Dehydrogenation of Methyl 12-Hydroxystearate to Methyl 12-Ketostearate with Raney Nickel

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Abstract

Suitable conditions have been found for the dehydrogenation of methyl 12-hydroxystearate to methyl 12-ketostearate with Raney nickel. Crude reaction mixtures contained 95% product when analyzed by gas-liquid chromatography (GLC). Isolated yields were 83%. Both catalyst concentration and type strongly influence the reaction. Laboratory-made methyl 12-hydroxystearate gave significantly better yields than commercial material, but satisfactory conversions were obtained from citrate-free commercial material. The extent of the dehydrogenation was determined by hydrogen evolution and GLC. Synthetic and analytical techniques used in studying this reaction are discussed.

Introduction

OUR PREVIOUS STUDY of the conversion of methyl ricinoleate to methyl 12-ketostearate with Raney nickel demonstrated that this process occurs in steps; hydrogenation precedes dehydrogenation (1). Methyl 12-hydroxystearate was shown to be an intermediate, and 50 weight percent or more Raney nickel is required as a hydrogen source in the first step. Since hydrogenation of methyl ricinoleate to methyl 12-hydroxystearate at low catalyst levels is a common commercial practice, we investigated dehydrogenation of methyl 12-hydroxystearate to methyl 12-ketostearate with Raney nickel. Consecutive use of these two processes would provide a stepwise catalytic hydrogenation-dehydrogenation system of commercial promise.

Although various investigators have examined dehydrogenation of secondary alcohols with Raney nickel (2–5), this catalyst apparently has not been used for dehydrogenation of hydroxy fatty esters. We have determined the effect of catalyst concentration on yield. Raney cobalt and four types of Raney nickel were evaluated for this reaction. When various starting materials were evaluated, commercial methyl 12-hydroxystearate behaved differently than that made in our laboratory; conditions were determined which gave maximum conversion[2] of the commercial material.

Experimental

Starting Materials

Methyl 12-Hydroxystearate. The laboratory-made ester was prepared by hydrogenating distilled methyl ricinoleate (6). The product was recrystallized from Skellysolve B and melted 57.6–58.0C. Reported mp 57.5–58C (7). Two types of commercial methyl 12-hydroxystearate (methyl esters of hydrogenated castor oil) were evaluated, both provided by The Baker Castor Oil Company, Bayonne, N. J. Sample A contained 81% methyl 12-hydroxystearate by gas-liquid chromatography (GLC) as well as small amounts of very polar components as shown by thin-layer chromatography. The second, specially prepared, commercial material, sample B, contained 83% methyl 12-hydroxystearate. It was free of citric acid and contained less glycerine and monoglycerides than sample A.

Raney Nickel. Two commercial types and two laboratory-made Raney nickels were evaluated. Both commercial nickels were provided by W. R. Grace & Co., Raney Catalyst Division, Chattanooga, Tenn. and are designated "No. 28 Raney Active Nickel Catalyst in Water," and "No. 24 Raney Active Nickel Chromium Catalyst in Water." The latter is a chromium-promoted nickel catalyst. W-4 Raney nickel was prepared by the method of Adkins et al. (8) except that the catalyst was washed with and stored under tap water. The other laboratory-made Raney nickel was prepared by the same method (9) used for the commercial Raney nickel and will be called "commercial type Raney nickel."

Raney Cobalt. This catalyst, labeled "No. 27 Raney Active Cobalt Catalyst in Water," was also provided by W. R. Grace & Co.

Gas-Liquid Chromatography

The reaction was followed initially by connecting the reaction flask to a wet test meter and observing gas evolution. When the gas evolution became very slow or ceased, samples were taken from the reaction mixture for GLC analysis. The reaction was considered complete when GLC indicated little or no starting material peak was present. GLC instrumentation was described earlier (1). Three types of packed columns were used: 1) 8 ft, ⅛ in., aluminum or stainless-steel columns containing 15% diethylene glycol succinate (DEGS) on 60–80 mesh Gas-Chrom P at 232–238C with a helium flow of 30 ml/min and a filament current of 200 ma; 2) 8 ft or 3 ft, ⅛ in., aluminum or stainless-steel columns packed with 7% polyethylene glycol succinate on 70–80 mesh, acid-washed dimethyldichlorosilanized (AW-DMCS), Chromosorb G used at 231C, helium flow 90 ml/min; 3) 3 ft, ⅛ in., stainless-steel columns containing 5% Carbowax 20 M on 70–80 mesh, hexamethyldisilazanized (HMDS), Chromosorb W used at 210C, helium flow 50 ml/min. The last two columns gave adequate resolution of starting material and product and were more stable to heat than the DEGS column. Samples of the reaction mixture were diluted to a 10% solution with chloroform and injected directly onto the columns.

Reaction Procedure

A typical reaction was run as follows: A tared 50-ml Ace "Mini-Lab" reaction flask was charged with 12.0 g of methyl 12-hydroxystearate and 3.0 g of moist Raney nickel. The flask head was fitted with a mechanical stirrer, thermometer, inlet tube for nitrogen and outlet tube which led first to a small trap and then to the wet test meter. The system was flushed with nitrogen for about 10 min, and the inlet opening

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[2] Conversion as used throughout this paper refers to the uncorrected area under the methyl 12-ketostearate curve relative to the total area as determined on crude reaction mixtures by GLC.

TABLE I

Effect of Catalyst Concentration on Yield [a]

Wt % catalyst	Time, hr	Temp, °C	Conversion, % (GLC)	Product [b] yield, %	Melting point, °C
50	0.68	181–214	> 95	77	46.5–47.0
25	0.85	177–219	> 95	83	47.0–47.2
12.5	1.10	188–233	95	77	46.8–47.0
5	1.66	195–222	95	78	46.8–47.0
1	1.5	191–250	85	62	46.2–47.0

[a] Moist commercial Raney nickel was used with 12.0 g of laboratory-made methyl 12-hydroxystearate.

[b] Once-recrystallized product.

was then stoppered. The contents of the flask were heated until the starting material melted, and then stirred vigorously. Good contact between catalyst and starting material is essential for maximum yield. The temperature was kept at 171–219C for 51 min at which point hydrogen evolution ceased and GLC showed greater than 95% conversion of starting material to product. The mixture was cooled to ca. 50C, treated with ether, and filtered through Celite on a sintered glass funnel. The filtrate was concentrated on the steam bath under a stream of nitrogen. The solid product was recrystallized from methanol to yield 9.9 g (83%) methyl 12-ketostearate, mp 47.0–47.2C; reported mp (10) 45.3–46C. GLC showed this product contained 98.6% methyl 12-ketostearate. From the mother liquor an additional 1.9 g (16%) of impure product was obtained, mp 42.6–43.0C.

Results and Discussion

Effect of Catalyst Concentration on Yield

Table I shows the variations in the yield of product as the concentration of Raney nickel was decreased. Fifty weight percent catalyst was the lowest satisfactory catalyst concentration with methyl ricinoleate (1), so we began these experiments at that concentration. Even at this level the yield from methyl 12-hydroxystearate (77%) was greater than the 60% from methyl ricinoleate (1). Only with less than 5% catalyst did the product yield begin decreasing, and with 1% catalyst, the yield was still superior to the 60% from methyl ricinoleate. Raney nickel is probably more efficient with methyl 12-hydroxystearate because it has only to catalyze dehydrogenation, which it apparently does quite efficiently. With methyl ricinoleate, hydrogenation must be catalyzed first. As previously shown (1), the hydrogen must come from the Raney nickel itself; the loss of this hydrogen may reduce the activity of the catalyst. The methyl 12-hydroxystearate thus formed must then be dehydrogenated in the presence of the now somewhat deactivated catalyst. The result is less conversion, higher by-product formation and lower yield. Thus, starting with methyl 12-hydroxystearate rather than methyl ricinoleate, better yields of methyl 12-ketostearate can be obtained with much less catalyst.

TABLE II

Effect of Catalyst Type on Conversion [a]

Catalyst type	Time, hr	Temp, °C	% of Compounds by GLC		
			Product	Starting material	By-product [b]
Commercial Raney Ni	1.5	191–250	85	15	0
Chromium-promoted Raney Ni	3.0	191–262	89	11	0
Raney cobalt	1.0	250–300	55	0	45
W-4 Raney Ni	3.2	191–302	30	10	60
Commercial type Raney Ni	2.4	240–260	56	24	24

[a] 1.0% of catalyst was used with 12.0 g of laboratory-made methyl 12-hydroxystearate.

[b] The by-product is probably a mixture of dehydration and hydrogenolysis products (cf Ref. 1).

TABLE III

Dehydrogenation of Commercial Methyl 12-Hydroxystearate [a]

Starting material	Wt % comm Raney Ni	Time, hr	Temp, °C	% of Compounds by GLC [b]		
				Product	Starting material	By-product
Sample A	1	1.2	250	44	14	42
Sample A	5	2.5	250	63	6	31
Sample A	10	1.2	250	73	0	27
Water washed Sample A	5	1.5	250	54	33	13
Sample A	10	2.0	200 [c]	50	0	50
Sample A	10	5.5	170 [c]	80	18	2
Sample B	10	1.0	245–262	95	0	5
Sample A	10	1.0	245–262	69	0	31

[a] Moist commercial Raney nickel was used with 12.0 g of starting material.

[b] Adjusted for the amount of methyl 12-hydroxystearate present in the starting material.

[c] Nitrogen atmosphere.

Effect of Catalyst Type on Conversion

Of the four types of Raney nickel previously investigated with methyl ricinoleate, W-4 was the most effective, commercial Raney nickel was satisfactory, and W-6 and W-7 were unsatisfactory (1). To determine which catalyst was most effective for the dehydrogenation of methyl 12-hydroxystearate, four types of Raney nickel were evaluated in addition to Raney cobalt. Each catalyst was run at 1% concentration for comparison with commercial Raney nickel which had given an 85% conversion of starting material to product at this level. The results are shown in Table II. Only chromium-promoted Raney nickel was better than commercial Raney nickel; the others gave unsatisfactory conversions. Although W-4 was the best catalyst with methyl ricinoleate, it was the least effective with methyl 12-hydroxystearate.

To see if W-4 was more active at a higher concentration, the reaction was also run with 12.5% catalyst. The 70% conversion thus obtained was still unsatisfactory compared to the 95% conversion with 12.5% commercial Raney nickel. Since this W-4 catalyst was used within 8 days of its preparation, catalyst age apparently was not a factor. However, this W-4 catalyst was more effective than commercial Raney nickel when used in systems similar to those described in reference 1. Thus it appears that W-4 is best for the hydrogenation-dehydrogenation reaction, but commercial Raney nickel is best for the dehydrogenation reaction alone. The slight increase in conversion noted with the chromium-promoted Raney nickel probably resulted from longer reaction time.

Since the commercial Raney nickel used in these experiments was at least 7 months old, we prepared fresh commercial type Raney nickel and evaluated it for increased activity. It was less active (56% conversion) than older preparations. Assuming that the commercial and commercial type Raney nickels were prepared in the same way, this result suggests that an older catalyst may be more effective than a fresher catalyst for this reaction. This possibility was not explored further. Raney cobalt is obviously inferior for this dehydrogenation.

Dehydrogenation of Commercial Methyl 12-Hydroxystearate

Sample A was first run with 1% catalyst for direct comparison with the 85% conversion obtained with the laboratory-made methyl 12-hydroxystearate at the same catalyst concentration. Considerably less product was formed (Table III). Five and 10% catalyst did not improve conversion satisfactorily. We suspected that glycerine possibly present in sample A might be partially poisoning the catalyst, since glycerine has been reported to be a nickel catalyst poison (11). A portion of sample A was washed with hot water to remove glycerine, but (Table III) by-product formation was still high and conversion low. We tried to reduce side reactions by lowering the temperature to 200C and by using a nitrogen atmosphere, but this attempt was unsuccessful. Although by-product formation was quite low at 170C under nitrogen, conversion rate at this temperature was very slow. If the reaction had been allowed to go to completion, the conversion might have been satisfactory.

Correspondence with the supplier of sample A revealed that this methyl 12-hydroxystearate contained citric acid, used to remove traces of nickel catalyst after hydrogenation of the castor esters. Since citric acid is known to poison nickel catalysts (11), we obtained purified commercial hydrogenated esters (sample B) which contained no citric acid. This purified material gave a 95% conversion to product (Table III) as well as a 91% crude yield. In contrast, the regular methyl 12-hydroxystearate (sample A) under identical conditions gave only a 69% conversion. Although these results implicate citric acid as a catalyst poison in these reactions, the lower glyceride content of sample B may also be at least partially responsible for its better performance. The high conversion and yield from sample B show that methyl 12-ketostearate can be prepared by low cost, catalytic dehydrogenation with Raney nickel from commercial as well as laboratory-made methyl 12-hydroxystearate.

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