Reduction with Zinc of Triple Bonds to *cis* Double Bonds in Long Chain Conjugated Fatty Acids[1]

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ABSTRACT

The methyl ester of santalbic acid (*trans*-11-octadecen-9-ynoic acid) was hydrogenated with powdered zinc in 50% propanol to yield 90% of the *cis*, *trans*-diene ester; similarly, 7,9-octadecadiynoic methyl ester was converted to *cis*, *cis*-diene ester but yields were no better than 75%.

INTRODUCTION

Lindlar (1) showed that his catalyst had specificity in the hydrogenation of acetylenic bonds. He reported the hydrogenation of a compound having only one acetylenic bond which in turn was in conjugation with a double bond.

Results of other investigators (1,2,4) and our own experience indicate that reduction of conjugated acetylenes produces complex mixtures of isomers. The presence of the CH_3 and OH groups may have delayed hydrogenation of the double bond and the formation of geometric isomers.

Allen (2) reported the hydrogenation of methyl 10,12-octadecadiynoate using Lindlar catalyst and revealed through IR examination that geometric isomers were present in the hydrogenated product after the theoretical amounts of hydrogen had been absorbed to form the diene ester. Recently Gunstone and Jie (3) obtained excellent results with the Lindlar catalyst when hydrogenating diynoic acids in which the acetylenic groups were well separated in the chain. However, when the acetylenic groups were conjugated they found only 40-45% diene in the hydrogenation mixture.

Aylward and Sawistowska (4), in a review of hydrazine reductions, stated that hydrazine and certain hydrazine derivatives can reduce acetylenic and olefinic bonds provided oxygen is present. The hydrazine-oxygen system is able to reduce multiple double bonds in stages with apparently no *cis* to *trans* isomeric changes or positional shifts in double bonds, typical of classical hydrogenation processes.

This paper reports our attempts to selectively hydrogenate the methyl ester of 7,9-octadecadiynoic acid to produce the maximum yield of *cis*, *cis*-diene and to produce the maximum yield of *cis*, *trans*-diene from the hydrogenation of *trans*-11-octadecen-9-ynoic acid methyl ester.

EXPERIMENTAL PROCEDURES

Materials

The 7,9-octadecadiynoic acid was synthesized by a procedure published elsewhere (5) and the *trans*-11-octadecen-9-ynoic acid (santalbic acid) was prepared from *Santalum album* seed (6). Four different samples of powdered zinc were used and designated by the numbers, 41, 52, 77, and 78. The purity of each as indicated on the manufacturer's label was 98, 97.3, 99+ and 99+% respectively. The solvents were aqueous solutions of each of the following: ethanol, 1-propanol, 2-propanol, methoxyethanol and ethoxyethanol.

Hydrogenation Procedure

A modification of the procedure suggested by Kuhn (7) was adopted. To 0.1 g of methyl ester of the acetylenic acid were added 25 ml of 50% (v/v) aqueous 1-propanol and the desired amount of powdered zinc. The reaction mixture was refluxed at 87 C and stirred with a Teflon-covered magnetic stirrer for the desired time. The ester was extracted with ethyl ether, washed with dilute hydrochloric acid and then with water. The ether was evaporated on a steam bath in a stream of nitrogen. Sample drying was aided by the addition of ethyl alcohol.

Chromatographic Analyses

Gas liquid chromatographic (GLC) analyses were performed with a dual column apparatus designed in this laboratory. It contained a 4-filament thermal conductivity cell detector. The column was an 8 ft x 3/16 in. OD (ID = 0.118 in.) stainless steel coiled tube packed with 42-60 mesh acid and base washed Chromosorb W coated with 25% ethylene glycol succinate polyester. It was heated isothermally at 200 C with helium as the carrier gas. The areas

TABLE I

Hydrogenation of Methyl Santalbate in 50% 1-Propanol and Zinc at Reflux Temperature (87 C)

		Zinc		GLC analysis[a]			
Exp. no.	Heating hr	no.	g	yne, t-ene %	t,t %	c,t %	monoene %
1[b]	16	41	10	14.7	7.0	76.8	1.0
2	16	41	10	6.6	1.5	90.4	1.4
2A[c]	5	41	10	2.3	2.2	93.2	2.2
3	20	41	15	1.1	5.7	77.7	15.5
4	15½	41	15	0.5	2.5	91.4	5.5
5[d]	24	41	15	64.0	0.0	28.0	8.0
6	13	77	15	3.6	3.5	91.9	0.9
7[e]	43	78	15	12.9	3.7	77.4	2.4

[a] t,-ene = *trans*-ene; t,t = *trans, trans*; c,t = *cis, trans*.
[b] Mixture includes 0.4 g calcium chloride.
[c] Extracted material from exp. 2.
[d] Heated at 75 C.
[e] Also contained 3.5% of an unidentified component.

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[1] Presented in part at the AOCS Meeting, Chicago, October 1967.

[2] East. Market. Nutr. Res. Div., ARS, USDA.

TABLE II

Hydrogenation of Methyl 7,9-Octadecadiynoate in 50% 1-Propanol and Zinc at Reflux Temperature (87 C)

		Zinc		GLC analysis[a]						
Exp. no.	Heating hr	no.	g	Diyne %	t,t %	c,t %	Monoene %	c,c + yne, ene %	yne, ene[b] %	c,c[c] %
8	23	41	8	1.1	3.8	1.4	0.0	93.6	75	19
8A[d]	19	41	10	---	---	---	---	---	---	---
8B[e]	16	41	10	0.0	5.6	8.6	1.1	84.7	10	75
9	61	52	8	0.0	5.4	27.8	12.3	54.4	0	54
10	50	41	15	0.0	0.0	27.0	17.0	55.0	0	55
11	17	52	15	23.0	2.7	9.3	3.0	61.0	15	46
12	24	52	20	3.5	1.9	13.7	3.1	77.6	35	43

[a] t,t = *trans, trans*; c,t = *cis, trans*; c,c = *cis, cis.*

[b] Estimated from UV analysis.

[c] (c,c + yne, ene) -yne, ene = c,c.

[d] Extracted ester from exp. 8.

[e] Extracted ester from exp. 8A.

under the peaks of the individual components were determined by an electronic integrator (Infotronics, Model CRS-11HSB, Houston, Texas) coupled to a digital printer.

RESULTS AND DISCUSSION

Our attempts to reduce conjugated acetylenic bonds selectively by the Lindlar procedure and noncatalytically with diimide reduction procedures were unsuccessful. Yields of the *cis, cis*-diene were usually less than 25%. Treatment of 7,9-octadecadiynoic acid with the Lindlar catalyst produced various isomers and use of hydrazine hydrate or hydrazine derivatives (8,9) resulted in a slow reduction of the diynoic acid. Furthermore, analysis of the hydrogenated products indicated little or no specificity of these reducing agents for the acetylenic bonds and thus considerable amounts of monoene and saturated acids were formed.

Reductions using the procedure auggested by Kuhn (7) showed promise. A study of various modifications was made, including changing concentration and type of solvent, varying temperature of reaction, and eliminating calcium chloride. This resulted in adoption of the procedure given above. The methyl esters rather than the free acids were hydrogenated in order to minimize zinc soap formation and to expedite GLC analysis.

Reduction of the methyl ester of santalbic acid was easily studied since reduction of the triple bond of this compound yields a *cis, trans*-diene ester which is readily separated from the yne, *trans*-monoene ester by GLC. However, the study of reduction of the methyl 7,9-octadecadiynoate presented a problem because the resulting yne, *cis*-monoene and *cis, cis*-diene esters have essentially the same retention time and are not readily separated. In this case UV spectrometry was used to follow the reaction. The yne, *cis*-monoene ester has a maximum absorption at 228 mμ while for the *cis, cis*-diene ester the maximum is at 235 mμ. During the early part of the hydrogenation reaction the absorption is essentially due to the yne, ene-ester, but as the concentration of *cis, cis*-diene ester increases the peak at 228 mμ shifts toward 235 mμ until only the absorption maximum at 235 mμ is present.

Although many experiments were performed, only a select few are shown to indicate the degree of success achieved and the problems encountered. The hydrogenation of methyl santalbate under various conditions is shown in Table I. The only difference between experiments 1 and 2 is the addition of 0.4 g of calcium chloride to number 1. Calcium chloride had no beneficial effect; in fact, it appears to have slowed the reaction. The yield of the *cis, trans*-diene ester was increased to 93% (experiment 2A) when the methyl santalbate from experiment 2 was extracted and retreated with a fresh portion of reducing reagent and heated an additional 5 hr. Although not shown, decreasing the amount of zinc resulted in a decrease in the rate of reduction. When the amount of zinc was increased from 10 g to 15 g (experiment 3) there was excessive hydrogenation even with a shorter reaction time as indicated by an increase of monoene from 2% to 15% and a loss of *cis, trans*-diene, 93% to 78%. Satisfactory results were produced with 15 g of zinc when the heating time was decreased as shown in experiment 4. When the temperature was decreased from reflux (87 C) to 75 C in a similar experiment (number 5) 64% of the sample remained unhydrogenated even after 24 hr of heating.

Experiments 6 and 7 illustrate the differences in activity for the reduction of methyl santalbate exhibited by different lots of zinc of the same commercial grade and from the same manufacturer. Zinc numbers 77 and 78 were of the highest purity (99+%) and mass spectrometric analysis revealed no difference in composition. Zinc number 77 reacted in a manner similar to number 41, but with zinc number 78 the yield of *cis, trans*-diene was only 27% after 22 hr heating and only 77% after 43 hr. We were unable to find the reason for the reduced activity of this sample of zinc.

The hydrogenation of methyl 7,9-octadecadiynoate requires a longer reaction time because of the two acetylenic bonds. This is shown by the results of experiment 8 in Table II. The ester was heated for 23 hr using 8 g of zinc. This reduced the ester to predominantly the yne, ene-isomer with relatively little of the *cis, cis*-form produced. It had been found that efficiency of the zinc as a reducing agent was often markedly diminished after about 20 hr of heating in the reaction mixture. Therefore the above ester was extracted and reheated for 19 hr (experiment 8A) and then extracted and reheated for an additional 16 hr (experiment 8B) with fresh 10 g portions of zinc added after each extraction. However, even after this long period of heating (58 hr) about 10% of the yne, ene-isomer was present. The yield of 75% *cis, cis*-diene was the best obtained. A similar experiment with zinc number 52 gave essentially the same results indicating no difference in the activity or selectivity of these two zinc samples. In experiment 9 the ester was treated as in experiment 8 but the time of heating increased. This resulted in a yield of 54% but excessive amounts of *cis, trans*-isomer and monoene were formed. Similar results were obtained (experiment 10) when the period of heating was reduced but the amount of zinc was increased to 15 g. The result of drastically reducing the heating time while keeping the same quantity of zinc is shown in experiment 11. Considerable amount of 7,9-octadecadiynoate remained unreacted. Increasing the heating time in experiment 11 and also increasing the zinc to 20 g resulted in reduction of the starting ester but no increase in the yield of *cis, cis*-isomer. These experiments are only representative of many variations of conditions tried in attempts to increase the yield.

Methoxyethanol, ethoxyethanol and 2-propanol were also used as solvents in the reaction in the effort to produce yields as high as those obtained for the reduction of santalbic acid esters but they revealed no advantage over 50% 1-propanol. This work has led to the use of other powdered metals as hydrogenating agents and the results will be published later.

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