

The Mechanism of the Aqueous Perchloric Acid Isomerization of Oleic Acid to γ -Stearolactone¹

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IAN S. SHEPHERD² and JOHN S. SHOWELL,³

Eastern Utilization Research and Development Division,⁴ Philadelphia, Pennsylvania 19118

Abstract

The migration of the double bond in the reaction of oleic acid with aqueous 67% deuteroperchloric acid occurs by the reversible intermolecular esterification of carboxylic acid by olefin; when a double bond reaches the $\Delta^{4,5}$ position and intramolecular carboxylic acid-olefin, esterification occurs to yield γ -stearolactone.

Introduction

γ -Stearolactone may be prepared by the reaction of oleic acid with aqueous 70% perchloric acid. The optimum yield (ca. 75%) is attained by running the reaction under nitrogen for 3 hr at 100 C with magnetic stirring, and using sufficient aqueous perchloric acid to ensure a 1.0 to 1.0 molar ratio of oleic acid to perchloric acid (1). In the present studies, aqueous 67% deuteroperchloric acid has been used on saturated and unsaturated fatty acids, γ -stearolactone, and secondary octadecyl stearate to investigate the reaction mechanism involved in the formation of γ -stearolactone. The results on isomerization and deuterated products in conjunction with the conclusions from a former study on *cis*-9-octadecene comprise the necessary evidence for a mechanism. The mechanism is accordingly shown to be reversible esterification of the carboxylic acid with the olefin, with double bond migration to the $\Delta^{4,5}$ followed by intramolecular esterification to form γ -stearolactone, according to schemes I and II below.

Experimental Procedures

Starting Materials

Caution. See Reference 1 for the safety precautions to be taken for all perchloric acid reactions.

Aqueous Deuteroperchloric Acid. All glassware was soaked overnight in nitric acid and washed with distilled water before use. Heavy water (25 g, 99.8 atom per cent) was added to Eastman Kodak aqueous 70% perchloric acid (100 ml) in a 500 ml round bottom flask fitted with a distillation head, condenser and receiving flask. A slight positive pressure of nitrogen was applied and the flask contents stirred with a magnetic bar. The flask was slowly heated by means of a Wood's metal bath and water distilled off (over 1 hr) in the bath in the temperature range 100–190 C. The bath temperature was allowed to fall to 90 C before the addition of more heavy water (25 g). Water was again distilled off by a slow rise in bath temperature to 190 C, followed by a cooling to 90 C. The procedure was repeated to give a total of eight separate additions of heavy water (25 g each) and eight removals of water (average of 22.5 ml each). The aqueous acid ($d^{25} = 1.7322$)

was calculated to be 90% deuterium enriched and contained 67.3% by weight of deuteroperchloric acid in the heavy water aqueous solution.

Stearic Acid, RCOOD. Stearic anhydride (10.0 g, 18.2 mmoles), mp 73 C, was dissolved in dry tetrahydrofuran (150 ml) containing heavy water (3.0 g, 150 mmoles, 7.5 molar excess) and pyridine (0.1 g). The solution was refluxed for four days, after which IR sampling indicated complete hydrolysis, and the solvent and water removed to yield 0-deuterostearic acid (9.9 g), mp 67.8–68.2 C.

γ -Stearolactone. γ -Stearolactone, mp 52–53 C, was supplied by W. R. Noble. The method of preparation has been reported (1).

Oleic Acid, RCOOD. Oleic acid (Applied Science Laboratories, 99%+, 60 g) was dissolved in dry tetrahydrofuran (300 ml, flushed with nitrogen) at room temperature. Water (ca. 85% deuterium enriched, 25 g) was added, and the solution stirred for 1 hr. Solvent and water were removed and the procedure repeated with 25 g of heavy water (99.8 atom per cent). Solvent and water were again removed by a rotary vacuum evaporator to leave the product (60 g).

Petroselinic Acid. This compound was prepared by J. R. Russell using the procedure of Fore et al. (2) by isolation of the crude material from parsley seed oil and recrystallization from petroleum ether to give a product of mp 29 C.

Trans-2-Octadecenoic Acid. Using the procedure of Myers (3), the preparative sequence stearic acid— α -bromostearic acid— α -iodostearic acid—*trans*-2-octadecenoic acid + α -hydroxystearic acid was followed. The α -hydroxystearic acid was removed as the copper chelate, as done by Palameta and Prostenik (4), and *trans*-2-octadecenoic acid, mp 57.2–57.5 C, was obtained by recrystallization of the crude compound from ethanol-petroleum ether.

Stearolic Acid. Stearolic acid, mp 46.0–46.5 C, was prepared following the method of Adkins and Burks (5).

Analytical Techniques. Oxidative cleavages were carried out by the Subbaram and Youngs (6) modification of the von Rudloff method (7); the methylated (boron-trifluoride-methanol) mono- and dicarboxylic acid products were analyzed by gas liquid chromatography (GLC) on a Silicone gum rubber column. Fusions with alkali were used for the cleavage of γ -lactone to a carboxylic acid containing three carbon atoms less (8). The reactions were carried out in a nickel pot at 300 C for 1 hr under nitrogen and with mechanical stirring. The cooled melt was dissolved in water, acidified and ether extracted.

The amount of deuterium in the γ -stearolactone and octadecenoic acid products was estimated by measuring the intensity of the infrared (IR) absorption in the region 2145 cm^{-1} (carbon tetrachloride as solvent). Some fatty acid methyl esters of known deuterium composition were available and these were used as standards to relate peak area in the region

¹ Presented in part at the AOCs Meeting, Houston, Texas, 1965.

² Present address: Unilever Research Laboratory, The Frythe, Welwyn, England.

³ Present address: National Science Foundation, Washington, D.C. 20550.

⁴ Agricultural Research Service, U.S.D.A.

2145 cm^{-1} to deuterium composition. (The method was tested and found reliable by examining some deuterated octadecenes. Estimation of deuterium content by IR spectroscopy was in good agreement with that found by mass spectrometric analysis). The IR spectra were run on a Beckman IR 7 IR Spectrophotometer.

The deuterium content of stearic acid products (after methylation with boron trifluoride methanol) was found by comparison of the mass spectra with the spectrum of normal methyl stearate. Mass spectra were run on a Consolidated Electrodynamics Corporation Model 21-103 C Mass Spectrometer.

Reaction Procedure. The reactions with aqueous perchloric acid are heterogeneous, there being an organic upper layer and an inorganic lower layer. In the typical procedure the fatty material (ca. 5.0 g) was weighed into a jacketed reaction vessel containing a magnetic stirring bar. The vessel was then flushed out with nitrogen before the drop by drop addition of the required amount of aqueous 67% deuteroperchloric acid. Reactions (100 C, 3 hr) were carried out under slight positive pressure of nitrogen and with magnetic stirring, using sufficient aqueous acid to ensure a 1.0 to 1.0 molar ratio of inorganic acid to fatty material. The reaction mixture was poured into water (200 ml) and continuously extracted with benzene (under nitrogen) for 17 hr. The benzene layer was separated off and evaporated to leave the crude reaction product. A small portion of the latter was withheld for various analytical examinations (GLC, TLC, IR) and the remainder chromatographed on a Florisil column in order to isolate the deuterated γ -stearolactone product. The acidic material recovered from the Florisil chromatography was methylated (diazomethane) and rechromatographed on a Silicic acid column to isolate monomeric methyl octadecenoates. The γ -stearolactone and methyl octadecenoates were examined for deuterium content; the methyl octadecenoates were also subjected to oxidative cleavage.

Results and Discussion

Stearic acid was recovered in almost quantitative yield from 3 hr, 100 C reactions with aqueous 67% deuteroperchloric acid (1.0 to 1.0 molar ratio of reactants). The recovered stearic acid contained only 0.02 deuterium atoms per molecule. (The work up procedure was such that almost all the original carboxyl deuterium was exchanged out. An equilibrium distribution of hydrogen-deuterium in the work-up mixture would result in fatty acid product containing approximately 0.005 carboxyl deuterium atoms per molecule).

The reaction of γ -stearolactone, under the same conditions, gave an 87% recovery of a deuterated γ -stearolactone containing 3.9 deuterium atoms per molecule (compare the reaction of hexan- and undecan-4-olide with hot 50% deuteriosulfuric acid). The reaction also gave a 3.5% yield of octadecenoic acids (5.3 deuterium atoms per molecule) consisting of approximately equal amounts of all isomers from $\Delta^{3,4}$ to $\Delta^{16,17}$. The deuteration of the olefinic acid and γ -stearolactone product may be contrasted with the result of the stearic acid reaction. It is apparent that the γ -stearolactone undergoes reversible ring-opening to yield olefinic acids, although with the above reaction conditions the equilibrium lies heavily in favor of the lactone.

Some information on the distribution of the

deuterium in the above γ -stearolactone product was given by reacting the lactone in molten alkali. The crude fusion product was chromatographed on a Florisil column to give pentadecanoic acid (67%, GLC purity of methyl ester 95%), mp 48-49 C, containing 2.4 deuterium atoms per molecule. This indicates that in the deuterated γ -stearolactone 1.5 deuterium atoms in the molecule are between the C_2 and C_5 positions [deuterium in the α -methylene group of the fusion product would be exchanged (10)].

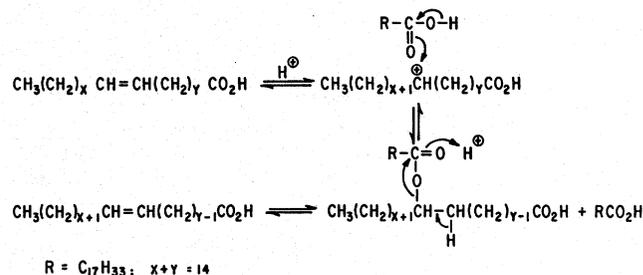
Oleic acid (RCOOH) in a 3 hr, 100 C reaction with aqueous 67% deuteroperchloric acid gave a 72% yield of a deuterated γ -stearolactone (5.6 deuterium atoms per molecule) and a 4.2% yield of octadecenoic acids (4.7 deuterium atoms per molecule) consisting of approximately equal amounts of all isomers from $\Delta^{3,4}$ to $\Delta^{16,17}$. Petroselinic acid similarly reacted to yield γ -stearolactone (70%, 4.7 deuterium atoms per molecule) and a small amount of deuterated isomeric octadecenoic acids.

Studies (11) on the reaction of *cis*-9-octadecene with aqueous 67% deuteroperchloric acid (1:1 molar ratio), both in the absence and presence of stearic acid, suggest the mechanism by which the double bond of olefinic acids undergoes isomerization. The 3 hr, 100 C reaction of *cis*-9-octadecene gave an octadecene product (0.4 deuterium atoms per molecule) which consisted of increasing amounts of positional isomers from $\Delta^{2,3}$ to (0.9%) through to $\Delta^{9,10}$ (25.1%).

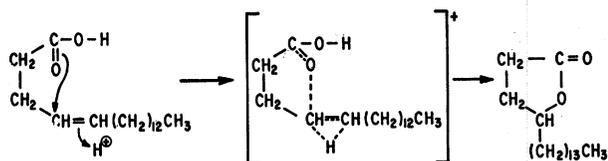
When a molar equivalent to stearic acid was included as a third reactant the isomerization occurred more rapidly and extensively, and gave a comparatively heavily deuterated product by a different reaction mechanism. For the 3 hr, 100 C reaction the octadecene product contained 3.3 deuterium atoms per molecule (equilibrium exchange value would be 4.8) and approximately equal amounts of all isomers from $\Delta^{2,3}$ to $\Delta^{9,10}$. An equilibrium amount (24%) of secondary isomeric octadecyl stearates is also formed in this reaction. It was shown that the isomerization of the octadecene occurs by a series of reactions involving direct esterification of the carboxylic acid by the octadecene followed by breakdown of the secondary ester to re-form acid and (isomerized) olefin.

By analogy with *cis*-9-octadecene studies it is suggested that, in the reaction of a monoethyleric fatty acid with aqueous 70% perchloric acid, migration of the double bond back and forward along the fatty acid chain occurs by a reversible intermolecular esterification of carboxylic acid by olefin, as illustrated by Scheme I.

A double bond on reaching the $\Delta^{4,5}$ position in the fatty acid chain will undergo an intramolecular carboxylic acid-olefin reaction, with formation of γ -



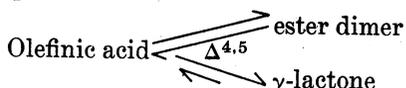
Scheme I



Scheme II

stearolactone. The lactonization mechanism (Scheme II) may be as suggested by Ansell and Palmer (12).

The heavy deuteration of γ -stearolactone products and octadecenoic acid by-products, and double bond distribution in octadecenoic acid by-products, is consistent with the proposed mechanism for double bond migration prior to lactonization:



Further supporting evidence is provided by some previous (1) observations using milder reaction conditions. The methylated (diazomethane) products from a reaction of oleic acid with aqueous 70% perchloric acid (1.0 to 1.0 molar ratio of fatty to inorganic acid) at 85 C for 1 hr were separated by countercurrent distribution. The products (weight per cent) obtained were polymeric hydroxy material (1.1%), lactones (39.1%), methyl octadecenoates (20.2%), dimer (33.7%) and trimer (5.9%). IR spectroscopy indicated that the dimer contained a C-O-C linkage; it was proposed that it was formed by the intermolecular addition of the carboxyl of one octadecenoic acid molecule to the double bond of another. The dimer was reacted further with aqueous 70% perchloric acid (1.0 to 2.0 molar ratio) at 85 C for 24 hr to give a 67% yield of γ -stearolactone.

It may be mentioned that when secondary octadecyl stearates (isolated from an octadecene-stearic acid-aqueous deuteroperchloric acid reaction mixture) were reacted (11) in a 100 C, 3 hr, reaction with a 1.0 molar ratio of aqueous deuteroperchloric acid

the products recovered were octadecyl stearates (26%), stearic acid (63.9%) and octadecenes (49.4%). In this system, of course, the equilibrium between olefin and ester cannot be disturbed by the possibility of lactone formation.

The 3 hr, 100 C reaction of *trans*-2-octadecenoic acid with aqueous 67% deuteroperchloric acid (1.0 to 1.0 molar ratio of reactants) is of interest in light of the proposed intermolecular carboxylic acid-olefin esterification mechanism of Scheme I. The recovered *trans*-2-enoic acid (87%) contained no detectable amount of deuterium; the γ -stearolactone product (5.7%) and a third product (1.5%, IR suggests estolide dimer) contained respectively 6.0 and 4.2 deuterium atom per molecule. The low yield of γ -lactone may be interpreted as due to α,β -unsaturation deactivating the carboxylic acid function or α -carboxyl deactivating the double bond.

Aqueous 70% perchloric acid reacted violently with stearolic acid; a 3 hr, 100 C reaction of 58% perchloric acid with stearolic acid produced a black, oily product. It is conceivable that intermolecular addition of carboxyl to triple bond produces a vinyl ester which then undergoes polymerization.

ACKNOWLEDGMENT

The Agricultural Research Service, in association with the National Academy of Sciences, National Research Council, provided a Resident Research Associateship for I. S. Shepherd. C. T. Leander and C. J. Dooley provided the infrared and mass spectra, respectively.

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[Received March 10, 1969]