Hydrogenation of Triple Bonds to Double Bonds in Conjugated Methyl Octadecadiynoate and Methyl Santalbate[1]

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ABSTRACT

A study was made of the noncatalytic hydrogenation of acetylenic bonds in fatty esters to *cis* double bonds using various metals in different solvent systems. The best results were obtained with 15% propanol in water using iron. The yields of *cis* double bonds for the nonconjugated diynoate and monoynoate ranged from 90% to 99% and for the conjugated diynoate the yields ranged from 56% to 77%. In the reduction of methyl santalbate to a conjugated diene, the yields were ca. 85%.

INTRODUCTION

The work previously reported (1) on the noncatalytic hydrogenation of acetylenic bonds to double bonds described the results obtained by using powdered zinc and 50% *n*-propanol and water solution as the reducing agent. The study has been expanded to include a variety of metals such as aluminum, iron and zinc, with varying concentrations of acetic and propionic acids in water and in water alone. These metals plus chromium and cobalt were also studied in 15% *n*-propanol.

In the present study the hydrogenation procedures were varied to determine optimum conditions for reduction of conjugated octadecadiynoates to the corresponding *cis,cis*-octadecadienoates. Similarly, in the hydrogenation of methyl santalbate (methyl *trans*-11-octadecen-9-ynoate), the desired product was methyl *cis*-9, *trans*-11-octadecadienoate. In addition, methyl 6-octadecynoate and methyl 7,10-hexadecadiynoate were reduced to their respective olefinic esters.

EXPERIMENTAL PROCEDURES

Materials

The synthesis of the conjugated diynoic acids has been described (2). The nonconjugated 7,10-hexadecadiynoic acid, starting with 1-heptyne and 7-octynoic acid, was prepared according to the method of Osbond et al. (3). The 6-octadecynoic acid was a commercial product. The santalbic acid (4) was prepared from *Santalum album* seeds and purified by crystallization from acetone at -20 C.

The methyl esters of the ynoic acids were prepared by the procedure for acid-catalyzed esterification of fatty acids (5).

Powdered metals were used in all the hydrogenations with water or aqueous propanol. In acid solvents large lumps were formed by powdered metals during hydrogenation. Therefore a granular form (20-40 mesh) was used for all metals except iron, which was 100 mesh or finer.

Procedures

In general the hydrogenation procedures differed only in the composition of the hydrogenation mixtures. A typical procedure is described.

To a 0.1 g sample of the methyl ynoate in a 250 ml round-bottomed flask were added 50 ml of 15% *n*-propanol and water solution (v/v) and 10 g powdered iron (100 mesh and finer). The flask was connected to a condenser and the contents heated to reflux temperature (93 C) on a sand bath.

The course of the hydrogenation was followed by removing 50-100 mg of the powdered metal from the reaction mixture and extracting with ethyl ether on a suction filter. At low concentrations of organic solvents, practically all the fatty sample was absorbed on the powdered metal. The metal was readily removed from the reaction flask by means of a glass rod flattened at the end and bent at an angle of ca. 110 °. Metal spatulas were avoided to prevent contamination with other metals.

The ether filtrate was washed with dilute hydrochloric acid and water. The ether was evaporated, and the sample was then dried on a hot water bath with a stream of nitrogen. A portion of the dried sample was used for analysis by gas liquid chromatography (GLC), and another portion was dissolved in hexane for UV analysis. The conditions for GLC analysis were the same as previously reported (1).

Reduction of the methyl santalbate was easily followed by GLC, since the reduction of the triple bond of this compound yields a *cis, trans* diene which is readily separated from the yne, *trans*-ene ester. Likewise the products from nonconjugated methyl ynoates were easily separated. The separation of the products from the reduction of conjugated diynoates presented a problem. The intermediate product, yne, *cis*-ene ester, and the final product, *cis, cis* diene ester of 8,10- and 9,11-diynoates, could be partially separated and quantitated on the GLC column. Similar products from the reduction of 6,8- and 7,9-diynoates had essentially the same retention on the GLC column and were not separated, so UV spectrophotometry was used to follow the reaction.

The changes in UV absorption between 225 mμ and 240 mμ with the extent of hydrogenation of conjugated octadecadiynoate are shown in Figure 1. At the beginning of the hydrogenation the starting material had a weak absorption at 226 mμ and is not shown in the Figure. As yne, *cis*-ene ester was formed, a strong absorption appeared

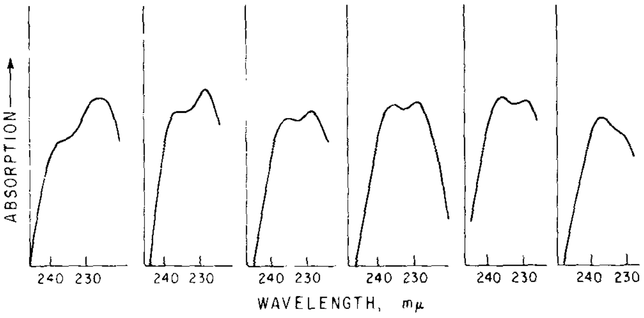

FIG. 1. A series of UV absorption spectra, showing the changes in absorption of conjugated methyl octadecadiynoate during hydrogenation to octadecadienoate. The first curve on the left is the spectrum after some yne, *cis*-ene had formed.

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TABLE I

Hydrogenation of 0.1 g Methyl Santalbate with Metals in 50 ml, 15% *n*-Propanol Solutions

Metal	Heating, hr[a]	Gas liquid chromatographic analyses, %			
		yne,*trans*-ene	*t,t*-[b] diene	*c,t*-[b] diene	monoene
Chromium, 10 g	22	52.2	3.7	31.4	8.3
Aluminum, 10 g	22	40.7	2.1	45.3	11.8
Cobalt, 5 g	7.5	30.2	9.7	54.8	5.3
Zinc,[c] 15 g	22	34.1	0.5	64.8	6.0
Zinc,[d] 15 g	22	71.2	0.8	26.8	1.1
Iron, 15 g	7[e]	1.6	1.0	85.5	11.9
Iron, 10 g	0.75	16.4	1.4	75.2	6.5
Iron, 10 g	1	1.2	4.0	85.7	9.0
Iron, 10 g	1.25	0.2	2.3	86.5	10.0
Iron, 10 g	1.5	0.0	2.5	85.8	11.6

[a] At reflux temperature, 93 C.
[b] *t,t* = *trans, trans-* ; *c,t* = *cis, trans-*.
[c] Practical, 92.3% zinc.
[d] 99+% Zinc.
[e] Temperature, 70 C.

at 228 mμ. Another peak appeared at 235 mμ as the concentration of *cis, cis* diene increased with further hydrogenation. Finally as the desired degree of reduction was attained, a single maximum remained at 235 mμ. The shoulder seen in the final curve in Figure 1 is indicative of a minor quantity of yne, *cis*-ene ester remaining in the mixture.

A similar UV scan was made during hydrogenation of methyl santalbate to determine quickly the extent of reduction that had taken place. The shift of absorption from 229 mμ to 233 mμ resulted from reduction of the yne, *trans*-ene group to conjugated *cis, trans* diene.

RESULTS AND DISCUSSION

Iron, of all the metals tested in 15% *n*-propanol and water solutions, had the highest activity and selectivity in the reduction of acetylenic bonds to *cis* double bonds. In general the action of acetic and propionic acids on metals showed high activity but lacked sufficient specificity for our purpose.

The data in Table I shows that iron in 15% *n*-propanol reduced methyl santalbate to high yields of *cis, trans* diene in much shorter time than did any of the other metals tested. Although chromium, aluminum and cobalt in 15% *n*-propanol hydrogenated only 50-70% of the sample, a relatively large amount of the undesired *trans, trans* diene and monoene esters was produced. Zinc also reacted slowly, but the hydrogenated product contained considerably smaller amounts of the *trans, trans* diene and monoene esters.

Reductions in which the only variable was time indicated that more complete hydrogenations cause more monoene to be formed. For example, in Table I, iron reacted for 45 min produced a total of ca. 6.5% monoene, while after 1.5 hr reaction a total of ca. 11.5% was produced. This suggests that the desired product could be more easily pruified if the hydrogenation was terminated while a considerable amount of the starting material was still present. The acetylenic compounds can be readily crystallized from a number of solvents which would then leave the desired product relatively pure.

In the hydrogenation of the conjugated diyne compounds reported in Table II, the hydrogenations were stopped when the UV scan indicated that all or nearly all the yne, *cis*-ene compounds had been eliminated. Hydrogenation of the 9,11-diynoate ester yielded 16.2% of the intermediate yne, *cis*-ene compound after 2 hr of heating, but only 1.8% after 4 hr of heating. For a 5% increase in yield of *cis, cis* diene, 8% of *cis, trans* diene and monoene esters were produced. Hydrogenation of the nonconjugated methyl hexadecadiynoate was much simpler, yielding 89.8% methyl *cis*-7, *cis*-10-hexadecadienoate; the methyl monoynoate yielded 99.6% methyl *cis*-6-octadecenoate. Determinations of isolated trans by IR indicated that little or none was present in either ester.

TABLE II

Hydrogenation of Various Methyl Ynoates with 10 g Iron in 50 ml, 15% *n*-Propanol Solution

Methyl ester	Heating, hr[a]	Gas liquid chromatographic analyses, %						
		diyne	*t,t*-[b] diene	yne, *cis*-ene	*c,c*-[b] diene	*c,t*-[b] diene	unidentified	monoene
6,8-Octadecadiynoate	6	0.0	0.4	0.0[c]	75.9	8.3	2.2	13.2
6,8-Octadecadiynoate	6.5	0.0	0.0	0.0[c]	77.1	7.5	1.7	13.7
7,9-Octadecadiynoate	6.5	0.0	0.5	0.0[c]	71.3	10.4	2.3	15.4
8,10-Octadecadiynoate	3	0.0	0.0	1.3	65.2	12.2	0.0	21.2
9,11-Octadecadiynoate	2	0.0	Trace	16.2	55.9	8.9	1.7	17.2
9,11-Octadecadiynoate	4	0.0	0.0	1.8	61.1	12.5	1.0	21.7
7,10-Hexadecadiynoate[d]	4	1.4	0.0	0.0	89.8	0.0	7.2	1.6
6-Octadecynoate	2	0.4[e]	0.0	0.0	0.0	0.0	0.0	99.6[f]

[a] At reflux temperature, 93 C.
[b] *t,t* = *trans, trans*; *c,c* = *cis,cis*; *c,t* = *cis, trans*; All products are conjugated except where indicated.
[c] Determined by UV analysis.
[d] All products nonconjugated.
[e] Monoyne.
[f] *cis* Monoene.

The rate of hydrogenation was very rapid in the experiments with acids and metals as compared to reactions with aqueous propanol and metals. When methyl santalbate was hydrogenated by heating for 30 min in the presence of 50% acetic acid and 4 g zinc, analysis showed the major products were 23% *cis, trans*-octadecadienoate and 76% octadecenoate. The hydrogenation was excessive, since more monoene than *cis, trans* diene had been produced. The rate of hydrogenation was diminished by reducing the amount of zinc to 2 g and the time to 15 min. Analysis revealed 48.9% *cis, trans* diene and 48.6% monoene esters. In other experiments the hydrogenation was diminished still further by varying the amount of metal and time of heating. Replacement of some water with propanol was also tried until too little reduction had taken place. There was some preferential hydrogenation of the triple bond but it was not sufficient to give more than a 50% yield of the desired product.

Since a slower reaction of the acids with metals might increase selectivity of the hydrogenation, two extremes were used: a high and a low concentration of acids. For both acetic and propionic acids at concentrations of 90%, the reactions with the metals were slow and soon stopped. Addition of 1 ml of water at intervals kept the reactions going slowly, suggesting that water was consumed. This procedure did not improve the selectivity. When the concentration of the acid was lowered to 15% or when water alone was used, unexpectedly favorable results were obtained, especially with powdered iron.

The hydrogenation of 0.1 g methyl santalbate in 15% acetic acid with 10 g powdered iron and refluxing for 1.5 hr yielded 73.3% *cis, trans* diene and 17.3% monoene esters as major products. Similar results were obtained by heating the methyl santalbate with propionic acid and iron. When only water and 10 g of iron were used as the reducing agent and the mixture was heated for 2.25 hr, the best analysis showed 85.0% *cis, trans* diene and 6.2% monoene esters. The results were quite erratic when water alone was used; the *cis, trans* diene ranged from 74-85%, but in each case only a small amount of monoene was produced. More work is needed to determine the cause of the erratic behavior. The action of zinc in water alone was much slower than that of iron. The reduction of methyl santalbate by heating 10 g zinc in water for 7 hr yielded 29.0% *cis, trans* diene and 1.1% monoene esters, but 68.8% of the original ester was unchanged.

In most experiments the metals that were reacted with the acids had reducing power, but with few exceptions they lacked sufficient specificity.

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