Hydrogenation of Dienes with Cationic Rhodium Complexes

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ABSTRACT

Methyl *cis*-9,*cis*-12-octadecadienoate (methyl linoleate; *c*9,*c*12), its *t*10,*t*12 and *t*10,*c*12 isomers and methyl *cis*-9-octadecenoate (methyl oleate; *c*9) were hydrogenated with rhodium complexes, the active species of which consisted of $[RhL_2]^+$ and $[RhL_2H_2]^+$ with ligands L = $P(C_2H_5)_2C_6H_5$ (catalyst A), $P(i\text{-}C_4H_9)_3$ (catalyst B) and $P(CH_3)_3$ (catalyst C). Using these catalysts the influence of steric effects on the reaction mechanism of hydrogenation of dienes was studied. The reactions were carried out in 2-propanol at atmospheric hydrogen pressure and ambient temperature. During hydrogenation of *c*9 on catalysts A and B, geometrical isomerization mainly occurred, whereas on catalyst C some positional isomerization also took place. *C*9,*c*12 was almost exclusively hydrogenated via conjugated intermediates on catalyst A. On catalyst C, one of the double bonds was hydrogenated directly, in most cases. In the absence of hydrogen, catalysts A and B conjugated *c*9,*c*12 very fast. The conjugation activity of catalyst C was much lower. Catalyst C showed a high 1,5-shift activity for the conjugated *cis,trans* and *trans,cis* intermediates during hydrogenation, in contrast to catalysts A and B, which showed a poor activity in this respect. *T*10,*t*12 was hydrogenated almost exclusively via 1,4-addition of hydrogen to the *cisoid* conformation, whereas only a slight preference was found in this mechanism over 1,2-addition for the hydrogenation of *t*10,*c*12. On the sterically unhindered catalysts A and C, the *trans* double bond in *t*10,*c*12 was preferentially hydrogenated whereas on catalyst B, with its bulky ligands, the *cis* double bond was reduced faster than the *trans* double bond.

INTRODUCTION

Homogeneous hydrogenation of fats and oils has become an important field of research for 2 reasons: improvement of the selectivity of conventional heterogeneous catalysts and collection of fundamental information about the hydrogenation process. The various homogeneous systems investigated in fat hydrogenation have been reviewed among others by James (1) and more recently by Frankel (2).

In a number of papers, Schrock and Osborn (3-6) describe the powerful activity and selectivity properties of rhodium complexes in the hydrogenation of dienes. The ligands in these complexes, the solvent and substrate structure play important roles in the catalytic behavior. To obtain additional information on the influence of these parameters on the mechanism of hydrogenation and isomerization of unsaturated fatty esters, we hydrogenated some isomeric methyl octadecadienoates on similar rhodium complexes. The active species of the complexes, $[RhL_2]^+$ and $[RhL_2H_2]^+$ (L = ligand), were prepared in situ from the corresponding norbornadiene (NBD) complexes $(Rh(NBD)L_2]^+PF_6^-$. By using various types of ligand ($P(C_2H_5)_2C_6H_5$, $P(i\text{-}C_4H_9)_3$ and $P(CH_3)_3$) we studied the influence of steric effects on both the hydrogenation and isomerization reactions.

EXPERIMENTAL PROCEDURES

Preparation of Complexes

The $[Rh(NBD)L_2]^+PF_6^-$ complexes were prepared similarly to the method described by Schrock and Osborn (4-6). A typical example with L = $P(C_2H_5)_2C_6H_5$ (catalyst A) is as follows: a solution of $[Rh(NBD)Cl]_2$ (685 mg) in acetone (40 ml) was treated with a suspension of $AgPF_6$ (825 mg) in acetone (10 ml). Silver chloride was formed rapidly. The solution was filtered and the yellow filtrate was reduced to ca. 15 ml by a flow of argon. Diethylphenylphosphine (982 mg) was slowly added with stirring and the color immediately changed to deep red. The vol of the solution was further reduced to ca. 3 ml. Ethanol (4 ml) and diethyl ether (30 ml) were added to complete crystallization. The red crystals were filtered off, washed with diethyl ether and dried under argon. Recrystallization was achieved by dissolving in a minimal amount of dichloromethane and addition of an equal vol of ethanol followed by excess diethyl ether (yield: 1507 mg = 76%). The $[Rh(NBD)Cl]_2$ complex was prepared according to the Abel et al. method (7).

The yield of the other 2 complexes (L = $P(i\text{-}C_4H_9)_3$ and L = $P(CH_3)_3$, catalysts B and C, respectively) were considerably lower because of high solubilities and recrystallization problems.

Substrates

The following substrates were hydrogenated: methyl *cis*-9,*cis*-12-octadecadienoate (*c*9,*c*12; methyl linoleate), methyl *trans*-10,*cis*-12-octadecadienoate (*t*10,*c*12), methyl *trans*-10,*trans*-12-octadecadienoate (*t*10,*t*12) and methyl *cis*-9-octadecenoate (*c*9; methyl oleate).

*C*9,*c*12 and *c*9 were isolated from the methyl esters of safflower oil and olive oil, respectively, from the safflower oil by urea crystallization and from the olive oil by fractionated distillation. *C*9,*c*12 was purified by distillation (98.5%), *c*9 by urea crystallization prior to distillation (97% *c*9, 3% *c*11).

*T*10,*c*12 was synthesized according to Beerthuis et al. procedures (8). The ethyl ester of 10-undecynoic acid was condensed with triethyl orthoformate with zinc iodide as a catalyst (9). Reduction of the triple bond with Lindlar's catalyst, conversion of the ketal function in the free aldehyde and *cis-trans* rearrangement of the original *cis* double bond by boiling in acetone with a trace of sulfuric acid yielded ethyl 12-oxo-*trans*-10-dodecenoate. This aldehyde was *cis*-stereo-selectively coupled (Wittig) to hexylidenetriphenylphosphorane (10) under salt-free conditions (11,12) giving ethyl *trans*-10,*cis*-12-octadecadienoate. Part of the free acid was converted into the corresponding *trans,trans* acid with iodine as a catalyst (13). Both acids were finally esterified with methanol.

*T*10,*c*12 purity was 97.5% by gas liquid chromatography (GLC); double bonds at 10- and 12-position > 95%, at 9- and 11-position 1%; geometry: *trans,cis* (infrared [IR] and nuclear magnetic resonance [NMR]). The product was identical to that obtained via the method described by Nichols et al. (14) (alkali isomerization of *c*9,*c*12 and isolation of *t*10,*c*12 from the mixture via crystallization).

*T*10,*t*12 purity was 99.8% (GLC); geometry: *trans,trans* (IR, NMR). Prior to hydrogenation, the esters were purified by chromatography over activated alumina under argon with hexane as eluent.

Hydrogenation

Hydrogenations were performed at ambient temperature and atmospheric hydrogen pressure. Hydrogen gas was purified over copper on magnesium silicate (BTS, ex

TABLE I

Hydrogenation of Methyl Octadecenoate and Various Methyl Octadecadienoates on Catalysts A, B and C

			Composition (%)				
					Diene		
Substrate	Catalyst	*t*/min	Saturated	Monoene	Nonconjugated	Conjugated	Degree of hydrogenation (%)
*c*9	A	5	21.8	78.2	-	-	21.8
	B	18	19.8	80.2	-	-	19.8
	C	11	24.7	75.3	-	-	24.7
*t*10,*t*12	A[a]	1	-	64.5	-	35.5	32.2
	B	2	2.1	97.9	-	-	51.0
*t*10,*c*12	A	3.5	13.3	86.7	-	-	56.6
	B	86	28.4	71.6	-	-	64.2
	C	4	13.8	86.2	-	-	56.9
*t*10,*c*12[b]	A	2	10.5	89.5	-	-	55.2
	B	66	27.7	72.3	-	-	63.8
*c*9,*c*12	A	2	8.2	91.8	-	-	54.1
	B	30	17.4	72.5	5.5	4.6	53.6
*c*9,*c*12[b]	A	< 2	6.9	90.4	-	2.7	52.1
	B	18	12.1	75.9	-	12.0	50.0
	C	4	7.5	92.0	0.5	-	53.5

[a] 0.003 mmol complex was used, instead of 0.03 mmol.

[b] In these experiments, the substrates were treated with the complex in the absence of hydrogen for 5 min prior to hydrogenation. During this period, catalysts A and B conjugated *c*9,*c*12 almost completely, whereas catalyst C conjugated the substrate for less than 10%.

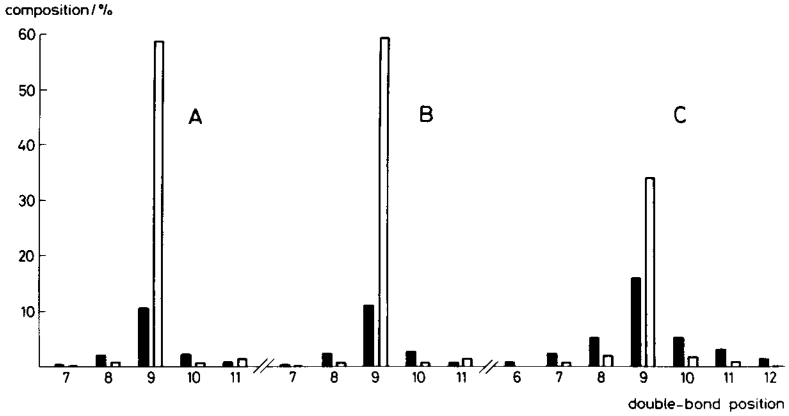


FIG. 1. Monoenes (■ *trans*; □ *cis*) obtained from partial hydrogenation of *c*9 on catalysts A, B and C.

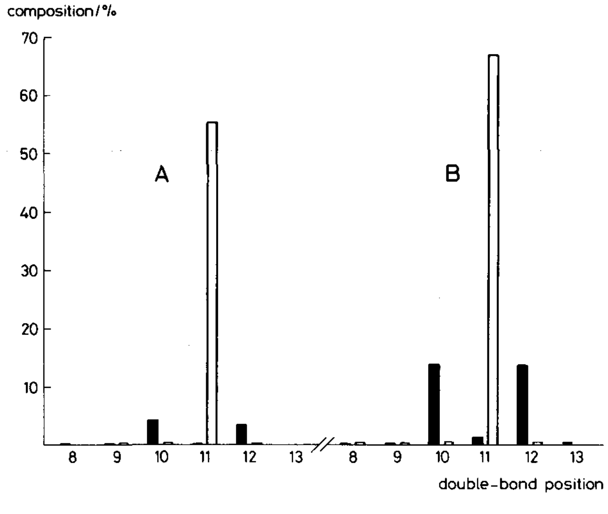


FIG. 2. Monoenes (■ *trans*; □ *cis*) obtained from partial hydrogenation of *t*10,*t*12 on catalysts A and B.

BASF) and dried over a molecular-sieve column. In a typical experiment, a solution of 0.03 mmol catalyst in 11 ml oxygen-free 2-propanol was activated by stirring under hydrogen for 30 min. During this treatment the red color changed to pale yellow. Immediately after admission of substrate (0.75 ml), the hydrogenation was started by stirring hydrogen gas into the solution.

In some experiments, stirring was delayed for 5 min after admission of substrate, often resulting in specific isomerization reactions such as conjugation of *c*9,*c*12 and 1,5-shift of hydrogen in conjugated *trans,cis* dienes in the absence of hydrogen. In these cases, the pale yellow solutions immediately turned orange-red and kept this color as long as conjugated dienes were present. The removal of these dienes was evident when the orange-red color faded to pale yellow. When *c*9,*c*12 was hydrogenated directly after admission, the pale yellow solution changed to yellow and this color persisted as long as *c*9,*c*12 was present. The original pale color returned after hydrogenation of the 1,4-diene to monoene.

The reaction was stopped by poisoning the catalyst with

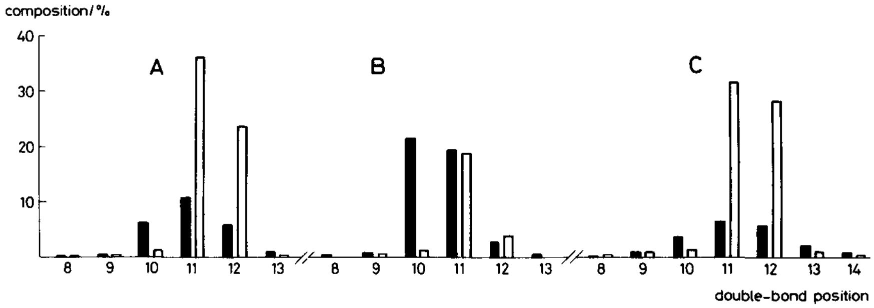


FIG. 3. Monoenes (■ *trans*; □ *cis*) obtained from partial hydrogenation of *t*10,*c*12 on catalysts A, B and C.

excess pyridine. Solvent and excess pyridine were removed by purging with nitrogen. The residue was diluted with pentane and the methyl esters were filtered off.

Analysis

The composition of the hydrogenation products was determined by a combination of the following techniques. *GLC*: determination of saturated, monoene and diene contents; 10% DEGS on chromosorb W(80-100 M); column length, 1.5 m; temperature, 165 C. *IR*: determination of *trans* contents. *TLC*: isolation of *cis* and *trans* monoene fractions (15); active layer, $SiO_2/AgNO_3$ (70:30); eluent, benzene/light petroleum (70:30). Although with this technique the monoene fractions could not be freed from conjugated dienes present in the sample, the method used for the determinations of the double-bond distribution could account for these contaminations in our experiments. In one experiment, *cis* and *trans* monoene fractions could not be separated because of a large amount of *cis,trans* conjugated diene present. In this case, monoenes and conjugated dienes were first separated by reversed-phase column chromatography, on Lipidex 5000 and a solvent system of chloroform/methanol/water (15:85:15) (16). Double-bond distribution: determination of the double-bond distribution in the *cis* and *trans* monoene fractions and in some conjugated diene fractions by oxidative degradation of these fractions via ozonolysis and GLC analysis of the aldehyde and aldehydic esters obtained (17).

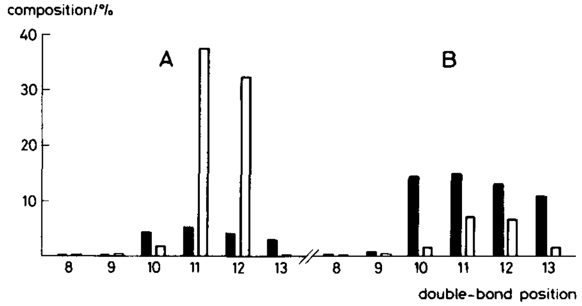


FIG. 4. Monoenes (■ *trans*; □ *cis*) obtained from partial hydrogenation of *t*10,*c*12 on catalysts A and B after isomerization in the absence of hydrogen for 5 min. (Mainly *t*10,*c*12 and *c*11,*t*13 were found in the reaction mixture prior to hydrogenation in a [10,12]/[11,13]-ratio of 2.0 and 1.2 for A and B, respectively).

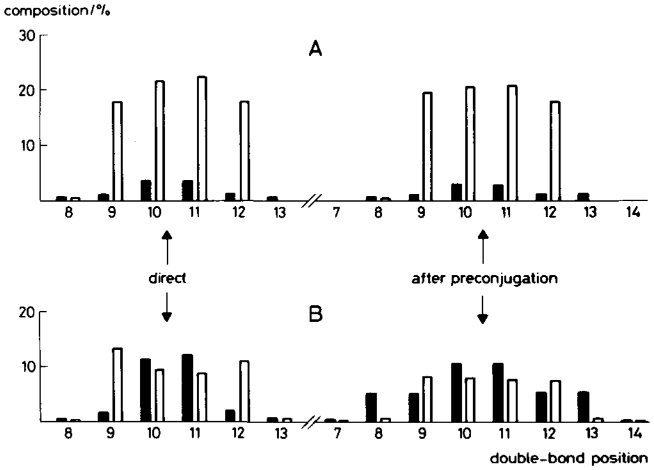


FIG. 5. Monoenes (■ *trans*; □ *cis*) obtained from partial hydrogenation of *c*9,*c*12 on catalysts A and B, directly and after preconjugation in the absence of hydrogen for 5 min. (After preconjugation, the residual diene fraction contained practically equal amounts of *c*9,*t*11, *t*10,*c*12, *t*8,*c*10 and *c*11,*t*13).

RESULTS AND DISCUSSION

Hydrogenation

On $[Rh(NBD)L_2]^+PF_6^-$ (catalyst A: L = $P(C_2H_5)_2C_6H_5$; catalyst B: L = $P(i\text{-}C_4H_9)_3$; catalyst C: L = $P(CH_3)_3$) *t*10,*t*12 is hydrogenated considerably faster and more selectively than *t*10,*c*12, which is hydrogenated about as fast as *c*9,*c*12 (Table I). The activity, as well as the selectivity sequence of the catalysts is A ≈ C > B. In this paper, we limit our attention to the detailed monoene compositions, as given in Figures 1-6. We can draw the following qualitative conclusions: (a) *c*9 isomerizes geometrically on catalysts A and B, most of the time, whereas on catalyst C, positional isomerization also occurs (Fig. 1); (b) on catalyst A, *t*10,*t*12 is hydrogenated almost exclusively via 1,4-addition of hydrogen to the *cisoid* conformation of the diene. The behavior of catalyst B does not deviate much from that of catalyst A in this respect, although on catalyst B, 1,2-addition increases. Monoene hardly isomerizes, if at all, in the presence of active diene (Fig. 2); (c) in contrast to the hydrogenation behavior of *t*10,*t*12, that of *t*10,*c*12 is largely influenced by ligands (Fig. 3); (d) in the absence of hydrogen a large amount of *c*11,*t*13 is formed from *t*10,*c*12. This can be concluded from the increased amount of 13-monoene, especially on catalyst B, after hydrogenation of the diene mixture obtained, and from the diene composition of this mixture (Fig. 4). On catalyst C, this diene isomerization also occurs to a considerable extent in the presence of hydrogen. The formation of *c*11,*t*13 can be explained easily by a process identical to a 1,5-shift of hydrogen (18,19); in this case only *c*11,*t*13 can be formed from *t*10,*c*12; (e) on catalyst A, hydrogenation after preconjugation of *c*9,*c*12 gives almost the same product composition as by direct hydrogenation (Fig. 5). This implies that the hydrogenation proceeds almost exclusively via conjugation. Also on catalyst B, the hydrogenation of *c*9,*c*12 proceeds mainly through conjugated intermediates;

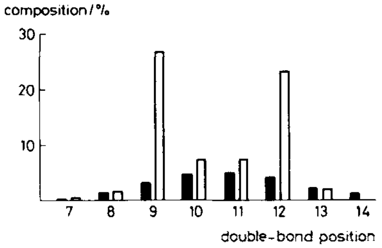
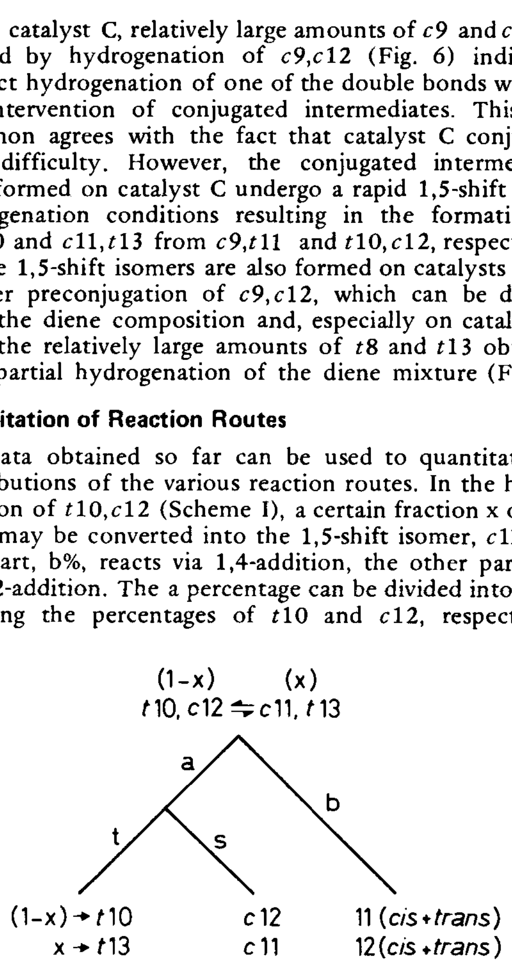


FIG. 6. Monoenes (● *trans*; □ *cis*) obtained from partial hydrogenation of *c*9,*c*12 on catalyst C after preconjugation in the absence of hydrogen for 5 min. (During preconjugation, less than 10% conjugated isomers arose).

(f) on catalyst C, relatively large amounts of *c*9 and *c*12 are formed by hydrogenation of *c*9,*c*12 (Fig. 6) indicating a direct hydrogenation of one of the double bonds without the intervention of conjugated intermediates. This phenomenon agrees with the fact that catalyst C conjugates with difficulty. However, the conjugated intermediates once formed on catalyst C undergo a rapid 1,5-shift under hydrogenation conditions resulting in the formation of *t*8,*c*10 and *c*11,*t*13 from *c*9,*t*11 and *t*10,*c*12, respectively; (g) the 1,5-shift isomers are also formed on catalysts A and B after preconjugation of *c*9,*c*12, which can be derived from the diene composition and, especially on catalyst B, from the relatively large amounts of *t*8 and *t*13 obtained after partial hydrogenation of the diene mixture (Fig. 5).

Quantitation of Reaction Routes

The data obtained so far can be used to quantitate the contributions of the various reaction routes. In the hydrogenation of *t*10,*c*12 (Scheme I), a certain fraction x of this diene may be converted into the 1,5-shift isomer, *c*11,*t*13. One part, b%, reacts via 1,4-addition, the other part, a%, via 1,2-addition. The a percentage can be divided into t and s, giving the percentages of *t*10 and *c*12, respectively.



SCHEME I. Hydrogenation of *t*10,*c*12 via various reaction routes: a and b are percentages of molecules reacting via 1,2- and 1,4-addition of hydrogen, respectively; t and s are the percentages *trans* and *cis* monoenes, respectively, formed by hydrogenation via 1,2-addition. Prior to hydrogenation, a fraction x of *t*10,*c*12 can isomerize to *c*11,*t*13 via a 1,5-shift mechanism.

Neglecting positional (positional isomerization rarely occurs on catalysts A and B, as can be concluded from Figure 1; on catalyst C, some positional isomerization occurs, so that in this case the calculations are somewhat less accurate) and geometrical isomerization (the sum of geometric isomers is used) and assuming that *cis* and *trans* monoenes are hydrogenated equally fast, we can solve a, b, t, s and x from the experimental data (see Appendix). These values (Table II) show that the 3 catalysts have a slight preference for 1,4-addition over 1,2-addition of hydrogen to conjugated *trans,cis* double-bond systems. However, a great ligand influence is observed on 1,5-shift activity and on the choice between the *cis* and *trans* double bond in the case of 1,2-addition of hydrogen: the 1,5-shift activity of the catalysts under hydrogenation conditions decreases in the order C > A > B; the sterically unhindered complexes A and C hydrogenate the *trans* double bond preferentially, whereas catalyst B, which is provided with rather bulky ligands, has a strong preference for the *cis* double bond on selective hydrogenation of conjugated *trans,cis* diene via 1,2-addition.

The values, derived for a, b, t and s can be applied for the calculation of the monoene composition obtained from partial hydrogenation of mixtures of conjugated dienes. This is exemplified in Table III for mixtures of *t*10,*c*12 and *c*11,*t*13 obtained from *t*10,*c*12 on catalysts A and B in the absence of hydrogen (Fig. 4). Also in these experiments, catalyst A shows a small 1,5-shift activity under hydrogenation conditions, whereas catalyst B is rather inactive in this respect (catalyst A starts hydrogenation with a mixture consisting of 67% *t*10,*c*12 and 33% *c*11,*t*13; after hydrogenation these values are 62 and 38%, respectively). The calculated compositions agree reasonably well with the experimental ones, indicating the reliability of the values for the parameters used.

We can now evaluate the hydrogenation routes of *c*9,*c*12, using the data derived from the conjugated dienes. In Scheme II, d is the percentage of diene that reacts via direct hydrogenation of one of the double bonds. The rest (i %) is hydrogenated via conjugated intermediates. A certain fraction x of the primary conjugated dienes (*c*9,*t*11 and *t*10,*c*12) can be isomerized via the 1,5-shift mechanism to *t*8,*c*10 and *c*11,*t*13. Finally, these dienes are converted into monoenes in the same way as described in Scheme I. From the monoene composition, the variables i, d and x can be calculated, using the values of a, b, t and s given in Table II. The results are compiled in Table IV.

We find rather large differences in the contribution of the conjugation mechanism to the hydrogenation of conjugatable *cis,cis* dienes. On catalyst A, the methylene-interrupted diene is hydrogenated almost exclusively through conjugated intermediates, whereas catalyst C largely hydrogenates one of the double bonds directly, without the intervention of conjugated intermediates. In this respect, the behavior of catalyst B is between that of A and C. As for the hydrogenation on catalyst C, we should take into

TABLE II

Contribution (%) of Various Reaction Routes to the Formation of Monoenes from *t*10,*c*12 by Hydrogenation on Catalysts A, B and C According to Scheme I

Catalyst	a	b	t	s	1,5-Shift[a]
A	40.6	59.4	10.4	30.2	14.4
B	44.5	55.5	34.5	10.0	0.0
C	43.2	56.8	10.7	32.5	40.0

[a] 1,5-shift = 100 times value of x.

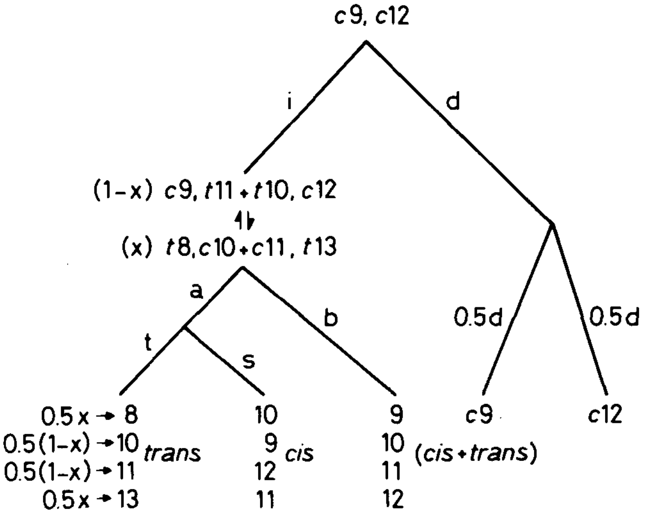
TABLE III

Calculated and Experimental Compositions (%) of Monoenes Obtained from Partially Hydrogenated *t*10,*c*12 Which Was Isomerized in the Absence of Hydrogen for 5 Minutes prior to Hydrogenation on Catalysts A and B

Double bond position	A		B	
	Calcd.[a]	Exp.	Calcd.[b]	Exp.
10	5.7	6.2	13.3	16.1
11	42.7	42.6	24.6	22.0
12	36.6	36.5	21.4	19.7
13	3.5	3.2	10.9	12.4

[a] Based on 62% *t*10,*c*12 and 38% *c*11,*t*13.

[b] Based on 55% *t*10,*c*12 and 45% *c*11,*t*13.



SCHEME II. Hydrogenation of *c*9,*c*12 via various reaction routes: d is the percentage of *c*9,*c*12 that is reduced via direct hydrogenation of one of the double bonds and i represents that percentage which is reduced through conjugated intermediates. The meaning of a, b, t, s and x is given in Scheme I.

consideration that hydrogenation was started 5 min after the addition of the substrate; in this period, ca. 10% conjugated intermediates were formed. This implies that hydrogenation of *c*9,*c*12, started immediately after addition, should result in a d/i ratio higher than one.

Comparison with the Literature

It is of interest to compare our results with those described by Frankel and Butterfield (19) who used arene-$Cr(CO)_3$ complexes as catalysts. These catalysts were used under completely different conditions from those applied for the rhodium catalysts described in this paper. Temperatures of 125-175 C and hydrogen pressures of 3000 kPa (30 atm) were necessary to hydrogenate 1,3- and 1,4-dienoic fatty esters. Upon hydrogenation of *c*9,*t*11 with benzene-$Cr(CO)_3$ at 165 C and 3000 kPa hydrogen pressure, 8-, 9-, 10- and 11-monoenes were found in relative amounts of 5.5, 43.6, 42.2 and 8.7%, respectively. We used these data for the quantitation of the various reaction routes. The following values (%) were found:

1,5-shift (100 x):	39.0
1,2-addition (a):	60.5
1,4-addition (b):	39.5
formation of *trans* monoene (t):	14.2
formation of *cis* monoene (s):	46.3

From these values and Table II it can be concluded that the benzene-$Cr(CO)_3$ catalyst resembles catalyst A to a certain extent in the contribution of the various reaction routes, and even more so as both catalysts hydrogenate *c*9,*c*12 almost exclusively through conjugated intermediates. The conclusion that benzene-$Cr(CO)_3$ reduces *c*9,*t*11 preferentially via 1,2-addition of hydrogen is not supported by the results of deuteration experiments.

On the contrary, using deuterium for the reduction of *c*9,*t*11, Frankel et al. (20) found with ^{2}H-NMR that 95% of the deuterium in the monoenes obtained was on the α-methylene carbons. This result is a compelling evidence that deuteration proceeds almost exclusively via 1,4-addition of deuterium across a *cis,trans* 1,3-diene. It shows that the neglect of positional isomerization in our evaluation is not allowed for Frankel's hydrogenation experiments.

Mechanism of the Hydrogenation of 1,3- and 1,4-Dienes

According to Schrock and Osborn (6), 2 hydrogenation cycles can be distinguished for the hydrogenation of 1,3- and 1,4-dienes (Fig. 7). In reaction path I, the rate-determining step is the attack of hydrogen to $[Rh(1,3\text{-diene})L_2]^+$. Before this attack, various reactions can occur: if desorption can take place, 1,4-dienes can isomerize completely to conjugated dienes; the conjugated dienes can isomerize via a 1,5-hydrogen shift; conjugation of 1,4-dienes in the absence of hydrogen can be blocked by a low desorption rate of conjugated diene. In this connection, a conjugation experiment with 1,4-cyclohexadiene on $[Rh(P(C_6H_5)_3)_2S_2]^+$ carried out by Schrock and Osborn (6) is notable. The diene is conjugated stoichiometrically in the absence of hydrogen to form $[Rh(1,3\text{-cyclohexadiene})(P(C_6H_5)_3)_2]^+$ which does not dissociate because the complex is too stable. This implies that excess 1,4-cyclohexadiene is not conjugated by $[Rh(1,3\text{-cyclohexadiene})(P(C_6H_5)_3)_2]^+$ and that the complexed diene can only be removed by hydrogenation. 1,5-Shift may be retarded in the presence of hydrogen, because of occupation of the essential vacant sites for this reaction by hydrogen. The

TABLE IV

Contribution (%) of Various Reaction Routes to the Formation of Monoenes from *c*9,*c*12 by Hydrogenation on Catalysts A, B and C According to Scheme II

Catalyst	d	i	b	a	t	s	1,5-Shift
A	7.9	92.1	54.7	37.4	9.6	27.8	25
B	29.6	70.4	39.1	31.3	24.5	6.8	12
C[a]	49.5	50.5	28.7	21.8	5.4	16.4	40[b]

[a] Hydrogenation after contact with the catalyst in the absence of hydrogen for 5 min.

[b] Because of the influence of monoene isomerization, the 1,5-shift activity could not be calculated exactly.

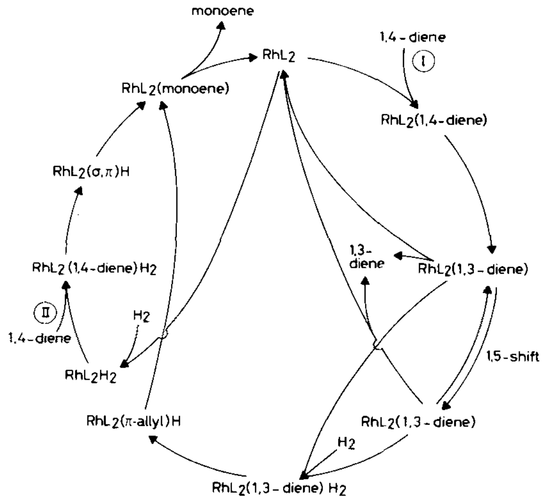


FIG. 7. Reaction routes for the selective hydrogenation of 1,4- and 1,3-dienes. Positive charge and coordinated solvent molecules have been omitted.

reduction proceeds at last by hydride transfer to the conjugated dienes, resulting in π-allyl complexes which are further reduced to monoenes.

In reaction route II, 1,4-diene reacts with a dihydride species: one of the double bonds is reduced directly via an ethylene-bridged σ,π-complex (21) as intermediate. The contribution of this reaction route to the hydrogenation process depends on the concentration of $RhL_2H_2^+$. Relatively high concentrations will be obtained when hydrogen competes successfully with 1,4-diene for RhL_2^+.

The low conjugation rate of *c*9,*c*12 on catalyst C in the absence of hydrogen may be ascribed to a low desorption rate of conjugated diene resulting from a fairly stable $[Rh(1,3\text{-diene})(P(CH_3)_3)_2]^+$ moiety. The lifetime of this intermediate may be long enough for 1,5-shift equilibrium (or nearly) of conjugated dienes in the coordinated state, even in the presence of hydrogen (Table II). However, despite the assumed stable conjugated diene complex, *c*9,*c*12 is not preferentially hydrogenated through this intermediate on complex C. On the contrary, the direct hydrogenation of one of the double bonds predominates over the conjugation route.

In this light, we do not quite understand why catalyst A almost exclusively hydrogenates through conjugated intermediates (route I), whereas catalyst B also reduces via route II, although both catalysts conjugate *c*9,*c*12 very fast in the absence of hydrogen. Apparently, both electronic and steric factors play a role in the rate of formation of conjugated diene- and σ,π-complexes as intermediates in the hydrogenation process.

Another remarkable phenomenon is the regioselective hydrogenation of one of the double bonds in *cis,trans* 1,3-dienes via 1,2-addition of hydrogen. The question why catalysts A and C preferentially hydrogenate the *trans* double bond, whereas catalyst B predominantly reduces the *cis* double bond, cannot be answered adequately with our present knowledge. In any case, we observe that the 3 catalysts hydrogenate the conjugated *cis,trans* dienes mainly via a *cisoid* conformation; we find roughly a ratio *cisoid*/*transoid* conformation of 6 on complexes A and C and a ratio of 2 on complex B. On hydrogenation, one of the hydrides in $Rh(1,3\text{-diene})L_2H_2$ is transferred to the adsorbed diene, resulting in π-allyl complex as intermediate. In complex B, the α-methylene group of the *cis* double bond probably experiences a strong steric interaction with one of the bulky $P(i\text{-}C_4H_9)_3$ ligands. This interaction may be reduced when one of the hydrides is transferred preferentially to the *cis* double bond, finally resulting in the accumulation of *trans* double bonds at 1,2-addition of hydrogen. For the complexes A and C, the steric interaction in question may be considerably smaller; the *cis* double bond may interact more strongly than the *trans* double bond with the rhodium ion, so that the *trans* double bond may be attacked preferentially by one of the hydrides. This reaction route results in the formation of *cis* monoene at 1,2-addition of hydrogen.

APPENDIX

The calculations applied are illustrated with 2 examples.

Example 1

Hydrogenation of *t*10,*c*12 with catalyst A (Fig. 3): we found relative amounts of 10-, 11-, 12- and 13-monoenes of 8.9, 55.2, 34.4 and 1.5% (total 100%), respectively. According to Scheme I, the following equations can be derived:

$$\begin{aligned}
&(10)\quad (1-x)t &&= 8.9\\
&(11)\quad x\,s + (1-x)b &&= 55.2\\
&(12)\quad (1-x)s + x\,b &&= 34.4\\
&(13)\quad x\,t &&= 1.5
\end{aligned}$$

These equations result in a = 40.6, b = 59.4, t = 10.4, s = 30.2 and x = 0.144.

Example 2

Direct hydrogenation of *c*9,*c*12 on catalyst A (Fig. 5): we found 8-, 9-, 10-, 11-, 12- and 13-monoenes in relative amounts of 1.2, 20.6, 27.6, 28.6, 21.1 and 0.9% (total 100%), respectively. Assuming a symmetrical double-bond distribution, we derive the following equations (mean values of 8/13- and 9/12-monoenes are used) on the basis of Scheme II:

$$\begin{aligned}
&(8)\quad 0.5\,x\,t &&= 1.1\\
&(9)\quad 0.5\,x\,b + 0.5\,(1-x)s + 0.5\,d &&= 20.8
\end{aligned}$$

We can solve x and d when we further assume that the conjugated dienes, formed prior to hydrogenation, are hydrogenated in the same way as in example 1. This means that the values for b, t and s given in example 1 can be used when we multiply these values by a balance factor f. Thus,

$$\begin{aligned}
&0.5 \times f\,10.4 &&= 1.1\\
&0.5 \times f\,59.4 + 0.5\,f\,(1-x)\;30.2 + 0.5\,d &&= 20.8\\
&f + 0.01\,d &&= 1
\end{aligned}$$

From these equations it follows that d = 7.9, i = 92.1, a = 37.4, b = 54.7, t = 9.6, s = 27.8 and x = 0.25.

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Hydrogenation of Methyl Sorbate and Soybean Esters with Polymer-bound Metal Catalysts[1]

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ABSTRACT

New polymer-bound hydrogenation catalysts were made by complexing $PdCl_2$, $RhCl_3 \cdot 3H_2O$, or $NiCl_2$ with anthranilic acid anchored to chloromethylated polystyrene. The Pd(II) and Ni(II) polymers were reduced to the corresponding Pd(O) and Ni(O) catalysts with $NaBH_4$. In the hydrogenation of methyl sorbate, these polymer catalysts were highly selective for the formation of methyl 2-hexenoate. The diene to monoene selectivity decreased in the order: Pd(II), Pd(O), Rh(I), Ni(II), Ni(O). Kinetic studies support 1,2-reduction of the Δ4 double bond of sorbate as the main path of hydrogenation. In the hydrogenation of soybean esters, the Pd(II) polymer catalysts proved superior because they were more active than the Ni(II) polymers and produced less *trans* unsaturation than the Rh(I) polymers. Hydrogenation with Pd(II) polymers at 50-100 C and 50 to 100 psi H_2 decreased the linolenate content below 3% and increased *trans* unsaturation to 10-26%. The linolenate to linoleate selectivity ranged from 1.6 to 3.2. Reaction parameters were analyzed statistically to optimize hydrogenation. Recycling through 2 or 3 hydrogenations of soybean esters was demonstrated with the Pd(II) polymers. In comparison with commercial Pd-on-alumina, the Pd(II) polymers were less active and as selective in the hydrogenation of soybean esters but more selective in the hydrogenation of methyl sorbate.

INTRODUCTION

Polymer-bound catalysts have attracted much attention recently because they can offer the selectivity advantage of homogeneous catalysts and the ease of separation from products of heterogeneous catalysts (1-4). Bruner and Bailar (5,6) used a polymeric ligand containing diphenylbenzylphosphine complexed with either $PtCl_2$ or $PdCl_2$ to prepare heterogeneous catalysts that are analogs of the homogeneous catalysts $PtCl_2(Ph_3P)_2$ and $PdCl_2(Ph_3P)_2$. The $PdCl_2$ polymeric complex proved to be an active hydrogenation catalyst of soybean esters. Pittman et al. (7) prepared a crosslinked polystyrene complex with $Cr(CO)_3$ that was active as a stereoselective catalyst for the hydrogenation of methyl sorbate to *cis*-3-hexenoate. This type of stereoselectivity was previously observed with the homogeneous arene-$Cr(CO)_3$ complexes (8-10). Although the crosslinked polystyrene-$Cr(CO)_3$ was less active than the homogeneous analogs, it was reportedly recycled as often as 7 times. In our laboratory, depending on conditions, this same catalyst could be recycled from 2 (11) to 10 times with methyl sorbate (Friedrich et al., unpublished results). However, this catalyst lost its activity and could not be recycled when used with soybean oil esters at 180-200 C, the temperature necessary to hydrogenate the unconjugated fatty esters (9,12).

Our interest in more stable, active and recyclable catalysts for the selective hydrogenation of unsaturated fats led us to this investigation on new polymer-bound catalysts made by complexing $PdCl_2$, $RhCl_3$, or $NiCl_2$ with anthranilic acid anchored to chloromethylated polystyrene. The Pd(II) polymer-bound catalyst was active for the hydrogenation of alkenes, dienes, benzene, nitrobenzene and benzonitrile (13,14). The Rh(I) polymer-bound catalyst reduced olefinic and aromatic hydrocarbons and carbonyl, nitrile and nitro functional groups (15). Although hydrogenation of corn oil and soybean esters was indicated with these catalysts, no product analyses were made. In this report, Pd(II), Pd(O), Rh(I), Ni(II) and Ni(O) polymer catalysts were evaluated in the hydrogenation of methyl sorbate and soybean esters. The recyclability of the Pd(II) polymer catalyst also was tested.

EXPERIMENTAL

Materials and Methods

Preparation of the Pd(II) and Rh(I) polymer catalysts was described previously (13-15). One Pd(II) polymer preparation was sieved into 3 fractions of different mesh size: 20, 40 and higher than 100. The Ni(II) catalyst was prepared the same way by reacting anthranilic acid anchored chloromethylated styrene with $NiCl_2 \cdot 6H_2O$ in ethanol. The Ni(O) catalyst was prepared by treating the Ni(II) catalyst with excess $NaBH_4$ in ethanol (N. Holy, unpublished work). The Pd(O) catalyst was prepared similarly using a methanolic solution of $NaBH_4$. Methyl sorbate and soybean esters were prepared as described elsewhere (11). Methyl *cis*-3-hexenoate (98% pure plus 2% methyl 2-hexenoate by GC) was prepared by stereoselective hydrogenation of methyl sorbate with methyl benzoate-$Cr(CO)_3$ (10). Gas chromatographic (GC) analyses of hydrogenated methyl sorbate were carried out with a 72 x 1/8 in. column packed with 15% EGSS-X on Gas Chrom P 100/120 mesh (Applied Science Labs, State College, PA), programming between 80 and 130 at 2 C/min at 30 ml/min carrier flow rate; for analyses of hydrogenated soybean esters, a 10% DEGS column was used isothermally at 190 C. For kinetic studies with methyl sorbate, a more efficient GC column was used to separate 2-, 3- and 4-hexenoates: 10% SP2330 (68% cyanopropyl

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