Alkaline Cleavage of Hydroxy Unsaturated Fatty Acids and Derivatives. II. 10-Hydroxydecanoic Acid from Ricinoleates and 1,10-Decanediol from Ricinoleyl Alcohol

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Abstract

The 10-hydroxydecanoic acid is formed in good yield when raw castor oil or methyl ricinoleate is fused with alkali in the presence of a high-boiling unhindered primary or secondary alcohol at 185–195C bath temperature. When non-reducing solvents or hindered alcohols are used, large amounts of sebacic acid form. Iso-octanol (mixed isomers) is a suitable and potentially economical medium for producing high yields of 10-hydroxydecanoic acid. Cleavage of ricinoleyl alcohol produces 1,10-decanediol.

Introduction

WIDESPREAD APPLICATION of potentially useful 10-hydroxydecanoic acid has been restricted by lack of simple synthetic procedures. Most published methods are multistep, proceeding through either oxidation of undecylenic acid (1–9) or reduction of sebacic acid (10). Both starting materials are derived from castor oil in no greater than 70–85% yields (5,11–27). Several investigators report the preparation of 10-hydroxydecanoic acid directly from castor oil (11,14,15,19,28–32), but their reaction conditions and complex purification procedures give low over-all yields (<50%). Usually sebacic acid is the preferential product when castor oil or its derivatives are fused with alkali, but it has recently been found that 10-hydroxydecanoic acid predominates when the fusion is carried out in the presence of excess 2-octanol (33). Now means are reported for improving the isolated yield of 10-hydroxydecanoic acid which result from the direct alkaline cleavage of ricinoleic acid derivatives in the presence of certain high-boiling alcohols. The influence of some inorganic reducing agents also was investigated but resulted in no added yield improvement.

Experimental Section

Materials

Castor Oil. Raw castor oil, Baker AA(R), containing 89% ricinoleic acid, was used directly as received.

Methyl Ricinoleate. This ester was prepared, according to Swern and Jordan (34), by alcoholysis of castor oil, followed by fractional distillation of the mixed methyl esters under reduced pressure to give a product of >98% purity.

Ricinoleyl Alcohol. This diol was prepared by reducing methyl ricinoleate with lithium aluminum hydride in ethyl ether (35,36).

Diluents. The following solvents were used directly as received: 2-octanol (ketone-free), 1-octanol, benzyl alcohol, phenethyl alcohol, ethylene glycol, propylene glycol, 3-methylcyclohexanol, and decalin purchased from Eastman Kodak; iso-octanol (mixed isomers), isodecanol (mixed isomers), 2-ethylhexanol, diisobutyl carbinol, 1,5-pentanediol, 2,6,8-trimethyl-4-nonanol, and methyl carbitol supplied by the Union Carbide Company; 2-methyl-2-nonanol, cyclo-octanol, and 4-isopropylcyclohexanol purchased from the Aldrich Chemical Company; γ-phenylpropyl alcohol supplied by UOP Chemical Company; and dl-α-methylbenzyl alcohol purchased from the Matheson, Coleman, and Bell Company.

Analytical Techniques

Programmed-temperature, gas-liquid chromatographic analyses were run on an F & M Gas Chromatograph, Model 720 with a thermal conductivity detector. The column was 3-ft, 0.25-in. OD stainless steel packed with 10% ECNSS-S (Applied Science Laboratories Inc., State College, Pa.) on 100–120 mesh Gas-Chrom P.

A helium flow-rate of 50 ml per min with programming from 100–220C at 5C per min was used.

Cleavage of Castor Oil and Methyl Ricinoleate

Analytical-Scale Procedure. A 100-ml, thick-walled Pyrex glass reaction vessel was fitted with a stirrer, dropping funnel, and reflux condenser. The glass reactor was capable of withstanding five or six runs with concentrated caustic before etching became so extensive that further use was deemed unsafe. The reactor was charged with 24.0 ml of organic diluent, 1.8 ml of water, and 6.8 g of sodium hydroxide; the dropping funnel was charged with 6.5 g of methyl ricinoleate or castor oil. An electrically heated silicone oil bath was used to heat the reactor to 185–195C, and the ricinoleate then was introduced drop by drop. After all the reactants were added, the mixture was stirred at 185–195C for 12.5 to 13 hr longer. A 3-g portion of the mixture was dissolved in 20 ml of hot water, acidified to pH 1 with 50% aqueous sulfuric acid, and extracted with ether. The ether solution was dried with sodium sulfate, and the ether was removed on a rotary evaporator to yield an oily residue which was converted to mixed methyl esters in refluxing excess methanol with 0.5% of concentrated sulfuric acid. The resultant ester mixture was examined by GLC. Table I summarizes the data obtained in experiments by using different diluents.

Preparative-Scale Procedure. A one-liter nickel resin kettle and top were fitted with a twisted-blade stirrer (similar to Ace Glass Company, No. 9076), dropping funnel, and reflux condenser. The kettle was charged with 480 ml of octanol, 36 ml of water, and 136 g of sodium hydroxide; the dropping funnel was filled with 130 g of castor oil or 126.5 g of methyl ricinoleate. The temperature of the kettle was raised to 185–190C, and the ricinoleate was introduced drop by drop. After all the reactants were added, the mixture was stirred at 185–190C for 12.5 to 13 hr longer. At shorter reaction times, larger amounts of uncleaved ricinoleate remain. The solid pot charge was acidified with 180 ml of 50% aqueous sulfuric acid with water cooling to obtain a 2-layered liquid

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TABLE I

Alkaline Cleavage of Methyl Ricinoleate in the Presence of Organic Diluents[1,2,3]
(6.5 g of methyl ricinoleate, 6.8 g of sodium hydroxide, 1.8 ml of water, 24 ml of diluent, 185–195C, 12–13 hr)

Diluent	Percentage Composition of Crude Product			
	10-Hydroxydecanoic acid	Sebacic acid	Ricinoleic acid	Unidentified
1-octanol	82.6	16.5	0.5	0.4
2-octanol	80.0	11.0	0	9.0
iso-octanol	73.0	15.4	0	11.6
2-ethylhexanol	39.2	35.4	1.3	24.1
diisobutyl carbinol	53.0	34.0	6.3	6.6
isodecanol	62.0	28.6	4.8	4.8
2,6,8-trimethyl-4-nonanol	43.6	52.1	4.3	......
2-methyl-2-nonanol	18.7	75.0	6.3	......
decalin	31.0	55.0	14.0	......
decalin:2-octanol (1:1 solution)	53.0	33.0	14.0	
cyclo-octanol	63.0	22.8	3.2	11.0
3-methylcyclohexanol	67.0	3.0	22.0	8.0
4-isopropylcyclohexanol	15.6	24.4	6.7	53.3
phenethyl alcohol	14.0	31.0	51.0	4.0
α-methylbenzyl alcohol	15.0	20.0	12.0	53.0
1,5-pentanediol	34.8	3.5	15.7	46.1

[1] When ethylene glycol, propylene glycol, or methyl carbitol was used, the reaction resulted in a complex mixture with major unidentified components.

[2] When benzyl alcohol was used, a higher ratio of 10-hydroxydecanoic acid:sebacic acid resulted than the best result in the table, but the major component of the reaction mixture was benzoic acid.

[3] Use of γ-phenylpropyl alcohol also gave a high 10-hydroxydecanoic acid:sebacic acid ratio, but the major component was a single unidentified compound, probably resulting from decomposition of the alcohol.

mixture. The mixture was heated to boiling and transferred while hot to a 2-1. separatory funnel. The lower aqueous layer was withdrawn, and the upper organic layer was washed with 4 × 300 ml of boiling water. The organic solution was cooled to room temperature and dried with solid sodium sulfate. After removal of the drying agent, 1,500 ml of petroleum ether (90–100C) were added, and the slightly turbid solution was cooled to −23C overnight. The crystals were removed by filtration in the cold, washed with cold low-boiling petroleum ether, and dried in air to yield 45–56 g (69–74%) solid; mp 69–73C. Further purification can be accomplished by recrystallizing this product from benzene (8 ml/g) to obtain 41–45 g (62–67%) crystals; mp 72.5–75.0C (Lit. 75C).

Use of Solid Additives or Nonoxidizing Atmosphere. When analytical-scale runs were performed in 2-octanol with the addition of 5–300 mg of one of the following solids: sodium sulfite, sodium bisulfite, sodium hypophosphite, aluminum isopropoxide, stannous chloride, or triphenylphosphine; the proportion of 10-hydroxydecanoic acid was never greater than if the additive was omitted. Similarly, when the reaction was performed while bubbling in nitrogen or hydrogen, there was no improvement in the yield of the ω-hydroxy acid.

Cleavage of Ricinoleyl Alcohol

The apparatus described under analytical-scale procedure was used. The reactor was charged with 24.0 ml of 2-octanol, 1.8 ml of water, and 6.8 g sodium hydroxide; then 6.6 g of ricinoleyl alcohol were placed in the dropping funnel. After the oil bath was heated to 185C, the ricinoleyl alcohol was added drop by drop. After the addition of all reactants, the mixture was stirred at 176–183C for 12.5 hr. The hot mixture was transferred to a separatory funnel and washed with 6 × 20 ml boiling water. The alcohol solution was acidified with 50% aqueous sulfuric acid, washed with 4 × 20 ml hot water, and dried with sodium sulfate. After removal of the drying agent, 50 ml of petroleum ether (90–100C) were added, and the turbid solution was cooled to −23C overnight. The mixture was filtered cold. The solid was washed with low-boiling petroleum ether, then dried to yield 0.9 g of white product; mp 58–69C. Recrystallization three times from ether at 5C yielded white crystalline 1,10-decanediol; mp 70–72.5C (Lit. 72–74C). Calcd. for $C_{10}H_{22}O_2$; C: 69.0%, H: 12.6%, O: 18.4%. Found; C: 69.0%, H: 12.7%. The bis-N-phenylcarbamate of the diol (37) was prepared, according to Shriner, Fuson, and Curtin (38), by treating 100 mg of 1,10-decanediol with 137 mg of phenylisocyanate at 60C. The white solid mass was recrystallized twice from carbon tetrachloride to yield white crystals; mp 163–166.5C (Lit. 170C). Calcd. for $C_{24}H_{32}N_2O_4$; C: 69.9%; H: 7.8%, N: 6.8%, O: 15.5%. Found; C: 69.1%, H: 7.6%, N: 6.7%.

Discussion

On the basis of previously published results (33) and data presented herein, the following generalizations can be stated concerning the effectiveness of various media for enhancing terminal hydroxyl group formation in preference to carboxyl group during alkaline cleavage.

Aliphatic primary or secondary alcohols in the C_8 to C_{13} range are the most suitable reaction media. Aliphatic alcohols with branches α or β to their hydroxyl groups have reduced effectiveness apparently because of steric hindrance. Tertiary alcohols and phenylethyl alcohols are ineffective, owing to ease of dehydration in strong alkali at high temperatures (28). Glycols and polyether alcohols are unsuitable because of undesirable side-reactions with caustic. Benzyl alcohol and γ-phenylpropyl alcohol enhance ω-hydroxyl formation but are themselves converted to products that are difficult to separate from ω-hydroxy acid. Alicyclic alcohols are less effective than acyclic alcohols. Addition of solid or gaseous inorganic reducing agents, or inert atmosphere provides no added enhancement of ω-hydroxyl formation.

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