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Reactions of Conjugated Fatty Acids. VII. Catalytic Cyclization and Aromatization of *cis,trans*-Octadecadienoic Acid with Selenium[1]

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When *cis,trans*-conjugated methyl linoleate was heated at 250° with selenium, the product consisted of a mixture of isomeric *cis*- and *trans*-octadecenoates and cyclized material that appeared to be a mixture of dialkylbenzene and dialkylcyclohexene and could be converted to *o*-phthalic acid in 54% yield. In the presence of hydrogen acceptors, the ratio of octadecenoate to cyclic product was decreased. Results of a kinetic study suggest that the first step in the reaction is a rapid isomerization of *cis,trans*-conjugated methyl linoleate to the *trans,trans* isomer and that it is the latter that cyclizes.

During studies[3] of the use of selenium as a catalyst in preparing Diels-Alder adducts from dienophiles and *cis,trans*-conjugated methyl linoleate, it was observed that when the *cis, trans*-conjugated ester was heated to 250° with selenium, but in the absence of a dienophile, it was converted to a material no longer containing significant amounts of diene conjugation. At first it was presumed that polymerization could account for this result, but when it was found that the reaction product left a negligible residue upon conventional vacuum distillation, it was evident that a reaction of unanticipated nature had taken place. This paper reports the results of our investigation of the effect of selenium upon *cis, trans*-conjugated methyl linoleate.

The reaction product obtained by heating *cis, trans*-conjugated methyl linoleate with selenium at 250° was separated by complexing with urea into a complex-forming fraction (A, 67%) and a non-complex-forming fraction (B, 31%). On the basis of iodine number, ultraviolet and infrared spectra, fractional crystallization of its component fatty acids, and the dibasic acids resulting from oxidation with permanganate-periodate,[4] Fraction A appears to be a mixture of isomeric methyl *cis*- and *trans*-octadecenoates having unsaturation in positions 7 through 14, with little or no stearate present.

Since Fraction B did not complex with urea, it was presumably some type of cyclized fatty acid derivative. If cyclization and aromatization of the *cis,trans*-conjugated methyl linoleate had taken place, the product would be a dialkylbenzene that would show characteristic absorptions in its ultraviolet and infrared spectra. In the ultraviolet, an absorption peak was observed at 272 mμ and a shoulder at 242.5 mμ. A very strong absorption was found at 752 cm.$^{-1}$ in the infrared and a weaker absorption at about 700 cm.$^{-1}$ A band in the range of 735 to 770 cm.$^{-1}$ would be expected for a dialkylbenzene.[5] Infrared absorption for isolated *trans* bonds was not present.

Fraction B was aromatized by successive treatment with *N*-bromosuccinimide and *N,N*-dimethylaniline and then oxidized with potassium permanganate. *o*-Phthalic acid was obtained in 54% yield.

The strong infrared absorption at 752 cm.$^{-1}$ shown by Fraction B, its ultraviolet spectrum, low iodine number (approx. 22), and conversion in good yield to *o*-phthalic acid, are consistent with the interpretation that this fraction is a mixture of aromatic and hydroaromatic compounds, specifically a dialkyl benzene and a dialkyl cyclohexene. From the iodine number, about 25% of Fraction B appears to be dialkylcyclohexene.

A recent paper by Floyd *et al.*[6] describes the aromatization of nonconjugated linoleic acid with palladium as a catalyst. Stearate (18%), monoolefins (40%), aromatic compounds (30%), and polymers (7%) were obtained. Dialkyl cyclohexene–type products were not reported. The aromatic fractions obtained by these workers had infrared spectra similar to those of the noncomplexing fraction of the present report. Absorption near 273 mμ was prominent in all aromatic fractions.

A brief study was made of the kinetics of the reaction of selenium with *cis,trans*-conjugated methyl linoleate. It was found that total conjugation is lost during the reaction at essentially the same rate as *trans,trans* conjugation whereas *cis,trans* conjugation is lost at a considerably more rapid rate (Figure 1). These results suggest that the first step in the reaction is a rapid isomerization of the *cis,trans* isomer to the *trans,trans* and that it is the latter that cyclizes. Construction of molecular models shows that cyclization by joining the two α-positions of a diene should occur readily with the *trans,trans* configuration but not with the *cis,trans*.

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[1] Presented at the fall meeting of the American Oil Chemists' Society, Cincinnati, Ohio, Sept. 30–Oct. 2, 1957.

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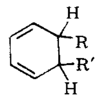
[3] H. M. Teeter, E. W. Bell, J. L. O'Donnell, M. J. Danzig, and J. C. Cowan, *J. Am. Oil Chemists' Soc.*, **35**, 238 (1958).

[4] E. P. Jones and J. A. Stolp, *J. Am. Oil Chemists' Soc.*, **35**, 71 (1958).

[5] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, 1954, p. 55.

[6] D. E. Floyd, R. F. Paschke, D. H. Wheeler, and W. S. Baldwin, *J. Am. Oil Chemists' Soc.*, **33**, 609 (1956).

The detailed mechanism whereby selenium brings about ring closure of *trans,trans*-conjugated methyl linoleate is not known. However, the over-all effect must be abstraction of a hydrogen atom from each of the methylene groups adjacent to the diene system to produce a cyclohexadiene derivative such as I. The hydrogen abstracted is presumably transferred to another molecule of conjugated linoleate, reducing it to an octadecenoate. The cyclohexadiene I could then be further dehydrogenated by another conjugated linoleate to yield the dialkylbenzene and a second octadecenoate molecule. Alternatively, I could disproportionate to dialkyl benzene plus dialkyl cyclohexene. This disproportionation appears to be the only way in which the latter could be formed.



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The molecular ratio of octadecenoate to cyclized product would be 2:1 if aromatization were complete and no dialkylcyclohexene were formed. This ratio would be 1:1 if aromatic and cyclohexene derivatives were formed only by disproportionation of the cyclohexadiene I. Intermediate ratios would be expected if both routes to aromatic were followed. The ratio observed in our experiments is about 2.2:1. If one stearate is considered equivalent to two oleate molecules, the results of Floyd[6] indicate a ratio of about 2.5:1. The ratio of octadecenoate to the cyclized product observed in our work, together with the iodine number and spectral properties of the cyclized material, suggest that aromatic substances were probably produced by both routes.

If a hydrogen transfer process is involved in the cyclization and aromatization of conjugated methyl linoleate, the ratio of octadecenoate to cyclized product would be expected to change if the reaction were carried out in the presence of a hydrogen acceptor. When crotonic acid was used as a hydrogen acceptor, a ratio of about 1.3:1 was observed. With nitrobenzene as acceptor, cyclized product was obtained in 29% yield, but no appreciable amount of octadecenoate was recovered. However, this reaction appeared to be very complex, and considerable amounts of unidentified tarry by-products were obtained. Cyclic material found in this reaction showed a strong band at 273 mμ in the ultraviolet as well as strong bands at 752 and 704 cm.$^{-1}$ in the infrared. Identification of aniline in the reaction mixture shows that hydrogen transfer to nitrobenzene took place during the reaction.

EXPERIMENTAL

Methyl linoleate (n_D^{30}, 1.4578; iodine number, 172.3) was prepared by debromination of tetrabromostearic acid in methanol solution.[7] Alkali-isomerization[8] gave conjugated linoleic acid: a = 100 l.g.$^{-1}$ cm.$^{-1}$ at 233 mμ; n_D^{30} 1.4793. The methyl ester of the conjugated linoleic acid (n_D^{30} 1.4694; acid value 2.4) showed 90.5% *cis,trans* and 12.8% *trans,trans* conjugation as determined by infrared analysis.

Reaction of cis-trans-conjugated methyl linoleate with selenium. A Parr medium pressure, stainless-steel, hydrogenation apparatus was charged with 50 g. of conjugated methyl linoleate, 250 ml. of heptane, and 1 g. of selenium. The apparatus was flushed with nitrogen, and nitrogen was then introduced to 40 p.s.i. The vessel was then sealed and heated with constant stirring at 250° for 4.5 hr. After cooling, the reaction mixture was filtered, and the solvent was removed under reduced pressure. The residue (49.9 g.) had an iodine number of 67 and 0.0% conjugation as determined by ultraviolet analysis.

To remove selenium, this residue was stirred with mercury for 3 hr. and decanted from the metal; 44.4 g. of ester was recovered.

Urea separation of deselenized product. The deselenized residue was separated into an urea-complexing fraction (I, 67%) n_D^{30} 1.4523, and a nonurea-complexing fraction (II, 30.8%) n_D^{30} 1.4868, by the following procedure:

The deselenized residue (44.4 g.) was added to a warm solution of 310 g. of urea and 500 ml. of methanol. The mixture was allowed to crystallize at room temperature overnight. The precipitate containing the urea-complexing fraction was filtered with suction and washed with a saturated methanol solution of urea. The urea complex was then decomposed by mixing with about 200 ml. of 10% aqueous hydrochloric acid. The mixture was extracted four times with 50-ml. portions of ethyl ether. The combined ether extracts were washed neutral with water and dried over anhydrous sodium sulfate. An ester (29.7 g.) was recovered (Fraction A).

Urea-complexing fraction. Distillation of 28.6 g. of Fraction A *in vacuo* yielded fractions as shown in Table I.

TABLE I

FRACTIONAL DISTILLATION OF UREA-COMPLEXING FRACTION FROM SELENIUM-TREATED CONJUGATED METHYL LINOLEATE

Fraction No.	B.P., °C./Mm.	Weight, G.	Iodine Number	n_D^{30}
A-1	118–127°/0.25	8.1	86.5	1.4496
A-2	132–140°/0.1	8.0	82.3	1.4497
A-3	134–140°/0.025	10.8	86.8	1.4509
Residue	—	1.5	—	—

Because fractions A-1 to A-3 differed only slightly in properties they were combined and saponified to obtain the acids (iodine number 90; neut. equiv. 280; diene conjugation <1%). When a sample of these acids was recrystallized from ethanol, the highest melting fraction isolated had m.p. 39–44°. This fraction is presumed to be elaidic acid, since a mixed melting point with authentic elaidic acid showed no depression.

Another sample of the acids was submitted to analytical oxidation with permanganate-periodate in accordance with the procedure of Lemieux and Von Rudloff[9] as modified by Jones and Stolp.[4]

Total recovery of mono- and dibasic acids was 93%. The following dibasic acids were recovered in the mole percentages shown: C_7, 3.9%; C_8, 8.1%; C_9, 11.4%; C_{10}, 14.0%; C_{11}, 13.6%; C_{12}, 12.0%; C_{13}, 10.1%, C_{14}, 8.0%. In

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(7) J. W. McCutcheon, *Org. Syntheses*, **22,** 77 (1942).

(8) J. P. Kass and G. O. Burr, *J. Am. Oil Chemists' Soc.*, **61,** 3293 (1939).

(9) R. V. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33,** 1701 (1955).

chromatography the monobasic acid peak showed contamination with dibasic acids of still longer chain length.

The infrared spectrum of Fraction A showed the presence of *trans* bonds. Since the data obtained do not permit exclusion of the presence of *cis* isomers, this urea-complexing fraction was tentatively identified as a mixture of isomeric methyl *cis*- and *trans*-octadecenoates.

Nonurea-complexing fraction. The filtrate from the urea separation yielded 13.7 g. of nonurea-complexing ester (Fraction B). A portion of this dark brown ester (12.6 g.) was fractionally distilled (Table II).

TABLE II

FRACTIONAL DISTILLATION OF NONUREA-COMPLEXING FRACTION FROM SELENIUM-TREATED METHYL LINOLEATE

Fraction No.	B.P., °C./Mm.	Weight, G.	Iodine Number	n_D^{30}
B-1	117–130°/0.025	1.00	21.6	1.4842
B-2	130–160°/0.025–0.1	1.37	21.8	1.4849
B-3	160–192°/0.025–0.05	7.18	22.1	1.4849
B-4	192–195°/0.025	0.99	—	—
Residue	—	1.59	—	—

Fraction B-3 was treated with mercury and decolorized by passing an ethereal solution through a column packed with a mixture of carbon (10%) and activated alumina (90%). The recovered product (5.9 g.) contained no conjugation. Infrared analysis of the fraction showed very strong absorption at 752 cm.$^{-1}$ and some absorption at 700 cm.$^{-1}$ In the ultraviolet, this fraction showed a peak at 272 mμ (a, 1.45 l.g.$^{-1}$ cm.$^{-1}$) and a shoulder at 242.5 mμ (a, 2.93 l.g.$^{-1}$ cm.$^{-1}$).

Aromatization and oxidation of the nonurea-complexing fraction. The non-urea-complexing fraction (B, 1.5 g.), 30 ml. of carbon tetrachloride, and 4.45 g. of *N*-bromosuccinimide were refluxed for 3.5 hr. and allowed to cool overnight. The solids were removed by filtration, and 2.63 g. of brominated material was recovered from the filtrate.

A mixture of this product and 7 ml. of *N,N*-dimethylaniline was heated to 125° for 1 hr. Water was added to the reaction mixture, and the organic layer was taken up in ether. The ethereal solution was extracted with 10% aqueous hydrochloric acid, washed twice with water, and dried over anhydrous sodium sulfate.

After removal of solvent, the debrominated product, 4 g. of sodium hydroxide, 80 ml. of water, and 10 g. of potassium permanganate were stirred and heated to reflux for 5 hr. Additional permanganate (5 g.) was then added, and heating was continued until the permanganate was used up. The cooled reaction mixture was acidified with 50% sulfuric acid, and sulfur dioxide was added to reduce the manganese dioxide present.

The *p*H of the reaction mixture was adjusted to 7 by the addition of sodium hydroxide. The solution was then acidified with 10% hydrochloric acid and extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. There was obtained 0.45 g. (53.6%) of solid; m.p. 187–188° after sublimation *in vacuo*. Ultraviolet spectra of the product and of pure *o*-phthalic acid were identical. A sample of the product was converted to phthalic anhydride, m.p. 129–130°. Mixed melting point with pure phthalic anhydride (m.p. 130–131°) was 129–130°.

Reaction of conjugated methyl linoleate with selenium in the presence of hydrogen acceptors. (*a*) *Crotonic acid.* A Carius tube was charged with 5.0 g. of conjugated methyl linoleate, 2.9 g. of crotonic acid, 0.1 g. of selenium, 10 ml. of benzene, and 0.05 g. of hydroquinone. The tube was sealed in a nitrogen atmosphere and heated at 250° for 3 hr. When the tube was cooled, it was opened, and the contents were extracted with a saturated aqueous solution of sodium bicarbonate. The residue (iodine number 39) was recovered from the benzene layer and treated with urea as previously described. An urea-complexing fraction (53.2%) and a nonurea-complexing fraction (41.7%) were obtained. Handling loss was 3%.

(*b*) *Nitrobenzene.* A mixture of conjugated methyl linoleate (10 g.), 24 g. of nitrobenzene, and 0.25 g. of selenium was refluxed for 6.5 hr. Distillation of the nitrobenzene left 12.3 g. of viscous black residue. This residue was flash distilled, yielding a reddish brown product (3.4 g.) boiling at 116–225°/0.025 mm. This product was treated with urea as previously described. No appreciable amount of urea-complexing material was recovered.

The nonurea-complexing fraction (2.9 g.) was distilled, yielding two fractions. The first fraction (0.8 g.) showed b.p., 120–140°/0.025 mm.; n_D^{30}, 1.4954; iodine number, 23.8; 0.0% conjugation. A strong band at 273 mμ was present in the ultraviolet spectrum. Strong absorptions at 752 cm.$^{-1}$ and at 702 cm.$^{-1}$ were observed in the infrared spectrum. The second fraction (1.8 g.) showed b.p., 140–160°/0.025 mm.; n_D^{30}, 1.4922; iodine number, 16.7; 0.0% conjugation. A strong band at 273 mμ was present in the ultraviolet spectrum, and a strong absorption at 752 cm.$^{-1}$ was noted in the infrared spectrum. The residues from the distillations were very viscous black materials from which no additional fatty material could be isolated. The nitrobenzene fraction recovered from the original reaction mixture was treated with anhydrous hydrogen chloride. Crude aniline hydrochloride (1.5 g.; hot stage m.p., 178°) was recovered. This product was recrystallized twice from ethanol; m.p. 195–196°. The melting point of pure aniline hydrochloride is 198°.

Kinetic study of the reaction of selenium with conjugated methyl linoleate. A mixture of conjugated methyl linoleate (34.9 g.; 44.3% *trans,trans* and 32.7% *cis,trans* conjugation) and 0.9 g. of selenium was stirred and heated at 250° under nitrogen at atmospheric pressure. Samples were withdrawn at 5-min. intervals. Total conjugation and *cis,trans* and *trans, trans* conjugation were obtained on each sample by infrared analysis. The results are shown in Fig. 1.

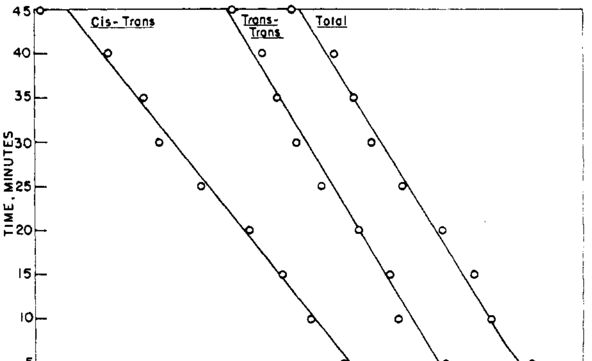

Fig. 1. Effect of selenium treatment on diene content of conjugated methyl linoleate

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