Homogeneous Hydrogenation of Methyl *cis*-9,*cis*-15-Octadecadienoate Catalyzed by Platinum-Tin, Palladium and Nickel Complexes

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ABSTRACT

Methyl *cis*-9,*cis*-15-octadecadienoate was used as a model for the hydrogenation of methyl linolenate. Homogeneous catalysis by platinum, palladium and nickel complexes produced a mixture of isomeric monoenes similar to that from the hydrogenation of methyl linolenate. These catalysts are, therefore, capable of promoting isomerization of isolated double bonds and of producing conjugated dienes which are necessary for the formation of monoenes.

INTRODUCTION

In a previous study (1), homogeneous hydrogenation of methyl linolenate with various platinum-tin complexes produced dienes and monoenes as major products. Initial conjugation through platinum-tin diene adducts was postulated in the mechanism of homogeneous hydrogenation. The high selectivity of the platinum-tin catalysts for the formation of dienes from methyl linolenate was attributed to the unreactivity of the diene products with double bonds separated by several methylene groups. Investigation of this hypothesis was made possible by the availability of pure methyl *cis*-9,*cis*-15-octadecadienoate (2). This model diene was hydrogenated with various soluble platinum, palladium and nickel complexes. The isomeric hydrogenation products were characterized in detail to elucidate further the mechanism of homogeneous catalytic hydrogenation.

RESULTS AND DISCUSSION

Methyl *cis*-9,*cis*-15-octadecadienoate was selectively hydrogenated to monoenes with the mixed chloroplatinic acid and platinum(II)-tin(II) chloride complexes and with palladium and nickel complexes containing triphenylphosphine ligands (Table I). The platinum triphenylarsine complex (run 4) was less selective, and even at a lower temperature methyl stearate was a significant product. Isomerization of the partially hydrogenated diene was indicated by the appearance of a triple peak by gas liquid chromatography (GLC). The same triple diene peak was previously observed with hydrogenated methyl linolenate and was identified as due to a mixture of *trans,trans*-, *cis,cis*- and *cis,trans*-dienes with isomerized isolated double bonds (1). IR analysis showed the presence of considerable isolated *trans* unsaturation in the hydrogenation products. Rate curves indicated that the reduction of dienes to monoenes leveled off after 4 hr with the mixture of chloroplatinic acid and tin(II) chloride (Table I, run 1). Small amounts of conjugated dienes and methyl stearate were also produced with this catalyst system.

Hydrogenation products were separated by rubber liquid partition column chromatogrpahy into monoenes having 70-72% isolated *trans* unsaturation (IR), and dienes with 97-93% unconjugated unsaturation and the rest conjugated in the *cis,trans*- and *trans,trans*-configuration (GLC). Double bond positions in these fractions were determined by ozonolysis-GLC (1). The double bond in the monoene fractions was distributed between carbon 4 and carbon 16 with the maximum at carbon 11 (Table II). The diene fraction had double bonds scattered between carbon 4 and carbon 13 with one centered at carbon 10 and the other centered at carbons 7,8.

From previous studies with methyl linoleate (3), it was suggested that the conjugation reaction 1,4-diene→ 1,3-diene, via a platinum-tin adduct, occurred before hydrogenation to monoenes. This mechanism accounts for the high selectivity of these platinum complexes for

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TABLE I

Catalytic Homogeneous Hydrogenation of Methyl *cis*-9,*cis*-15-Octadecadienoate

	Conditions[a]					Composition, %[b]					
									CD		
Run	Catalysts	Cocatalysts	Solvents, ml	Temperature, C	Time, hr	S	M	D	*ct*	*tt*	*trans*
1	$H_2PtCl_6 \cdot 6H_2O$	$SnCl_2 \cdot 2H_2O$	MeOH(30) + PhH^c(20)	100	0.5	0.3	36.0	63.5	0.0	0.2	---
					1	0.4	42.9	55.8	0.0	0.9	---
					2	0.7	44.3	53.0	0.9	1.1	---
					4	0.9	44.6	52.5	0.7	1.3	---
					6	1.1	44.5	50.4	1.8	2.2	31.2
2	$PtCl_2(Ph_3P)_2$	$SnCl_2 \cdot 2H_2O$	MeOH(20) + PhH(30)	90	8	0.0	16.2	76.0	7.8	0.0	155.0
3	$PtCl_2(Ph_3P)_2$	$SnCl_2 \cdot 2H_2O$	CH_2Cl_2(50)	90	8	0.0	86.1	13.9	0.0	0.0	71.1
4	$PtCl_2(Ph_3As)_2$	$SnCl_2 \cdot 2H_2O$	MeOH(20) + PhH(30)	80	8	12.1	79.5	8.4	0.0	0.0	68.5
5	$Pd(CN)_2(Ph_3P)_2$	None	MeOH(20) + PhH(30)	90	11	0.0	83.2	16.8	0.0	0.0	82.0
6	$NiI_2(Ph_3P)_2$	None	THF^d(50)	90	6	0.0	44.6	55.4	0.0	0.0	50.0

[a] Run 1: 0.1 M catalyst and 0.5 M $SnCl_2$ per M substrate, 500 psi H_2; runs 2-6: 0.3 M catalyst and 0.5 M $SnCl_2$ (when used) per M substrate, 575 psi H_2.

[b] Determined by gas liquid chromatography (GLC) and IR on final reaction products (1); S = stearate, M = monoene, D = diene, CD = conjugated diene, *ct* = *cis, trans* and *tt* = *trans, trans.*

[c] PhH = benzene.

[d] THF = tetrahydrofuran.

hydrogenation of dienes to monoenes. With linolenate a more complex reaction scheme results from the participation of various isomeric dienes (1,6-, 1,5-, 1,4- and 1,3-dienes) found as intermediates (1). In a mixture of dienes, the 1,4- and 1,3-isomers would be expected to compete in complex formation with the catalyst over those dienes with double bonds separated by several methylene groups (4). In the hydrogenation of methyl linolenate this competition resulted in accumulation of the relatively unreactive 1,6- and 1,5-dienes in partially hydrogenated reaction mixtures (1). In the present study this competitive situation was evidently eliminated. We observed that methyl *cis*-9,*cis*-15-octadecadienoate is readily hydrogenated to a mixture of isomeric monoenes which is remarkably similar to that produced from the hydrogenation of methyl linolenate. Apparently, migration of double bonds occurs rapidly during hydrogenation with platinum-tin complexes and the intermediate conjugated dienes formed are hydrogenated to monoenes that have mainly the *trans* configuration.

The double bond isomerization ability of palladium and nickel complexes was also demonstrated in this study. In contrast, the arene-chromium tricarbonyl complexes were previously noted for their stereoselectivity in catalyzing the hydrogenation of 1,4- and 1,3-dienes to *cis*-monoenes and for being ineffective toward 1,5-hexadiene and methyl *cis*-9,*cis*-15-octadecadienoate (5). These results and those of others (6) suggest that homogeneous catalysts with the judicious choice of polyunsaturated substrates and reaction conditions may now provide improved routes to the synthesis of selected unsaturated natural products of given bond position, configuration and stereochemistry. Conjugated fats were prepared, on the one hand, by using the isomerization property of iron carbonyl (7) and of platinum-tin complex catalysts (8). Synthetic fats were made, on the other hand, by using the unique property of chromium carbonyl complex catalysts of catalyzing the hydrogenation of polyunsaturates to *cis*-monounsaturates (9).

EXPERIMENTAL PROCEDURES

The catalysts $PtCl_2(Ph_3P)_2$, $PtCl_2(Ph_3As)_2$, $Pd(CN)_2(Ph_3P)_2$ and $NiI_2(Ph_3P)_2$ were prepared as described previously (3). Methyl *cis*-9,*cis*-15-octadecadienoate was prepared according to Butterfield et al. (2). The hydrogenation procedure and analytical scheme used to characterize the hydrogenation products were the same as before (1). Runs summarized in Table I were carried out under optimum conditions established previously (1,3). Hydrogenation times were chosen to be 1 or 2 hr after the rate of conversion leveled off. For the Pt complex catalysts, $SnCl_2$ was required as cocatalyst and CH_2Cl_2 was a better solvent than the mixture of MeOH and PhH. This solvent mixture was effective for the Pd complex but not for the Ni complex in which it decomposed. Tetrahydrofuran (THF) was the only suitable solvent found for the Ni complex catalyst.

TABLE II

Double Bond Distribution in Fractions of Hydrogenated Methyl *cis*-9,*cis*-15-Octadecadienoate[a]

Bond positions, carbon no.	Monoene mole, % AE[b]	Diene mole, % AE[b]	Diene mole, % A[b]
4	2.0	4.0	
5	4.6	9.8	2.3
6	5.4	15.1	2.9
7	7.9	20.6	8.0
8	11.4	20.3	10.6
9	11.7	17.0	16.3
10	11.7	8.5	18.9
11	13.6	3.5	16.0
12	12.9	1.4	12.8
13	8.5		12.2
14	7.0		
15	2.1		
16	1.3		

[a] With $H_2PtCl_6 \cdot 6H_2O + SnCl_2 \cdot 2H_2O$ (run 1, Table I).

[b] AE = aldehyde esters, same as carbon no. (fragments determined by gas liquid chromatography [GLC] after ozonolysis) (1). A = aldehydes, 18-carbon number.

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