Catalytic Dehydrogenation of Methyl 12-Hydroxystearate to Methyl 12-Ketostearate[1]

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Abstract

Economically attractive catalytic methods for the conversion of methyl 12-hydroxystearate to methyl 12-ketostearate have been developed on a laboratory scale. With 1.0 wt% copper chromite catalyst, pure methyl 12-hydroxystearate is dehydrogenated at 180–263C to methyl 12-ketostearate in 99% yield and 97% purity. Commercial methyl 12-hydroxystearate required 3% catalyst but gave a 98% conversion to product and 100% crude yield.

Introduction

We have shown that methyl 12-hydroxysteaate can be dehydrogenated to methyl 12-ketostearate by the use of catalytic amounts of Raney nickel (1). Another catalyst that appears suitable for this dehydrogenation is copper chromite. This catalyst has several advantages compared to Raney nickel. It is less expensive on a weight basis, is nonpyrophoric, is less easily poisoned, and is an easily handled solid. Copper chromite should therefore be more economical and convenient than Raney nickel.

The literature contains several examples of the dehydrogenation of secondary alcohols to ketones by copper chromite catalysis (2–5), but this catalyst has apparently not been used in the dehydrogenation of hydroxy fatty esters. We have investigated this reaction to determine the influence of such parameters as catalyst type and concentration, starting material type, scale, and other factors. We also studied this process for the dehydrogenation of methyl ricinoleate, methyl ricinelaidate, and hydrogenated castor oil.

Experimental

Starting Materials

Methyl 12-Hydroxystearate. Four types of this ester were evaluated. Samples A, B, and C have been previously described (1). Sample A was commercial methyl 12-hydroxystearate. Sample B was commercial material which contains no citric acid and less glycerine than sample A. Sample C was laboratory-made material. Sample D was obtained by distilling sample B with a 3-ft, heated, Vigreux column; bp 206–210C/0.040 mm, mp 57.8–58.0C. The methyl 12-hydroxystearate content of sample D was 99% by gas-liquid chromatography (GLC).

Methyl Ricinoleate. This ester was prepared by base-catalyzed alcoholysis of castor oil and purified by fractional distillation of the mixed methyl esters under reduced pressure (6).

Methyl Ricinelaidate. Methyl ricinoleate was isomerized according to McCutcheon et al. (7), and the product had mp 29.0–29.2C. Reported (7) 28.5–29.8C.

Hydrogenated Castor Oil. This material was provided by the Baker Castor Oil Company, Bayonne, New Jersey.

Catalysts. The two copper chromite catalysts, Cu-1106 P and Cu-1800 P, and the copper carbonate catalyst Cu-2501 G4-10, were provided by the Harshaw Chemical Company, Cleveland, Ohio. Cu-1106 P contains barium, but Cu-1800 P does not. The copper carbonate catalyst contains 6% copper as copper carbonate mounted on a silica support. We ground it to a fine powder for better mixing.

Gas Liquid Chromatography

The GLC instrumentation (8) and columns (1) used were previously described.

Reaction Procedure

Methyl 12-Hydroxystearate. In general, the procedure described earlier (1) was employed. Benzene rather than ether was used during filtration because the copper chromite catalysts are somewhat soluble in ether but not in benzene. Where GLC indicated 95% or better product formation, products of satisfactory purity were obtained, without recrystallization, by simply removing the benzene from the filtered reaction mixture. Maximum yields were obtained by vigorous stirring, limited exposure to air, and avoidance of prolonged heating of the reaction mixtures. Specific examples are discussed below.

Methyl Ricinoleate. A mixture of 12.0 g of this ester and 0.360 g (3%) Cu-1106 P was heated 23 min at 220–300C with stirring. The mixture was then cooled to room temperature, 7% more catalyst was added, and heating was continued for an additional 47 min at 295–320C.

Methyl Ricinelaidate. Twelve grams of this ester and 1.2 g Cu-1106 P were first heated with stirring for 18 min at 269–310C. The mixture was cooled to room temperature, saturated with hydrogen during the remainder of the run, and heated with stirring an additional 32 min at 294–300C.

Hydrogenated Castor Oil. Two runs were made. In the first, 36.0 g of starting material and 3.6 g of Cu-1106 P were heated 30 min at 325C. The second run was made with 50% catalyst for 2 hr at 252–320C.

Results and Discussion

Dehydrogenation of Methyl 12-Hydroxystearate

Catalyst Type. Runs were first made to determine which of the three catalysts was most effective for this dehydrogenation reaction. The supplier indicated that barium in a catalyst such as Cu-1106 P (10% as BaO), stabilizes copper chromite for hydrogenation, but unstabilized copper chromites, such as Cu-1800 P are preferred for dehydrogenation (9). The copper carbonate catalyst, Cu-2501 G4-10, is used to effect the dehydrogenation of alcohols to aldehydes and ketones (9). The results we obtained with these catalysts are shown in Table I, runs 1–3. Each catalyst was used under similar conditions. Although the two copper chromite catalysts gave about the same reactant conversion, 70% by-product formed with the copper carbonate catalyst. Thus far it appeared the activities of the two copper chromite catalysts were

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TABLE I

Dehydrogenation of Methyl 12-Hydroxystearate

Run No.	Catalyst type	Wt % catalyst	Starting material		Time, hr	Temp, °C	% of Compounds by GLC[a]			Yield,[c] %	mp, °C
			Sample	Quantity, g			Product	Starting material	By-product[b]		
1	Cu-1106 P	2	A	12	0.50	220–309	75	8	17	(87)	....
2	Cu-1800 P	2	A	12	0.37	235–300	76	20	4	....	....
2A	Cu-1800 P	1	A	....	0.35	300	68	0	32	....	....
3	Cu-2501	2[d]	A	12	0.68	290–310	30	0	70	....	....
4	Cu-1106 P	3	A	12	0.50	251–313	98	1	1	(100) 87[a]	.... 43.5–44.0
5	Cu-1800 P	3	A	12	0.58	239–301	100	0	0	(98) 68[a]	.... 43.5–44.0
6	Cu-1800 P	1	B	12	1.2	285–310	71	20	9	(100)	....
6A	Cu-1800 P	1	B[e]	....	0.75	300	66	0	34	....	....
7	Cu-1800 P	2	B	12	0.72	262–290	88	0	12	(97) 68[a]	.... 46.0–46.1
8	Cu-1106 P	1	C	12	0.62	180–263	97	3	0	(99)[f]	46.1–46.8
9	Cu-1800 P	1	C	12	0.50	180–285	97	3	0	(99)[f]	46.0–46.8
10[g]	Cu-1800 P	10	C	12	0.27	220–257	95	5	0	....	....
10A[g]	....	....	....	....	1.0	257–314	75	0	25	57	46.0–46.5
11	Cu-1106 P	1	D	12	1.38	249–265	92	8	0	75	46.8–47.0
12	Cu-1106 P	3	D	100	1.28	228–268	96	4	0	88	46.9–47.1
13	Cu-1106 P	3	D	150	2.50	230–281	96	4	0	86	46.0–47.5
14[h]	Cu-1106 P	3	D	150	3.50	237–302	....	....	....	45	45.0–46.0
15[i]	Cu-1106 P	6	D	150	5.83	228–311	30	0	70	....	....

[a] Adjusted for the amount of methyl 12-hydroxystearate in samples A and B: sample A, 81% (GLC); sample B, 83% (GLC).
[b] The by-product is probably a mixture of hydrogenolysis and dehydration products.
[c] Yields in parentheses are crude yields. Other yields were obtained after one recrystallization.
[d] The amount of catalyst used was adjusted to give the equivalence of 2%.
[e] Sample B in this case was the filtered reaction mixture from run 6.
[f] These products contained 97% methyl 12-ketostearate by GLC.
[g] Run 10 is the first stage of heating, run 10A the second stage of heating.
[h] Stirring was inadequate in this run, and H_2 evolved was 83% of that expected.
[i] The hot reaction mixture was exposed to air.

about equivalent, but the copper carbonate catalyst was considered unsuitable for this reaction.

In run 2A we tried to convert the remaining 20% starting material from 2, but the amount of product decreased and the amount of by-product increased. Runs 6 and 6A gave similar results. Apparently, addition of catalyst is not helpful when reaction is incomplete.

Relationship Between Catalyst Concentration and Type of Starting Material. In the runs just discussed, sample A was not completely converted to product with 2% catalyst. As shown in runs 4 and 5, with either 3% of Cu-1106 P or Cu-1800 P conversion was essentially complete, and the catalysts were about equivalent in effectiveness. In contrast, the same type of starting material and 10% Raney nickel gave only an 80% conversion (1). These results indicate that the copper chromite catalysts are much less susceptible to poisoning by impurities in commercial methyl 12-hydroxystearate than is Raney nickel. Copper chromite catalysts also give high conversions at lower catalyst concentrations than Raney nickel. Since commercial methyl 12-hydroxystearate can be quantitatively converted to methyl 12-ketostearate at this low catalyst level and the product quantitatively recovered, this process should be economically attractive. Methyl 12-ketostearate was isolated in 87% yield (run 4) and 68% yield (run 5) from these crude products. However, by starting with distilled methyl 12-hydroxystearate from commercial material (sample D) better yields of pure methyl 12-ketostearate were obtained.

Because the second commercial material, sample B, contained fewer impurities than sample A, an attempt was made to catalyze the dehydrogenation of sample B with only 1% catalyst. As shown in run 6, conversion was only 71%, and an attempt to convert the remaining starting material (run 6A) with an additional 1% catalyst was unsuccessful. Since 2% catalyst (run 7) gave only 88% product, apparently 3% catalyst was required for complete reaction of sample B. Thus samples A and B behaved similarly when dehydrogenated in the presence of copper chromite but behaved very differently in the presence of Raney nickel (1).

Runs 8 and 9 demonstrate that laboratory-made methyl 12-hydroxystearate can be converted almost completely with only 1% catalyst. Because of this high conversion, the product was isolated in 99% yield and 97% purity without recrystallization. The high yield and simplicity of this process make it preferable to the chromic acid oxidation of methyl 12-hydroxystearate from which methyl 12-ketostearate has been obtained in 70% yield (10). Because the two copper chromite catalysts showed no significant difference in the runs in which they were compared, they were considered equally effective for this reaction.

Runs 10 and 10A exemplify the undesirability of heating the mixture beyond completion of the reaction. After the first stage of heating (run 10), GLC indicated 95% of the starting material was converted to product. While confirmation for this conversion was being sought, heating was continued (run 10A). At the end of this time, 20% of the product had converted to by-product. Less by-product formation might be expected with 1% than 10% catalyst under the same conditions.

Distilled methyl 12-hydroxystearate from commercial material (run 11) did not dehydrogenate as satisfactorily as laboratory-made methyl 12-hydroxystearate (run 8). Nevertheless, pure methyl 12-ketostearate was obtained in higher yield by the use of sample D than samples A or B.

Scale of Reaction. The dehydrogenation was next run with 100 g of starting material (rather than 12 g) to determine whether comparable yields could be obtained with the larger-scale reaction. Because the 12 g-scale reaction seemed to be exothermic, it was also necessary to determine whether the 100 g-scale reaction would be excessively exothermic. To insure a more complete reaction, 3% rather than 1% catalyst was used with sample D. As shown in run 12, the reaction was equally successful on the larger scale. Hydrogen evolution was smooth and there was no difficulty with temperature control. In run 13, 150 g of sample D gave essentially the same results.

Runs 14 and 15 illustrate reactions that were improperly conducted. In run 14, inadequate stirring slowed the reaction, and lowered the yield. Run 15 was undertaken to determine how 6% rather than 3% catalyst would influence the reaction. Inadvertent exposure of the hot reaction mixture to air apparently deactivated the catalyst, since very little gas evolution was observed after this. Even after an additional 6% catalyst was added to this cooled mixture, and the contents reheated, only a very slow conversion of starting material to by-product was observed. This behavior suggests that the oxidized products function as a catalyst poison, and/or the deactivated catalyst alters the course of the reaction.

Attempted Dehydrogenation of Methyl Ricinoleate, Methyl Ricinelaidate and Hydrogenated Castor Oil

Methyl Ricinoleate. The products expected from the dehydrogenation of this ester are methyl 12-ketooleate and/or methyl 12-ketostearate. We had previously prepared methyl 12-ketooleate (8), and subsequently found that this compound could be separated from methyl 12-ketostearate by GLC with an 8-ft, ⅛-in., column packed with 10% FFAP (Wilkens Instrument and Research, Inc.) on 70–80 mesh, AW-DMCS, Chromosorb W, used at 230C, 50 ml/min helium flow. When methyl ricinoleate was heated with 3% catalyst under conditions which gave substantial dehydrogenation of methyl 12-hydroxystearate, no reaction occurred. This was ascertained both by the absence of gas evolution and by GLC which showed only starting material. Further heating with 7% catalyst resulted in a slow distillation of an unknown liquid which appeared (GLC) to contain approximately 30% 12-hydroxystearyl alcohol, 30% dehydration and hydrogenolysis products, 22% methyl ricinoleate, 18% methyl 12-ketostearate, but no methyl 12-ketooleate. The reaction mixture contained an equal proportion of starting material and dehydration-hydrogenolysis products. Apparently these forcing conditions favor dehydrogenation less than other reactions. Possibly the double bond in the 9-position of methyl ricinoleate forms a pi complex with the catalyst, and this complex strongly retards the dehydrogenation reaction. With methyl 12-hydroxystearate such a complex is not possible.

Methyl Ricinelaidate. It seemed possible that because of the difference in stereochemistry between methyl ricinoleate and methyl ricinelaidate the latter compound might dehydrogenate satisfactorily. However, when methyl ricinelaidate was heated with 10% catalyst, very little hydrogen evolved, and GLC showed that practically no reaction had occurred. In the second stage of the heating, hydrogen was bubbled into the reaction mixture in an attempt to saturate the olefinic group and thus promote dehydrogenation. This attempt was not successful. The mixture of products formed was similar to that observed with the methyl ricinoleate reaction.

Hydrogenated Castor Oil. Gas evolution indicated this material dehydrogenated only slightly when heated with 10% catalyst. With 50% catalyst, gas evolved slowly. Water distilled from the reaction flask, which indicates that dehydration had occurred. This was confirmed by IR analysis; the crude product contained *trans* unsaturation (10.3 μ) and little hydroxyl absorption. The crude product was mostly intractable and was assumed to be polymeric when base-catalyzed methanolysis failed to solubilize most of the reaction mixture. The small amount of esters obtained showed very little methyl 12-ketostearate present by GLC and thin-layer chromatography. Steric effects may prevent effective approach of the bulky triglyceride to the catalyst surface.

We have shown that the saturated hydroxy fatty ester, unlike the unsaturated hydroxy fatty ester or saturated hydroxy glyceride derived from castor oil, can be readily dehydrogenated to the corresponding keto fatty ester. This process should be of commercial interest because it uses low levels of inexpensive catalysts, is simple, and converts starting material to product almost quantitatively. A continuous rather than batch system would make this process even more economically attractive.

REFERENCES

1. Freedman, B., and T. H. Applewhite, JAOCS *43*, 125–127 (1966).
2. Halasz, A., J. Chem. Educ. *33*, 624–625 (1956).
3. Dunbar, R. E., and M. R. Arnold, J. Org. Chem. *10*, 501–504 (1945).
4. Dean, F. (Imperial Chemical Industries), U.S. 2,746,993 (1956).
5. Winans, C. F. (Wingfoot Corp.), U.S. 2,218,457 (1940).
6. Swern, D., and E. F. Jordan, Jr., Biochem. Prep. *2*, 104–105 (1952).
7. McCutcheon, M. A., R. T. O'Connor, E. F. Dupre, L. A. Goldblatt and W. G. Bickford, JAOCS *36*, 115–118 (1959).
8. Freedman, B., J. S. Nelson, R. G. Binder and T. H. Applewhite, Ibid. *42*, 340–344 (1965).
9. Harshaw Catalysts, Catalog 100, The Harshaw Chemical Company, 1962, p. 18.
10. Calderon, R., H. P. Dupuy, E. R. McCall, R. T. O'Connor and L. A. Goldblatt, JAOCS *37*, 132–136 (1960).

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