Selective Hydrogenation with tris(triphenylphosphine) chlororhodium (I) Catalyst: Preparation of Octadecenoate Isomers

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Fractionation of products obtained from partial catalytic hydrogenation of methyl *cis*-9,*cis*-12-octadecadienoate (9c,12c-18:2) with tris(triphenylphosphine) chlororhodium [$RhCl(Ph_3P)_3$] provided a facile method for preparation of a nearly equal molar mixture of methyl *cis*-9- and *cis*-12-octadecenoate (9c-18:1 and 12c-18:1). Isolation of products was achieved by silver resin and C18 reverse phase liquid chromatography. Catalytic deuteration of 9c,12c-18:2 yields a mixture of 9c-18:1-12,13-d_2 and 12c-18:1-9,10-d_2 with an isotopic purity of 85%. Final isolated yield of the mixture of 9c- and 12c-18:1 products was 30%. Isolation of products from partial hydrogenation of conjugated octadecadienoates (9c,11t-18:2 or 10t,12c-18:2) provided a convenient method for synthesis of an almost equal molar mixture of methyl *trans*-10 and *trans*-11-octadecenoate (10t-18:1 and 11t-18:1). Characterization of the reaction products from hydrogenation of 9c,12c-18:2 indicates that the 9c- and 12c-18:1 products are formed by the expected 1,2-hydride addition. The presence of small amounts of 10t- and 11t-18:1 and conjugated octadecadienoates was evidence for a secondary isomerization-1,4-hydride addition pathway. Isolation and characterization of products from $RhCl(Ph_3P)_3$-catalyzed hydrogenation of 9c,11t-18:2 and 10t,12c-18:2 indicate that both 1,2- and 1,4-hydride addition to the conjugated diene isomers occurs at about equal rates, but only the *cis* bond is reduced by the 1,2-hydride addition pathway and the 1,4-hydride addition pathway yields only a *trans*-18:1. Because of this unusual selectivity for a *cis* bond conjugated with a *trans* bond, hydrogenation of both 9c,11t-18:2 and 10t,12c-18:2 yields the same mixture of t-18:1 isomers.

Wilkinson's catalyst, tris(triphenylphosphine) chlororhodium (I) [$RhCl(Ph_3P)_3$] has been used extensively for preparation of deuterium-labeled fatty acids (1-4) and for other applications (5-7). The catalyst is particularly useful because it incorporates nearly a stoichiometric number of deuterium atoms during the reduction of olefinic and acetylenic compounds. Thus, the deuterated products from $RhCl(Ph_3P)_3$ reductions generally have greater than 90% isotopic purity, which is in contrast to the extensive deuterium scatter that occurs when normal heterogeneous catalysts such as nickel, platinum or palladium are used (8,9).

The mechanism or pathway for reduction of double bonds by $RhCl(Ph_3P)_3$ has been described as proceeding through an octahedral *cis*-dihydridorhodium complex (10,11) and has been used to explain many of the properties of this catalyst.

In the course of using the $RhCl(Ph_3P)_3$ catalyst for deuteration of a wide variety of compounds containing olefinic and acetylenic structures, products from deuteration of *cis*-9,*cis*-12-octadecadienoate (9c,12c-18:2) were noted to contain lower isotopic purity than products from deuteration of mono-olefins and acetylenes. Data presented in this paper provide evidence for a secondary reaction pathway that explains this observation. Also, facile procedures are described for preparation of a mixture of *cis*-9-octadecenoate (9c-18:1) and *cis*-12-octadecenoate (12c-18:1) from 9c,12c-18:2 and of a mixture of *trans*-10-octadecenoate (10t-18:1) and *trans*-11-octadecenoate (11t-18:1) from *cis*-9,*trans*-11-octadecadienoate (9c,11t-18:2) or from *trans*-10,*cis*-12-octadecadienoate by partial catalytic hydrogenation with $RhCl(Ph_3P)_3$.

EXPERIMENTAL

Materials. $RhCl(Ph_3P)_3$ was obtained from Strem Chemicals, Inc. (Newburyport, Massachusetts), and methyl *cis*-9,*cis*-12-octadecadienoate was prepared in 99.9% purity from safflower oil methyl esters by silver resin chromatography (12-14). The absence of conjugated diene isomers was confirmed by UV spectroscopy. Samples enriched in methyl 9c,11t-18:2 and 10t,12c-18:2 were prepared by alkali conjugation of 9c,12c-18:2, and separation of the conjugated geometrical isomers was accomplished by silver resin chromatography and crystallization as described previously (15,16). The 9c,11t-18:2 sample contained 7.5% 10t,12c-18:2 and 9.7% conjugated t,t-18:2 as the major impurities. The 10t,12c-18:2 sample was 69.4% pure, with 9c,11t-18:2 (11.4%), conjugated c,t-18:2 (9.3%) and conjugated t,t-18:2 (2.8%) as the major impurities. Methyl oleate (9c-18:1) and methyl elaidate (9t-18:1) were purchased from Nu Chek Prep, Inc., Elysian, Minnesota. Deuterium gas (99% isotopic purity) was obtained from Matheson, Joliet, Illinois. Solvents were ACS or spectroscopic grade and were used as received.

Procedures. Previously described procedures and equipment were used for deuteration of 9c,12c-18:2 and 9c,11t-18:2 with $RhCl(Ph_3P)_3$ and for isolation of reaction products (1,3). Formation of the dioxygenated complex of $RhCl(Ph_3P)_3$ was avoided by careful deoxygenation of the benzene solvent before addition of the $RhCl(Ph_3P)_3$ catalyst (3,11). The catalyst was also completely prereduced in situ before addition of the 18.2 methyl esters. Deuterium gas uptake was monitored continuously as described previously (17), and the reaction mixture was sampled periodically.

The compositions of the partially deuterated 9c,12c-18:2 reaction mixtures were determined by using a Packard model 428 gas chromatograph, equipped with a 100 meter × 0.25 mm I.D. SP2560 fused silica capillary column (Supelco, Inc., Bellefonte, Pennsylvania) and operated isothermally at 170 C. Isolation of the deuterated products was achieved by a combination of silver resin and high performance C_{18} reverse phase chromatography (12-14). A 25 cm × 10 mm C_{18} reverse phase column (Altex Ultrasphere-ODS, 5 μ) was used for removal of conjugated 18:2 (18:2CD) isomers from

the 9c- and 12c-18:1-d_2 fraction obtained from silver resin chromatography. Elution of the sample from the reverse phase column was with 100% acetonitrile (18). Deuterium isotope distribution in the products was determined by mass spectrometry (19). Ultraviolet and infrared spectroscopy were used to confirm the presence of conjugated and *trans* structures in the isolated methyl conjugated octadecadienoate and *trans*-octadecenoate reaction products. *Trans*-18:1 and conjugated octadecadienoate isomers were identified by comparison of GC retention times to standards or mixtures of known composition. Reductive ozonolysis followed by GC analysis of the aldehyde and aldehyde-ester products was used to determine double bond distribution (20).

Preparation of mixture containing 9c-18:1-d_2 and 12c-18:1-d_2. Benzene (500 ml) in a one-l round bottom flask was thoroughly deoxygenated by purging with helium for 10 min and was then evacuated and flushed three times with deuterium gas. $RhCl(Ph_3P)_3$ (6.0 g) was added, flushing with deuterium gas was repeated and the mixture was stirred under one atmosphere of deuterium until the catalyst was completely dissolved and deuterium uptake had stopped. The resulting solution had a light amber color. The 9c,12c-18:2 (45.8 g) was added by injection through a septum, and the mixture was stirred vigorously. Total reaction time required to reach about 42% deuteration was 60 min. The reaction was stopped by flushing with nitrogen, and most of the benzene was then evaporated at reduced pressure. About 250 ml of petroleum ether was added to precipitate the catalyst. The mixture was filtered, and the filtrate was concentrated to ca. 50 ml. The entire solution was placed on a column containing 400 g silica gel, and the methyl esters were eluted with 2.5 l hexane:diethyl ether (85:15, v/v).

A 50 cm × 5 cm silver XN1010 resin column was used to separate ca. 15 g portions of the reaction mixture by elution of the sample with methanol (6 ml/min). The column eluant was monitored by a refractive index detector, and fractions were collected. The fraction containing the 9c- and 12c-18:1-d_2 esters also contained 5.7% each of 9c,11t-18:2 and 10t,12c-18:2. A C_{18} reverse phase column was used to separate the c-18:1-d_2 isomers from conjugated 18:2. Final isolated yield of the 9c-18:1-12,13-d_2 and 12c-18:1-9,10-d_2 product was 30% (13.8 g) based on the initial weight of 9c,12c-18:2.

Deuteration of 9c,11t-18:2. The same general procedure was used as described earlier for preparation of the 9c- and 12c-18:1-d_2 mixture. The only difference was that 4.5 g of a 9c,11t-18:2-enriched sample was used. All solvent volumes, catalyst weight, etc., were reduced proportionately. The reaction was stopped after 47% deuteration. The final reaction product contained no detectable *cis*-18:1 isomers, and only silver resin chromatography was required to isolate the *trans*-18:1-d_2 fraction. Isolated yield of 10t- and 11t-18:1-d_2 product was 1.6 g (35%).

Hydrogenation of 10t,12c-18:2. The previously described procedure was used for the hydrogenation of 10t,12c-18:2 with $RhCl(Ph_3P)_3$. Hydrogenation conditions were: 0.15 g of 10t,12c-18:2, 0.012 g of catalyst, room temperature, one atm hydrogen pressure, three ml degassed benzene. Small samples (1 mg) were removed at various times and the reaction was stopped at 40.6% reduction.

Hydrogenation of a mixture containing 9t-18:1 and 9c-18:1. Benzene (45 ml) was degassed, the apparatus was flushed with hydrogen, and 0.5 g of $RhCl(Ph_3P)_3$ catalyst was added as described previously. A sample containing 47.3% 9t-18:1 and 52.7% 9c-18:1 (3.79 g) was then introduced, and the reaction was followed by removal of 0.1-ml samples periodically until hydrogen uptake became negligible.

RESULTS

The composition of partially deuterated 9c,12c-18:2 and 9c,11t-18:2 samples and the isotopic purities of the unsaturated reaction products are summarized in Tables 1 and 2. The composition of samples taken at various

TABLE 1

Partial Deuteration of 9c,12c-18:2 and 9c,11t-18:2 with $Rh(Ph_3P)_3Cl$

	Composition (%) of reaction mixture[a]	
Methyl ester[c]	42% Reduced[b] 9c,12c-18:2	47% Reduced[b] 9c,11t-18:2
18:0	13.6	16.9
10t-18:1	3.6	24.6
11t-18:1	3.5	32.7
12t-18:1	–	0.9
9c-18:1	22.3	0
12c-18:1	27.1	0
9c,11t-18:2	1.7	12.0
10t,12c-18:2	1.8	1.2
9c,12c-18:2	22.9	–
t,t-18:2CD[c]	3.4	11.3

[a]t- and c-18:1 isomer distribution determined by both capillary GC and ozonolysis of fraction isolated by C_{18} HPLC.
[b]Percent reduced value calculated from total number of double bonds remaining in mixture.
[c]18:2CD, conjugated octadecadienoate.

TABLE 2

Isotopic Purity of the Unsaturated Fatty Ester Isomers Isolated from Partial Deuteration of 9c,12c-18:2 and 9c,11t-18:2

	Deuterium distribution (%)					
Fatty ester	d_0	d_1	d_2	d_3	d_4	d_5
t-18:1[a]	0.8	7.2	70.0	20.5	1.3	2.0
c-18:1[a]	0.8	12.6	85.3	1.0	0.3	–
18:2CD[b]	13.5	75.1	10.9	0.5	–	–
t-18:1[c]	0.5	6.1	86.4	6.8	0.2	–

[a]*cis* and *trans* octadecenoate fractions from partial deuteration of 9c,12c-18:2.
[b]Conjugated octadecadienoate fraction (18:2CD) isolated from partially deuterated 9c,12c-18:2.
[c]Fraction from partially deuterated 9c,11t-18:2.

stages of partial hydrogenation of a 10t, 12c-18:2-enriched sample are contained in Table 3. The chromatograms shown in Figure 1 illustrate the separation of the 9c- and 12c-18:1 mixture and the 10t- and 11t-18:1 pair. Although the 10t- and 11t-18:1 isomers were not completely separated, the percentage of areas under each peak was within 2% of the mean values obtained by GC analysis of the ozonolysis products. The standard deviation for the data obtained with the SP2560 capillary column was much lower than for the ozonolysis data and was much easier to obtain.

TABLE 3

Partial Hydrogenation of an Enriched 10t,12c-18:2 Conjugated Diene Mixture with $Rh(Ph_3P)_3Cl$

	Composition of samples (%)				
Methyl esters	0 min	5 min	10 min	25 min	35 min
18:0	0.0	0.2	0.6	5.4	12.2
8t-18:1	0.0	0.7	1.3	2.9	3.8
9t-18:1	0.0	0.7	1.2	2.5	3.2
10t-18:1	0.0	4.5	8.0	18.2	23.2
11t-18:1	0.0	3.6	6.6	18.1	22.0
12t-18:1	0.0	0.5	0.7	2.0	2.7
13t-18:1	0.0	0.3	0.7	1.5	1.9
c,t-18:2CD[a]	1.6	1.2	1.1	0.6	0.0
c,t-18:2CD[a]	1.0	0.8	0.8	0.5	0.0
9c,11t-18:2	11.4	10.1	8.9	4.7	2.7
t,c-18:2CD[a]	9.3	8.2	7.2	4.1	2.2
t,c-18:2CD[a]	2.1	1.8	1.6	1.1	0.6
10t,12c-18:2	69.4	61.7	54.0	29.8	16.3
18:2CD[b]	0.8	0.6	0.5	0.4	0.7
18:2CD[b]	1.6	1.0	1.7	1.1	1.0
t,t-18:2CD	2.8	4.1	5.1	7.1	7.5
Total					
Double bond	200.0	189.3	180.3	144.0	118.8
% Reduced	0.00	5.35	9.85	28.00	40.60

[a]Tentative identification based on relative GC retention times.
[b]These conjugated dienes are assumed not to have a *cis,trans or trans,cis* configuration because they were not reduced at the same rate as 9c,11t- and 10t,12c-18:2.

Deuteration of 9c,12c-18:2 was stopped at 42% total deuteration, which is near the theoretical value of 50% necessary for maximum yield of 18:1. Deuteration beyond 50% results in conversion of 18:1-d_2 to 18:0-d_4 at a rate faster than formation of 18:1-d_2 from 18:2 because the reaction follows pseudo-first-order kinetics (21).

In order to obtain a sample containing only c-18:1-d_2, it was necessary to remove 18:1, t-18:1, 18:2CD and unreacted 9c,12c-18:2 by a combination of silver resin and C_{18} reverse phase liquid chromatography. Products from deuteration of mono acetylenes and olefins by the procedures used normally have isotopic purities in excess of 95%. In comparison, the isotopic purity of products from deuteration of 9c,12c-18:2 was 85.3% for the c-18:1-d_2 fraction, 75.1% for the 18:2CD fraction

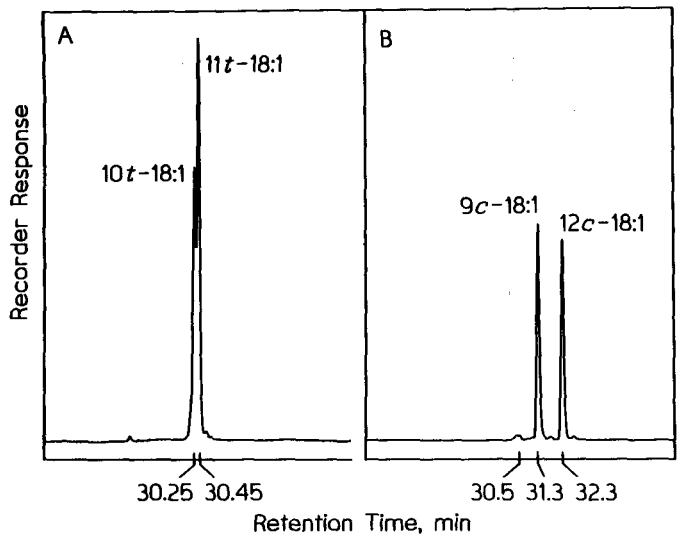

FIG. 1. Gas chromatograms of a 10t-18:1-d_2 and 11t-18:1-d_2 mixture and of a 9c-18:1 and 12c-18:1 mixture.

and 70% for the t-18:1 fraction, which also contained 20.5% of a d_3 species (Table 2). These combined isotopic purity data indicate that H-D exchange occurs during the formation of 18:2CD. GC analysis of the triphenylphosphine-reduced ozonolysis products and capillary GC analysis with a SP2560 column were used to determine double-bond location. The double bonds were located in the c-18:1-d_2 fraction at the 9 and 12 positions and were in nearly a 1:1 ratio. Mass spectrometric analyses of the reduced ozonolysis products indicate that the deuterium atoms were located at the 12,13 and 9,10 carbons of 9c-18:1-d_2, respectively.

The partially deuterated 9c,11t-18:2-enriched sample was purified by silver resin chromatography and yielded a t-18:1-d_2 fraction with an isotopic purity of 86.4%. Capillary GC analysis of the t-18:1 fraction and GC analysis of ozonolysis products indicated that 95% of the double bonds were located at the 10 and 11 positions. The higher percentage of 11t-18:1-d_2 (Table 1) in the t-18:1 isomers indicated that 1,2-addition was slightly faster than 1,4-addition.

Partially hydrogenated 10t,12c-18:2-enriched samples were analyzed by capillary GC, and the compositions of samples at various stages of reduction are summarized in Table 3. About 80% of the t-18:1 isomers formed were 10t- and 11t-18:1 and were present in about a 1:1 ratio. Other t-18:1 isomers identified were 8t-, 9t-, 12t- and 13t-18:1 and probably were formed from *cis,trans*- and *trans,cis*-18:2CD isomers present as impurities in the starting material.

Data for the hydrogenation rates of 9t-18:1 and 9c-18:1 were obtained by hydrogenation of a mixture containing 47% 9t-18:1 and 53% 9c-18:1. The compositions of samples taken at various stages of hydrogenation are summarized in Table 4 and indicate that the hydrogenation rates for 9c-18:1 and 9t-18:1 are 0.49 and 0.16 mmol/min/g of catalyst, respectively.

DISCUSSION

Partial deuteration of 9c,12c-18:2 with Wilkinson's catalyst followed by isolation of the c-18:1-d_2 fraction pro-

TABLE 4

Hydrogenation of a Mixture of 9c-18:1 and 9t-18:1 with $Rh(Ph_3P)_3Cl$

	Composition of samples (%)			mmol reduced		
Sample time (min)[a]	18:0	9t-18:1	9c-18:1	Total	9t-18:1	9c-18:1
0	0.0	47.3	52.7	0.00	0.00	0.00
5	21.9	41.5	36.6	2.50	0.14	0.40
10	43.8	36.3	19.8	4.99	0.55	1.64
22	68.8	26.3	4.9	7.84	1.65	3.75
90	93.9	5.9	0.1	10.70	4.43	5.63
145	98.8	1.1	0.0	11.26	5.20	5.94

Hydrogenation rate for 9t-18:1 = 0.16 mmol/min/g
Hydrogenation rate for 9c-18:1 = 0.49 mmol/min/g

[a]Time at which reaction mixture was sampled.

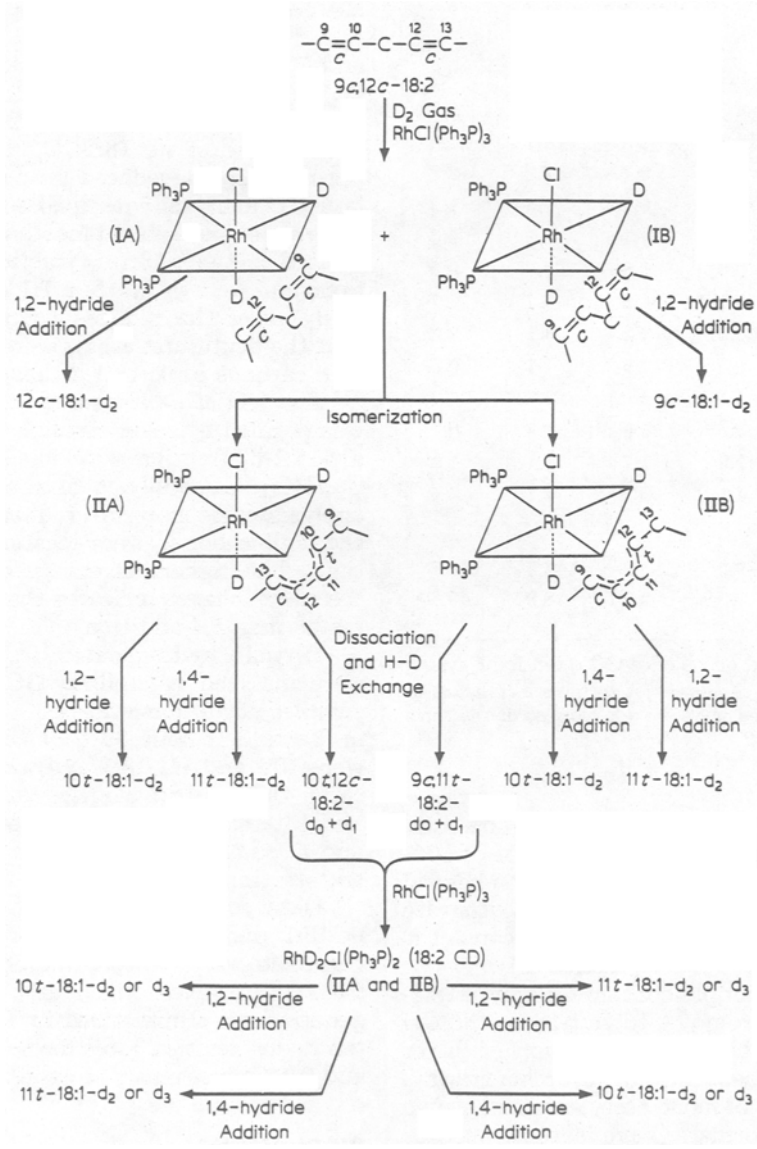

FIG. 2. Reaction pathways involved in the catalytic deuteration of 9c,12c-18:2 with $RhCl(Ph_3P)_3$.

vides a simple synthetic method for preparation of a mixture containing 9c-18:1-12,13-d_2 and 12c-18:1-9,10-d_2. In a similar manner, partial hydrogenation of 9c,11t-18:2 or 10t,12c-18:2 provides a convenient method for synthesis of a mixture containing 10t- and 11t-18:1. Since both of these conjugated dienes yield the same *trans* positional isomers, a mixture of these conjugated diene isomers would be a suitable starting material. The procedure described provides a rapid method for synthesis of either deuterium-labeled or non-labeled pairs of 18:1 isomers that can be incorporated into metabolic studies or used as analytical standards. The procedure has the advantage that it is easily adaptable for the synthesis of either multigram or mg quantities of these 18:1 isomers.

The compositions of the reaction products summarized in Tables 2 and 3 and the data for deuterium isotope distribution (Table 2) clearly indicate that the two reaction pathways shown in Figure 2 were involved in the deuteration of 9c,12c-18:2. The composition data in Table 1 indicate the 1,2-hydride addition pathway was the pathway responsible for most of the product formation. This is the pathway Wilkinson and others have well characterized (10,11). The 1,4-hydride addition pathway involves formation of a conjugated octadecadienoic fatty acid intermediate. Hydrogen-deuterium (H-D) exchange occurs either during formation of 18:2CD or when it dissociates from the catalyst. As indicated by the isotope data in Table 2, this H-D exchange lowers the isotopic purity of all the reaction products. The formation of 18:2CD-d_1 is evidence that this exchange occurs when 18:2CD dissociates from the rhodium catalyst. The 18:2CD is subsequently hydrogenated by both 1,4- and 1,2-hydride addition. The ratios of 10t- and 11t-18:1 from hydrogenation of both conjugated and non-conjugated 18:2 samples were similar, which indicates that the reaction rates for 1,2- and 1,4-addition to c,t- and t,c-18:2CD were nearly equal. Surprisingly, no *cis* 18:1 isomers were formed during the hydrogenation of the *cis,trans-* or *trans,cis*-conjugated octadecadienoate-enriched samples, which indicates that 1,2-hydride addition occurs only to the *cis* bond. Hydrogenation of a mixture of 9c- and 9t-18:1 was used to determine that this unusual selectivity did not occur with *cis* and *trans* monounsaturated fatty acids. The accumulation of t,t-18:CD impurity in the partially hydrogenated samples of 9c,11t- and 10t,12c-18:2 is further evidence that 1,2-hydride addition to a conjugated *trans* double bond is not rapidly catalyzed by $RhCl(Ph_3P)_3$.

The presence of a secondary isomerization-1,4-hydride addition pathway that produces t-18:1 and 18:2CD isomers and a primary 1,2-hydride addition pathway that forms c-18:1 isomers results in a mixture that cannot be completely separated by silver resin chromatography. Final purification of the c-18:1 fraction requires the use of a C_{18} reverse phase column. Isolation of the t-18:1 fraction from hydrogenated 18:2CD requires only the use of silver resin chromatography.

Because of the isomerization-1,4-hydride addition pathway, care should be taken in the interpretation of results obtained by analytical methods that use $RhCl(PH_3$ to catalyze deuteration of diglycerides as a means of determining molecular species (5). Also, this secondary reaction pathway may compromise the results of membrane fluidity studies where $RhCl(Ph_3P)_3$ is used to hydrogenate or deuterate intact phospholipids in the cell wall (6). Both of these techniques are based on the assumption that a theoretical addition of two deuterium atoms per double bond occurs. The data presented in Tables 1, 2 and 3 indicate that deuteration of polyunsaturated fatty acids produces both isomeric fatty acid structures and lower than expected isotopic purities.

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