Transfer Hydrogenation and Transfer Hydrogenolysis: XII. Selective Hydrogenation of Fatty Acid Methyl Esters by Various Hydrogen Donors

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ABSTRACT

The selective hydrogenation of methyl linoleate was studied using various organic compounds as hydrogen sources in the presence of homogeneous and metallic palladium catalysts. Complete selectivity to monoenes and relatively little formation of isolated *trans* double bonds were realized by the hydrogen transfer from L-ascorbic acid at 47% conversion of starting material to hydrogenation products. The hydrogenation by *trans*-1,2-cyclohexanediol catalyzed by $RuH_2(PPh_3)_4$ also showed rather high selectivity to *cis*-monoenes. In the reaction catalyzed by $RuH_2(PPh_3)_4$, the presence of these hydroxy compounds increased the isomerization of methyl elaidate to *cis*-monoenes.

INTRODUCTION

In the hydrogenation of oils, the formation of saturated products and *trans* double bonds is generally undesirable, and high selectivity to *cis*-monoenes is sought. In a previous paper (1), we reported that methyl linoleate was reduced by hydrogen transfer from indoline and 2-propanol, and the selectivity to *cis*-monoenes was varied not only by catalysts but also by hydrogen donors. These results suggest that the high selectivity to *cis*-monoenes in the hydrogenation of the diene is realized by appropriate combination of hydrogen donors and catalysts. This study was undertaken to find reaction systems to give high selectivity to *cis*-monoenes.

EXPERIMENTAL PROCEDURES

The hydrogenation procedure and methods of product analysis were described in a previous paper (1). When some natural polyols were used as hydrogen donors, tetrahydrofuran was used as a solvent, and the concentrations of the substrates were half as much as were mentioned previously (1) because of their poor solubility in aprotic solvents. The catalysts used were those which showed high activity in the hydrogen transfer from indoline to methyl linoleate. The yield of products was determined by gas liquid chromatographic (GLC) analyses, and the amount of isolated *trans* bonds was measured by IR analyses, using the peak at 968 cm^{-1} as elaidate (2). But the experimental errors of the percent *trans* were rather large when the product contained conjugated dienes.

Materials

The preparation of catalysts, methyl linoleate, alkali-conjugated methyl octadecadienoates, and methyl oleate was previoualy described (1). Methyl *trans*-9,*trans*-12-octadecadienoate was prepared by isomerization of methyl linoleate by sodium nitrite (3). Methyl elaidate was prepared from esterification of refined elaidic acid with methyl alcohol. The hydrogen donors, the additives, and the solvents were purified by the usual methods. Glucose, sucrose, inositol, and L-arabinose were purchased and used without purification.

Identification of Dehydroascorbic Acid

The reaction mixture (2 ml) containing 71 mg of added L-ascorbic acid was prepared by the procedure described in Table I, B. After heating at 140 C for 3 hr, the volatile compounds were removed from the reaction mixture under reduced pressure. The residue was dissolved in water and then washed by carbon tetrachloride to remove C_{18}-esters. This aqueous solution was treated with 2,4-dinitrophenylhydrazine (4). The mixture obtained was submitted to thin layer chromatography (TLC), which was performed using Wakogel-5 F as adsorbent and toluene-ethyl acetate mixture (1:1) as developer (5). The resulting thin layer chromatogram was compared with that of iodine oxidized dehydroascorbic acid (4). The dehydrogenated product eluted from the TLC plate was submitted to infrared analysis. Then the dehydrogenation product was qualitatively identified as L-dehydroascorbic acid by the Rf value, infrared spectrum, and melting point (4). The other spots on the thin layer chromatogram were not identified.

RESULTS

A part of the results is summarized in Table I. In the table, conversion shows the total yield of the hydrogenation products, and selectivity represents the percentage of monoenes in the hydrogenation products. *trans* percent (A) implies the supposed yield of *trans* isomers based on elaidate, and *trans* percent (B) exhibits the percentage of isolated *trans* double bonds in all the isolated double bonds in the reaction mixtures. The former notation has been used in most reports on the hydrogenation of oils, but the latter seems to be more useful in scientific discussions. As the rough tendency, selectivity decreased, and the *trans* percent (B) increased with an increment in conversion. Therefore, the comparison of selectivity and *trans* percent (B) at constant conversion is desirable to discuss the selectivity to *cis*-monoenes. For this purpose, reaction conditions were modified to obtain conversion ranging from 70% to 90%.

The combination of hydrogen donors and catalysts was determined by reference to the literature and our experience. Cyclohexene (6-10), dioxane (10-12), and 2,5-dihydrofuran (10,13) have been reported as hydrogen donors in transfer hydrogenation. Except for the case of cyclohexene-palladium carbon system, conversion and *trans* percent (B) were low in the reduction by these hydrogen donors. Selectivity was low in cyclohexene-palladium carbon system, though the conversion was high. In the hydrogenation by dioxane, the activity of catalysts expressed by conversion decreased in the order $RuH_2(PPh_3)_4 > RhH(PPh_3)_4 > RuCl_2(PPh_3)_3$. When tetrahydroquinoline was used, the order was $RuCl_2(PPh_3)_3 \gg PdCl_2 \approx (NH_4)_2PdCl_4$ and 5% palladium carbon. The activity decreased in the order $RuH_2(PPh_3)_4 > RuCl_2(PPh_3)_3 > RhH(PPh_3)_4 \approx RhCl(PPh_3)_3$, in the reaction of tetralin. In the reduction by 2,5-dihydrofuran, the conversion diminished in the sequence $RhH(PPh_3)_4 > PdCl_2 > RuH_2$-

TABLE I

Transfer Hydrogenation of Methyl Linoleate

Hydrogen donor	Dehydrogenation products	Catalyst	React.[a] cond.	Yield of products (%) S	M	CD	Conv.[c] (%)	Select.[d] (%)	*trans* (%)[e] A	B
Cyclohexene	Benzene	5% Pd-C[f]	A	48	40	0	88	45	40	63
Dioxane	Dioxene	$RuH_2(PPh_3)_4$	A	0	42	28	42	100	34	34
Tetrahydro quinoline	Quinoline	$RuCl_2(PPh_3)_3$	A	0	38	6	38	100	23	15
Tetralin	Naphthalene	$RuH_2(PPh_3)_4$	A	7	28	38	35	80	37	45
2,5-Dihydrofuran	Furan	$RhH(PPH_3)_4$	A	10	26	33	36	73		
		$RuH_2(PPh_3)_4$	A	0	26	51	26	100		
L-Ascorbic acid	Dehydroascorbic acid	$RuH_2(PPh_3)_4$	B	0	70	0	70	100	25	19
		$RuH_2(CO)(PPh_3)_3$	B	0	47	18	47	100	6	5
		$RhCl_3 \cdot 2H_2O$	B	0	40	18	40	100	34	25
		$RuCl_2(PPh_3)_3$	B	0	35	36	35	100	26	28
Glucose	Unidentified	$RuCl_2(PPh_3)_3$	B	0	91	0	91	100	58	53
		$RuH_2(PPh_3)_4$	B	0	42	37	42	100	25	29
L-Arabinose		$RuH_2(PPh_3)_4$	B	12	59	7	71	83	Trace	
Sucrose		$RuCl_2(PPh_3)_3$	B	0	48	26	48	100	24	25
		$RuH_2(PPh_3)_4$	B	0	33	49	33	100	21	30
Inositol[g]		$RuH_2(PPh_3)_4$	B	1	32	34	33	96	23	23

[a] A: methyl linoleate (0.2 M), a hydrogen donor (0.4 M), and a catalyst (20 mM) were heated in toluene at 140 C for 3 hr. B: methyl linoleate (0.1 M), a hydrogen donor (0.2 M), and a catalyst (10 mM) were heated in tetrahydrofuran at 140 C for 3 hr.

[b] S = methyl stearate. M = monoenes. CD = conjugated dienes.

[c] Conv. = conversion, which is given by $\frac{[\text{Stearate}] + [\text{Monoenoates}]}{[C_{18}\text{-esters}]} \times 100$.

[d] Select. = selectivity, which is given by $\frac{[\text{Monoenoates}]}{[\text{Stearate}] + [\text{Monoenoates}]} \times 100$.

[e] *trans* Percent (A) = $\frac{[\textit{trans} \text{ Isomers as elaidate}]}{[C_{18}\text{-esters}]} \times 100$ by IR analysis.

trans percent (B) = $\frac{[\textit{trans} \text{ isomers as elaidate}]}{[\text{Monoenes}] + [\text{Nonconjugated dienes}] \times 2} \times 100$

The compositions used in footnotes c,d, and e except for the *trans* isomers as elaidate were determined by gas liquid chromatographic (GLC) analysis.

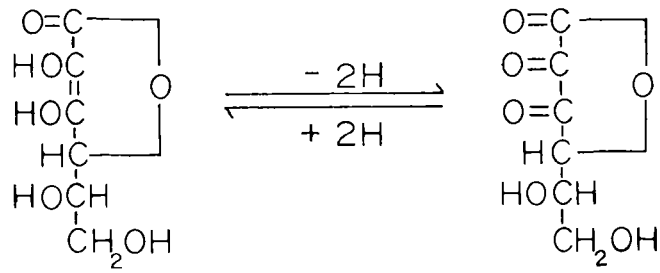
[f] The concentration of this catalyst was 10 g/l.

[g] This hydrogen donor did not dissolve completely.

$(PPh_3)_4 > RuH_2(CO)(PPh_3)_3 \approx RuCl_2(PPh_3)_3 \approx$ palladium carbon $> K_2PtCl_4 \approx (NH_4)_2PdCl_4 \approx RhCl_3 \approx RhCl(PPh_3)_3 \approx CuBr \approx IrCl_3$. In the reaction of this hydrogen donor, the analysis of *trans* isomers could not be performed, because the IR spectra of the reaction mixtures showed a broad peak at 960 ~ 1000 cm^{-1}. The fact that the total amount of C_{18}-esters and that of 2,5-dihydrofuran and furan diminished suggests that a Diels-Alder type reaction occurred. It was noteworthy that in spite of low conversion, a considerable amount of stearate was formed in the reaction of tetralin and 2,5-dihydrofuran. Diethyl 1,5-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate, which has been reported to reduce some organic compounds without catalysts (14), scarcely hydrogenated the linoleate.

Then we examined some naturally occurring polyhydroxy compounds including L-ascorbic acid, which is known to function as a reducing agent to give L-dehydroascorbic acid in vivo (15). In the reduction of linoleate with this reductant catalyzed by $RuH_2(PPh_3)_4$, conversion, selectivity, and *trans* percent (B) were 70, 100, and 19% respectively; and in the one catalyzed by $RuH_2(CO)(PPh_3)_3$, the parameters were 47, 100, and 5%. Not shown in Table I are reactions at 140 C for 6 hr and at 160 C for 3 hr with $RuH_2(CO)(PPh_3)_3$, in which the conversion changed little, but the *trans* percent increased to 20~30% while selectivity to monoenes remained high. In any case, with this hydrogen donor the selectivity was 100%. In these reactions L-dehydroascorbic acid was identified in the product mixture by TLC analysis. This result shows that endiol structure of the reductant was transformed to diketone form by the hydrogen transfer.

In the glucose-$RuH_2(PPh_3)_4$ system, conversion and



selectivity were high, but *trans* percent (B) was not so low. The L-arabinose-$RuH_2(PPh_3)_4$ system showed high conversion and very low *trans* percent (B), but the selectivity was not complete. Sucrose and inositol also reduced linoleate. It is worth noting that in almost all the reactions with conversions of less than 70%, significant amounts of conjugated dienes were detected. Among the reactions given in Table I, the L-ascorbic acid-$RuH_2(PPh_3)_4$ system seems to be best. Considering this and the remarkable result obtained in the reduction by 2-propanol (1), we undertook to examine the hydrogen transfer from hydroxy compounds catalyzed by $RuH_2(PPh_3)_4$ in more detail. Among the results shown in Table II, the reduction by *trans*-1,2-cyclohexanediol is noticeable becuase it realized lowest percent *trans* and relatively high selectivity. However, *cis*-1,2-cyclohexanediol did not show such superiority. Ethyl lactate, acetoin, and 2-methylcyclohexanol exhibited high selectivity and relatively low *trans* percents, but conversion was low.

The results described so far show that not only conver-

TABLE II

Transfer Hydrogenation of Methyl Linoleate by Alcohols[a]

Hydrogen donor	Yield of products (%)[b] S	M	CD	Conv.[b] (%)	Select.[b] (%)	*trans* (%)[b] A	B
2-Phenylethanol	11	40	25	51	74	25	28
1-Phenylethanol	34	56	0	90	62	69	79
3-Pentanol	22	57	0	79	72	91	92
Ethyl lactate	1	65	16	66	98	34	33
Benzoin	0	54	8	54	100	90	69
Acetoin	0	44	15	44	100	38	30
1,3-Butanediol	21	63	0	84	75	82	86
2,3-Butanediol	14	40	23	54	74	66	77
Glycerine	11	36	32	47	77	23	29
Cyclohexanol[c]	14	78	0	92	85	90	95
2-Methylcyclohexanol	0	65	0	65	100	49	48
3-Methylcyclohexanol[c]	18	77	0	94	82	59	66
cis-1,2-Cyclohexanediol	12	76	0	88	86	79	79
trans-1,2-Cyclohexanediol[d]	6	68	0	75	92	20	17

[a]Methyl linoleate (0.2 M), the designated alcohol (0.4 M), and $RuH_2(PPh_3)_4$ (20 mM) were heated at 140 C for 3 hr in toluene.

[b]Footnotes in this table are the same as those in Table I.

[c]Reaction temperature was 120 C. Other reaction conditions were the same as those indicated in footnote a.

[d]Reaction time was 2 hr. Other reaction conditions were the same as those indicated in footnote a.

TABLE III

Effect of Additives

Hydrogen donor	Additive	React[a] cond.	Yield of products[a] S	M	CD	Conv.[b] (%)	Select.[b] (%)	*trans* (%)[b] A	B
Indoline	None	A	8	83	0	91	91	63	62
	L-Ascorbic acid	B	0	81	Trace	81	100	29	24
	Dehydro-L-ascorbic acid	B	0	70	0	70	100	41	31
	Pyrocatechol	C	0	43	11	43	100	50	38
	Resorcinol	D	0	80	0	80	100	70	59
	o-Diaminobenzene	C	0	30	18	30	100	44	32
	m-Diaminobenzene	D	14	68	0	82	83	27	26
Cyclohexanol	L-Ascorbic acid	E	0	78	0	78	100	44	36
	Dehydro-L-ascorbic acid	E	0	77	0	77	100	68	55
	Pyrocatechol	C	0	28	22	28	100	43	34
	Resorcinol	C	0	52	7	54	100	136	102
	o-Diaminobenzene	C	0	22	33	22	100	22	20
	m-Diaminobenzene	D	21	65	0	80	76	18	19
L-Ascorbic acid	Triphenylphosphine	F	0	59	4	59	100	75	56

[a]A: methyl linoleate (0.2 M), hydrogen donor (0.4 M), additive (0.2 M), and $RuH_2(PPh_3)_4$ (20 mM) were heated at 120 C for 3 hr in toluene; B: heated at 120 C for 3 hr in THF; C: heated at 140 C for 3 hr in toluene; D: heated at 140 C for 2 hr in toluene; and E: heated at 140 C for 3 hr in THF. F: methyl linoleate (0.1 M), hydrogen donor (0.2 M), additive (10 mM), and $RuH_2(PPh_3)_4$ (10 mM) were heated at 140 C for 3 hr in THF.

[b]Footnotes in this table are the same as those in Table I.

sion but also product distirbution varied greatly. This fact suggests that hydrogen donors or dehydrogenated donors coordinated on catalysts as ligands participate in the transition states of hydrogen transfer. To inspect this suggestion, additives with hydrogen-giving ability lower than that of the hydrogen donors were added to the reaction catalyzed by $RuH_2(PPh_3)_4$ (Table III). The addition of L-ascorbic acid to the reduction by indoline and cyclohexanol improved considerably the selectivity to *cis*-monoenes; addition of L-dehydroascorbic acid and *m*-diaminobenzene did so moderately. Resorcinol raised selectivity but did not lower percent *trans*. Pyrocatechol and *o*-diaminobenzene lowered conversion. In the hydrogenation by L-ascorbic acid, the addition of triphenylphosphine lowered conversion a little and raised percent *trans* intensively shown in Table III). Perhaps the phosphine added may occupy coordination sites of active species and interfere with the coordination of the hydrogen donor which further promotes the formation of *cis*-monoenes.

To study the route leading to the formation of *cis*-monoenes, the hydrogen transfer from indoline, L-ascorbic acid, and *trans*-1,2-cyclohexanediol to methyl *trans*-9,*trans*-12-octadecadienoate, conjugated octadecadienoates, oleate and elaidate in addition to linoleate, was investiaged using $RuH_2(PPh_3)_4$ as a catalyst. The conjugated dienes, which were prepared from linoleic acid by the isomerization catalyzed by alkali, were shown to consist of 90% of *cis-trans* and 10% of *trans-trans* isomers by GLC analysis.

The results are given in Table IV. When L-ascorbic acid was used as a hydrogen donor, the selectivity to monoenes was 100% in every case, and *trans* percent (B) was about 30% in the reduction of dienes. Oleate and elaidate were hardly reduced in the presence of the acid even at 140 C. This means that L-ascorbic acid not only gives no hydrogen to monoenes but also inhibits the hydrogen transfer from $RuH_2(PPh_3)_4$ to monoenes. This may be responsible for its complete selectivity to monoenes. In the reaction of the monoenes, *trans* percent (B) was nearly equal and about 40%, showing that the ratio of *cis* to *trans* was about 3:2. (It might be speculated that *cis*- and *trans*-monoenes are equilibrated, based on the fact that the reaction of oleate

TABLE IV

Transfer Hydrogenation of Fatty Acid Methyl Esters by $RuH_2(PPh_3)_4$[a]

Hydrogen donor	Substrate	Yield of products (%)[b] S	M	CD	Conv.[b] (%)	Select.[b] (%)	*trans* (%)[b] A	B
L-Ascorbic acid	Nonconjugated t,t-dienoate[c]	0	66	8	66	100	37	31
	Conjugated dienoates[d]	0	96	4	96	100	30	25
	Oleate	0	100	0	---	---	36	36
	Elaidate	0	100	0	---	---	40	40
None	Oleate	13	87	0	---	---	57	67
	Elaidate	11	89	0	---	---	63	71
trans-1,2-Cyclohexanediol	Nonconjugated t,t-dienoate[c]	14	75	0	89	84	21	22
	Conjugated dienoates[d]	13	87	0	100	87	17	20
	Oleate	20	80	0	---	---	5	6
	Elaidate	12	88	0	---	---	7	8
Indoline	Linoleate	15	66	0	81	82	87	84
	Nonconjugated t,t-dienoate[c]	21	79	0	100	79	62	78
	Conjugated dienoates[d]	61	39	0	100	39	23	59
	Oleate	76	24	0	---	---	17	70
	Elaidate	81	20	0	---	---	11	58

[a] In the reactions of *trans*-1,2-cyclohexanediol, reaction time was 2 hr, and in those of indoline, reaction temperature was 100 C. Except for these modifications, reaction conditions were the same as those indicated in Tables I and II catalyzed by $RuH_2(PPh_3)_4$.

[b] Footnotes in this table are the same as those in Table I.

[c] Methyl *trans*-9,*trans*-12-octadecadienoate.

[d] Alkali-conjugated methyl octadecadienoates.

and elaidate showed nearly the same percent *trans* [B]). In the absence of hydrogen donors, the reaction of oleate and elaidate gives *trans* percent (B) of 67% and 71%. This result demonstrates that the *cis* to *trans* ratio in the absence of hydrogen donors was about 1:2. The formation of about 0.01 M of stearate may be attributable to the hydrogen transfer from $RuH_2(PPh_3)_4$.

The reduction of the dienes by *trans*-1,2-cyclohexanediol exhibited conversion a little higher and *trans* percent a little lower than the one by L-ascorbic acid, but the selectivity to monoenes was not complete. The values of percent *trans* were nearly equal, and the amount of *cis*-isomers was more than ten times that of *trans*-isomers in the reaction of oleate and elaidate with the diol (16). For comparison, the hydrogenations by indoline were carried out. This donor reduced both the dienes and monoenes effectively even at 100 C, and percent *trans* was higher than 50% in every case.

It is notable that the three hydrogen donors reduced the conjugated dienes in higher conversion than the nonconjugated dienes.

DISCUSSION

Although the mechanisms of the transfer hydrogenation of linoleate may differ depending on the combination of hydrogen donors and catalysts, we will try to discuss the mechanism of the hydrogen transfer from L-ascorbic acid and *trans*-1,2-cyclohexanediol catalyzed by $RuH_2(PPh_3)_4$.

Linoleate is assumed to be reduced by these hydroxy compounds via conjugation, for conjugated dienes were detected in the reactions with conversion lower than 65~70%, and conjugated dienes were hydrogenated faster than the nonconjugated dienes.

Previously, we thought that *cis*-monoenes were mainly formed in the hydrogenation step of dienes and discussed the mechanisms to form *cis*-monoenes directly from dienes in the case of $(NH_4)_2PdCl_4$-inoline, $PdCl_2$-indoline, and $RuCl_2(PPh_3)_3$-isopropyl alcohol systems (1). Now it is found that *trans*-monoenes isomerize to *cis*-monoenes in high conversion in the reaction systems being discussed. In these systems, the direct formation of *cis*-monoenes from dienes is not necessarily required. Further, we discussed the plausibility of the assumption that the hydrogen-donating ability of hydrogen donors affects the relative rates of the hydrogenation and the isomerization, which decide the final product distributions, though the hydrogen donors and the dehydrogenated donors are not involved in the transition states of the hydrogen transfers (1). However, this mechanism cannot explain the following facts concerning the system under discussion. (a) Product distribution was greatly varied by hydrogen donors, even if the hydrogen-donating power is comparable and conversion of the reduction was nearly equal. (b) Not only conversion but also selectivity and percent *trans* were influenced by additives such as triphenylphosphine, L-ascorbic acid, dihydroxybenzenes, and diaminobenzenes. (c) In the reactions of monoenes, the *cis* to *trans* ratio was influenced intensively by the addition of L-ascorbic acid and *trans*-1,2-cyclohexanediol. Accordingly, it is suggested that such hydrogen donors as L-ascorbic acid and *trans*-1,2-cyclohexanediol participate in the transition state of the hydrogen transfer from the catalyst to olefins and/or in that of the isomerization of olefins.

REFERENCES

1. Nishiguchi, T., T. Tagawa, H. Imai, and K. Fukuzumi, JAOCS 54:144 (1977).
2. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I & II, Third Edition, 1973, AOCS, Champaign, IL, Method Cd 14-61.
3. Harlow, R.D., C. Litchfield, and R. Reiser, JAOCS 40:505 (1963).
4. Herbert, R.W., E.L. Hirst, E.G.V. Percival, R.J.W. Reynolds, and F. Smith, J. Chem. Soc. 1270 (1933).
5. Kurata, T., and Y. Sakurai, Agric. Biol. Chem. 31:170 (1967).
6. Nishiguchi, T., H. Imai, Y. Hirose, and K. Fukuzumi, J. Catal. 41:249 (1976).
7. Braude, E.A., R.P. Linstead, and P.W. Mitchell, J. Chem. Soc. 3578 (1954).
8. Brieger, G., and T.J. Nestrick, Chem. Rev. 5:567 (1974).
9. Nishiguchi, T., H. Imai, Y. Hirose, and K. Fukuzumi, J. Catal. 41:2691 (1976).
10. Imai, H., T. Nishiguchi, and K. Fukuzumi, J. Org. Chem. 41:665 (1976).
11. Nishiguchi, T., K. Tachi, and K. Fukuzumi, Ibid. 40:237 (1975).
12. Imai, H., T. Nishiguchi, and K. Fukuzumi, Ibid. 41:2691 (1976).
13. Imai, H., T. Nishiguchi, and K. Fukuzumi, Chem. Lett. 807 (1975).

14. Zelinin, S.N., M.L. Khidekel, and V.F. Schuvalov, J. Ger. Chem. U.S.S.R. 39:2683 (1969).
15 White, A., P.Handler, and E.L. Smith, "Principles of Biochemistry," 5th Edition, McGraw-Hill, New York, 1973, p. 1181.

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