavage of methyl 12-methylricinoleate (III). Oxygen containing ozone was bubbled into a solution of 10 g. (0.031 mole) of methyl 12-methylricinoleate (III) in 70 ml. of chloroform (Baker Analyzed) at a rate of 0.36 mmole of ozone per min.[8] The reaction mixture was held at the temperature of solid carbon dioxide–kerosene. Ozonolysis was interrupted after 110 min., that is, after 0.040 mole of ozone had been introduced. At this time, the chloroform became blue, and iodine was liberated on passing the emergent gases into an acidified aqueous' solution of potassium iodide.

Most of the chloroform was removed by distillation at room temperature under reduced pressure. Water (300 ml.) was added to the viscous residue, and the mixture was boiled for 2 hr. Five per cent aqueous potassium permanganate (150 ml.) and 10% aqueous sodium hydroxide (25 ml.) were added to the cooled mixture, which was boiled again and then cooled in an ice bath. Excess 5% sulfuric acid (200 ml.) was slowly introduced followed by enough 5% aqueous sodium hydrogen sulfite to transform all the permanganate and manganese dioxide to manganese(II). The colorless, faintly turbid solution was extracted with six 50-ml. portions of ether, and the combined extracts were extracted in turn with two 10-ml. portions of 10% aqueous sodium hydroxide. After the combined alkaline solutions were washed with two 20-ml. portions of ether (discard), concentrated hydrochloric acid was added dropwise with cooling until the *p*H was close to 1. The white, precipitated azelaic acid (VI) was collected on the funnel, was washed free of inorganic acid with ice water, and was air dried.

This product (3.7 g.; m.p. 94–97°), on crystallization from water yielded 3.3 g. (57%) of pure material, which melted either alone or admixed with authentic azelaic acid (m.p. 104.5–106°) at 105–106°. The observed neutralization equivalent, 95.0, agreed with the value calculated (94.1) for azelaic acid. The cleavage azelaic acid (VI) mixed with 7-carbon pimelic acid (m.p. 104–105°) showed m.p. 85–95°. The reported melting points of the 8-carbon suberic acid and the 10-carbon sebacic acid are 140° and 133°, respectively.[9]

Pyrolysis of methyl 12-methylricinoleate (III).[10] A 25-ml. flask fitted with a 25-cm. Vigreux column and condenser, and containing 10.0 g. (0.031 mole) of methyl 12-methylricinoleate (III) was dipped into a metal bath at 400°. After 10 min., distillation became slower, and the bath was heated to 525° and held at this temperature for 5 min. The pyrolysis products, which came over at vapor temperatures fluctuating between 270 and 330°, were collected in a receiver cooled with solid carbon dioxide.

Redistillation of the products through a 5-cm. Vigreux column afforded the following fractions: (a) 0.61 g. of a colorless, pungent liquid, b.p. 64–75° (atm. press.), n^{25}_{D} 1.3767; (b) 1.3 g. of faintly yellow liquid, b.p. 97–101° (54 mm.), n^{25}_{D} 1.4192; (c) 1.82 g. of faintly yellow liquid, b.p. 137–140° (25 mm.), n^{25}_{D} 1.4392; and (d) 3.2 g. of brown residue.

Fraction (b) was shown to be 2-octanone (IV) by formation of the semicarbazone.[9] The 2-octanone (0.50 g.) furnished 0.61 g. of once-crystallized white needles, m.p. 114–117°, which were recrystallized once from water. The pure derivative melted at 121–122°; its melting point was unchanged on admixture with an authentic sample of 2-octanone semicarbazone, m.p. 121.5–122°. The derivative was crystallized twice from water before analysis.

Anal. Calcd. for $C_9H_{19}N_3O$: C, 58.34; H, 10.34; N, 22.68. Found: C, 58.6; H, 10.5; N, 22.5.

Distillate fraction (c) was taken as methyl undecylenate (V). Purification by chromatography was effected by placing 0.77 g. of fraction (c) dissolved in 10 ml. of petroleum ether (b.p. 30–60°) on a 1.7 cm. chromatography column containing 15 g. of alumina (Merck, acid washed) and eluting with 120 ml. of petroleum ether. Each 20-ml. portion of eluate was freed of solvent by exposure at 100° to a jet of pure nitrogen. In this way, 0.32 g. of analytically pure methyl undecylenate (V) was obtained.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.5; H, 11.2.

The index of refraction, n^{25}_{D} 1.4372, agreed with the value, n^{25}_{D} 1.43727,[11] reported for methyl undecylenate. Infrared absorption curves taken with neat samples of pyrolysis methyl undecylenate (V) and of authentic methyl undecylenate were the same.

Under similar pyrolysis conditions, methyl ricinoleate gave heptanal and methyl undecylenate in roughly double the yields of 2-octanone (IV) and methyl undecylenate (V) from methyl 12-methylricinoleate (III).

Acknowledgment. We wish to thank the Baker Castor Oil Co. for the grant under which this work was performed and to acknowledge the encouragement and assistance of Don S. Bolley, Technical Director, The Baker Castor Oil Co. Dr. Joseph Nichols, of Ethicon, Inc. very kindly provided us with directions for the preparation of keto acid II before their publication.[4]

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[8] The ozonolysis was modeled after the ozonolysis of ricinoleic acid (I), A. C. Noorduyn, *Rec. trav. chim.*, **38**, 323 (1919).

[9] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Fourth edition, John Wiley & Sons, Inc., New York, New York, 1956.

[10] *Cf.* G. A. Perkins and A. O. Cruz, *J. Am. Chem. Soc.*, **49**, 1070 (1927).

[11] J. T. Bornwater, *Rec. trav. chim.*, **26**, 409 (1907).

Alkaline Epoxidation of α,β-Unsaturated Aldehydes

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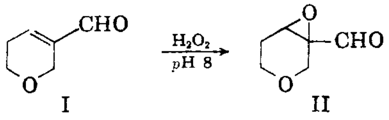
The technique recently described[1] for the epoxidation of acrolein and methacrolein by hydrogen peroxide has been applied to a variety of other α,β-unsaturated aldehydes. Table I summarizes the results obtained with crotonaldehyde, tiglaldehyde (2-methyl-2-butenal), cinnamaldehyde, citral, and the "acid dimer" of acrolein, 3-formyl-5,6-dihydro-2H-pyran (I).



I II

The epoxy aldehydes obtained from I, citral, and tiglaldehyde are new compounds. That from croton-

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[1] G. B. Payne, *J. Am. Chem. Soc.*, **81**, 4901 (1959).