Hydrogenation of Monounsaturated and Ethylene- and Methylene-Interrupted Diunsaturated Fatty Acid Esters on Nonmetallic Palladium-on-Resin[1] II

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ABSTRACT

Methyl *cis*-9-octadecenoate (methyl oleate; *c*9), methyl *cis*-9,*cis*-13-octadecadienoate (*c*9,*c*13) and a 50:50 mixture of this diene with methyl *cis*-9,*cis*-12-octadecadienoate (methyl linoleate; *c*9,*c*12) have been hydrogenated on a nonmetallic palladium-on-resin catalyst in acetone as a solvent at 40 C and atmospheric hydrogen pressure. The monoene is hydrogenated very slowly, but *c*9,*c*12 is reduced easily and quickly. The ethylene-interrupted diene reacts more slowly than *c*9,*c*12, but considerably faster than *c*9, because active methylene-interrupted dienes are intermediates by double-bond migration. This isomerization process also results in the formation of inactive polymethylene-interrupted dienes, which accumulate during hydrogenation. Also *c*9 isomerizes considerably during reduction. In the 50:50 mixture, *c*9,*c*12 is hydrogenated about eight times faster than *c*9,*c*13.

INTRODUCTION

In a previous paper (1), we have reported on the excellent selectivity properties of nonmetallic palladium-on-resin catalysts (Pd/resin) for the hydrogenation of methylene-interrupted diunsaturated fatty acid esters. This selectivity was attributed to the low activity of this type of catalyst for the hydrogenation of monoenes. It was also assumed that ethylene-interrupted dienes were difficult to hydrogenate. To verify these assumptions, the present study mutually compares the hydrogenation of the methyl esters of an ethylene- and a methylene-interrupted diunsaturated fatty acid and of a monounsaturated fatty acid on Pd/resin.

EXPERIMENTAL PROCEDURES

Substrates

The following substrates were hydrogenated: methyl *cis*-9,*cis*-12-octadecadienoate (*c*9,*c*12; methyl linoleate), methyl *cis*-9,*cis*-13-octadecadienoate (*c*9,*c*13), a 50:50 mixture of *c*9,*c*12 and *c*9,*c*13, and methyl *cis*-9-octadecenoate (*c*9; methyl oleate). *C*9 was isolated from the methyl esters of olive oil by fractionated distillation and purified by urea crystallization followed by distillation (b.p. 148-150 C/45 Pa; purity 97% *c*9, 3% *c*11). *C*9,*c*13 was prepared using corresponding procedures as described by Lam and Lie Ken Jie (2) (b.p. 145-147 C/26 Pa; purity 98.5% *c*9,*c*13, 1.5% *c*9,*c*14). *C*9,*c*12 was isolated as described in ref. 1. Prior to hydrogenation, the esters were purified by chromatography over alumina with hexane as an eluent.

Hydrogenation

The preparation of Pd/resin has been described elsewhere (1, 3). The reaction conditions of the hydrogenations are given in Table I.

Analysis

Samples of partially hydrogenated monoene and dienes were analyzed by GLC (DEGS on chromosorb W) and argentation TLC with benzene as an eluent. The esters in the various weighed fractions were identified and quantified on the basis of chromatographic data and oxidative degradation products. The double-bond distribution in the isolated *cis* and *trans* fractions was determined by GLC of the aldehydes and aldehydic esters, obtained by ozonolysis of these fractions and reduction of the ozonides formed with triphenylphosphine (4).

RESULTS AND DISCUSSION

Figure 1 shows the degree of hydrogenation (HD),

TABLE I

Reaction Conditions of the Hydrogenation of Methyl Octadecenoate and Octadecadienoates[a]

Ester	Catalyst	Reactor	Amount of catalyst/ (mg Pd/kg ester)	Time of catalyst addition *t*/min
*c*9	I	A	260	0
			+ 260	95
*c*9,*c*13	III	B	300	0
			+ 300	36
*c*9,*c*12	III	B	120	0
*c*9,*c*12/*c*9,*c*13	III	B	120	0
(50:50)			+ 180	55
			+ 300	78

[a] Reactor A (350 ml): 20 ml ester + 160 ml acetone. Reactor B (40 ml): 5 ml ester + 15 ml acetone. Temperature: 40 C; hydrogen pressure: 101 kPa (≅ 1 atm).

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[1] The activity of the catalyst for the *c*9,*c*12 hydrogenation described previously (1) is considerably higher than that derived from the present data. The experiments described in this study were carried out about eight months later, so that we have to deal with an older catalyst. However, reproduction of the catalyst resulted in the same activity. Furthermore, we used a new batch of *c*9,*c*12 for these experiments, which was purified in the same way as the previous one. The catalyst is probably sensitive to apolar compounds which may be present in *c*9,*c*12 and which are not removed by alumina. Small amounts of these compounds may have a drastic influence on the activity of the catalysts under investigation because the catalyst dosing is very low. We emphasize that, though the activity may vary to some extent (depending on substrate quality), the selectivity and the isomerization pattern do not change.

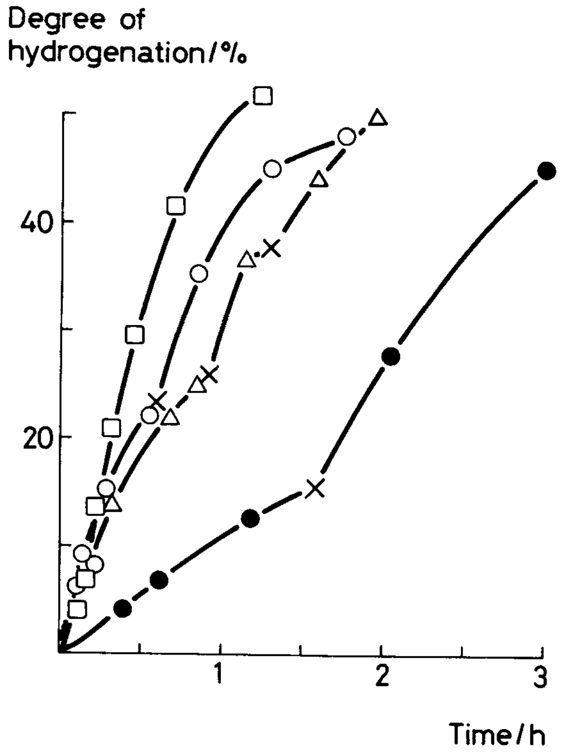

FIG. 1. Degree of hydrogenation as a function of time in the hydrogenation of: ● *c*9; ○ *c*9,*c*13; □ *c*9,*c*12; △ *c*9,*c*12/*c*9,*c*13 (50:50). The reaction conditions are given in Table I. "X" indicates the time of fresh catalyst addition.

defined as (hydrogen uptake/hydrogen uptake after complete hydrogenation) x 100, as a function of time for *c*9, *c*9,*c*13, *c*9,*c*12 and a 50:50 mixture of the diene. The rate curves indicate that *c*9 is hydrogenated very slowly and *c*9,*c*12 very quickly. The ethylene-interrupted diene is less reactive than *c*9,*c*12, but considerably more active than *c*9. The results of the hydrogenation of the 50:50 mixture suggest that *c*9,*c*12 is hydrogenated preferentially, because initially the hydrogenation rate of *c*9,*c*12 equals that of the mixture.

The higher hydrogenation acitivity of *c*9,*c*13 compared to that of *c*9 may be attributed to double-bond migration in the diene, resulting in active methylene-interrupted dienes as intermediates. This isomerization is accompanied by the accumulation of polymethylene-interruped dienes (Fig. 2). During the hydrogenation of *c*9,*c*12, fewer isomers are formed as is shown in Fig. 3. The composition of a sample of partially hydrogenated *c*9,*c*13 (HD = 22.2%) is given in Fig. 4.

Figure 5 shows the composition of the monoene fraction during hydrogenation of *c*9,*c*13. This composition supports the conclusion that the hydrogenation of *c*9,*c*13 mainly proceeds through active conjugatable intermediates.

Initially, mainly *c*9,*t*12 and *t*10,*c*13 will be formed, which will be hydrogenated either straightforwardly or via conjugated intermediates. These intermediates react immediately without desorptions so that they do not accumulate in detectable amounts. In a previous paper (1), we described the hydrogenation of *c*9,*t*12. The amounts of 9- and 10-isomers formed from this diene agree fairly well with the amounts of corresponding isomers formed from *c*9,*c*13 via *c*9,*t*12 as intermediate, bearing in mind that also *t*9,*t*12 contributes to the formation of *t*9, especially at high HDs, and that less than half the *c*9,*c*13 reacts via *c*9,*t*12.

Because of the formation of conjugatable intermediates the hydrogenation proceeds with a certain selectivity. At random hydrogenation of the double bonds in the diene, 20% methyl stearate should be formed at an HD of 45%,

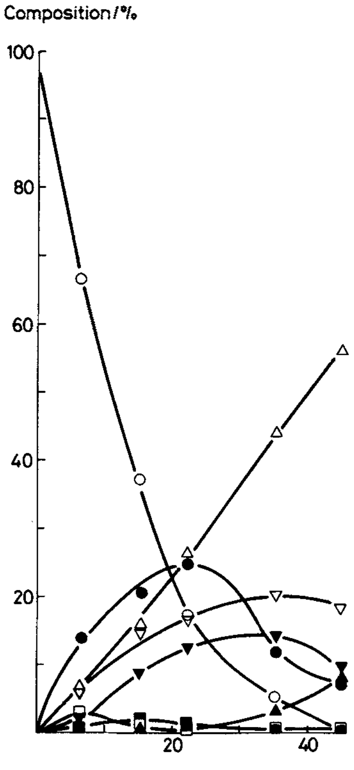

FIG. 2. Product composition during hydrogenation of *c*9,*c*13.△ *trans*-monoene; ▽ *cis*-monoene; ▲-saturated; ○ *c*9,*c*13; ● (*c*,*t*)- and (*t*,*c*)-nonconjugatable diene; □ (*c*,*t*)- and (*t*,*c*)-conjugatable diene; ■ (*t*,*t*)-conjugatable diene; ▼ (*t*,*t*)-nonconjugatable diene.

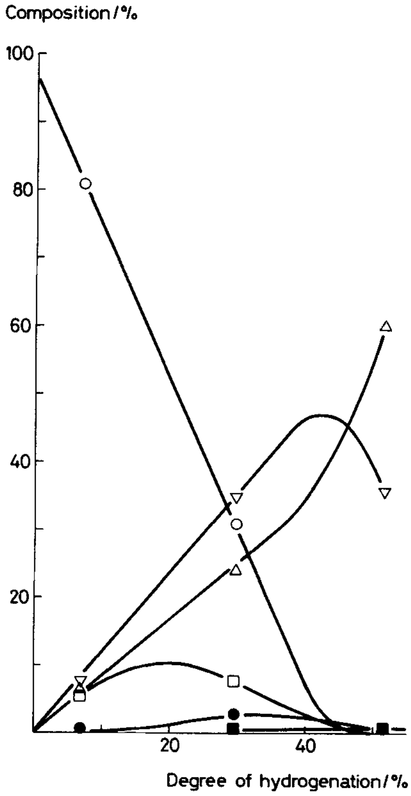

FIG. 3. Product composition during hydrogenation of *c*9,*c*12. △ *trans*-monoene; ▽ *cis*-monoene; ○ *c*9,*c*12; □ *c*9,*t*12 and *t*9,*c*12; ● *t*9,*t*12; ■ *t*9,*t*13 and *t*8,*t*12. The small (< 0.5%) percentages methyl stearate are ommitted; only an amount of 3.6% was present at HD = 51.6%.

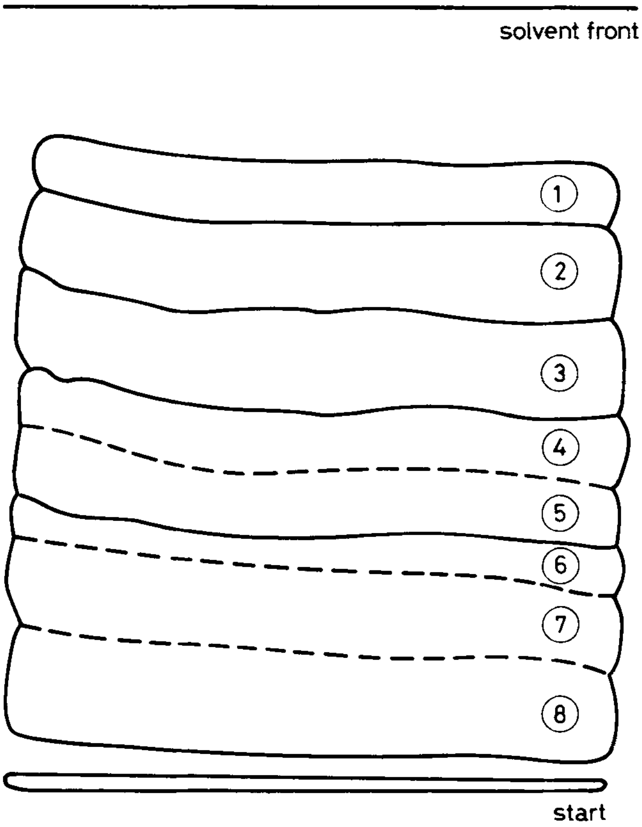

FIG. 4. Chromatoplate of partially hydrogenated *c*9,*c*13 (eluent: benzene; HD = 22.2%). The components were identified on the basis of R_f values, GLC-data and oxidation products. 1. saturated: 1.0%; 2. *trans*-monoene: 26.5%; 3. *cis*-monoene: 16.7%; *t*9,*t*12 and *t*10,*t*13: 1.1%; 4. *t*9,*t*14 and *t*8,*t*13, *t*10,*t*15 and *t*7,*t*12: 5.9%. *c*9,*t*12 and *t*10,*c*13: 0.3%; 5. *t*9,*t*13 and *t*8,*t*12 and *t*10,*t*14: 6.9%; 6. *c*9,*t*14 and *t*8,*c*13: 7.4%; 7. *c*9,*t*13 and *t*9,*c*13: 17.3%; 8. *c*9,*c*13: 17.2%.

whereas only 8.0% stearate is detected. At lower HDs the selectivity is even higher; at an HD of 22% we found 1.0% stearate, whereas 4.9% should be present at a statistical distribution of hydrogen.

We further observed that at an HD of 22% the percentages of *c*9 and *c*13 markedly decrease and those of the corresponding *trans* monoenes markedly increase (Fig. 5). These changes coincide with an increased contribution of *c*9,*t*13 and *t*9,*c*13 to the formation of monoenes (Fig. 2), whereas the disappearance rate of *c*9,*c*13 decreases. Apparently, at an HD of more than 20% the disappearance of *c*9 and *c*13 due to secondary reactions, such as isomerization and hydrogenation, is insufficiently compensated by the hydrogenation of dienes.

On hydrogenation of the 50:50 mixture of *c*9,*c*12 and *c*9,*c*13 we found at an HD of 13.9% only 0.1% stearate and further 13.8% *c*9,*c*12, 43.0% *c*9,*c*13 and 15.3% dienoic isomers in the reaction mixture. These isomers originate from *c*9,*c*12 as well as from *c*9,*c*13, so that we do not know exactly whether *c*9,*c*13 has contributed to the monoene formation or not. However, the double-bond distribution in the monoene fractions gives information about the origin of the monoenes.

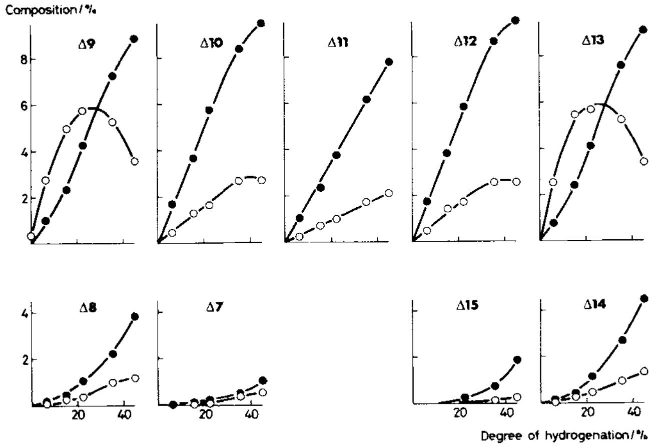

FIG. 5. Monoenes (● *trans*; ○ *cis*) obtained from the hydrogenation of *c*9,*c*13.

Table II gives the double-bond distributions of the monoene fractions obtained from *c*9,*c*12, *c*9,*c*13 and the 50:50 mixture at an HD of 13.9%. We can conclude that *c*9,*c*12 is the main source of the monoenes in the reaction mixture. Assuming that both dienes react independently, we can draw a more quantified conclusion. The sum of the double-bond distributions from *c*9,*c*13 and *c*9,*c*12 at HDs of 1.5 and 12.4% respectively (half of the distributions at 3.0 and 24.8% should be taken), agrees rather well with the experimental double-bond distribution from the 50:50 mixture at an HD of 13.9%. Thus, in the 50:50 mixture of *c*9,*c*12 and *c*9,*c*13, the latter diene is also hydrogenated from the beginning, but at a rate eight times lower than that of *c*9,*c*12.

As we already remarked, on Pd/resin the hydrogenation activity and selectivity behavior of *c*9,*c*13 originates mainly from the relatively high rate of double-bond migration with respect to the rate of hydrogenation. The isomerization activity also appears from the hydrogenation of *c*9. Figure 6 shows that a considerable amount of positional and geometric isomers arises. On a conventional nickel-on-silica catalyst (5), fewer isomers are formed (Table III and Fig. 7). The ratio of the rate of double-bond migration to that of hydrogenation is about 0.4 on nickel-on-silica at 50 C and 4.3 on Pd/resin at 40 C. This great difference is mainly due to the low hydrogenation rate found on the latter catalyst.

We may conclude that monoenes and polymethylene-

TABLE II

Double-bond Distribution from *c*9,*c*12/*c*9,*c*13 and a 50:50 Mixture of These Dienes at an HD of 13.9%. Calculated: Sum of the Distribution Data from *c*9,*c*13 at an HD of 1.5% and from *c*9,*c*12 at an HD of 12.4%

	Percentage of monoene											
	8		9		10		11		12		13	
Substrate	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
*c*9,*c*12	0.1	0.2	7.3	2.0	0.3	3.2	0.3	3.2	7.6	2.4	0.1	0.4
*c*9,*c*13	0.2	0.4	4.8	2.1	1.2	3.5	0.6	2.3	1.2	3.5	5.3	2.2
*c*9,*c*12/*c*9,*c*13 (50:50)												
Experimental	0.2	0.3	7.7	2.1	0.6	2.9	0.5	2.8	6.7	2.5	0.7	0.5
Calculated	0.1	0.2	7.2	1.9	0.4	3.2	0.4	3.1	6.8	2.4	0.7	0.5

TABLE III

Hydroisomerization in the Hydrogenation of $c9$ on Nonmetallic Palladium-on-Resin and on Nickel-on-Silica (5) at Atmospheric Hydrogen Pressure

Catalyst					
Type	amount/ (mg metal/kg ester)	Temperature/ C	$(dm/dt)^a$ $t \to 0$	$(d(t9)/dt)^b$/ $t \to 0$ (mol %/min)	(dsat/dt)/ $t \to 0$ (mol %/min)
Ni	700	50	0.47	0.42	1.2
Pd	260	40	0.77	0.53	0.18

[a] Rate of double-bond migration/(number of migrations per 100 molecules monoene per min).
[b] Rate of c/t rearrangement.

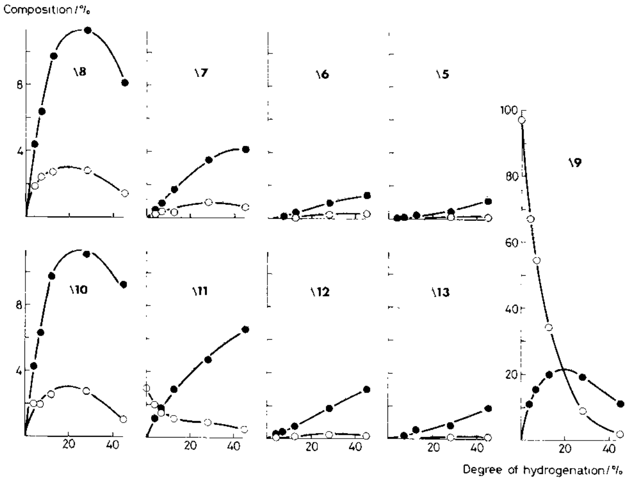

FIG. 6. Monoenes (● *trans*, ○ *cis*) obtained from the hydrogenation of $c9$.

interrupted dienes are difficult to hydrogenate on Pd/resin. During hydrogenation these substrates isomerize intensively. Thus, $c9,c13$ is hydrogenated faster than $c9$, because from the first ester, methylene-interrupted dienes are formed as active intermediates, which are reduced very fast.

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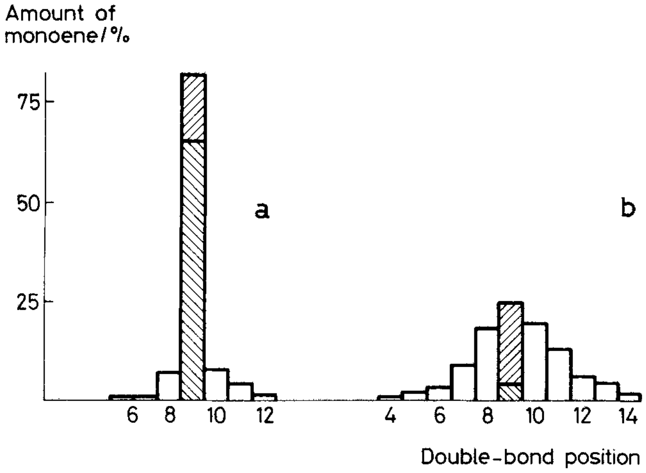

FIG. 7. Double-bond distribution of partially hydrogenated $c9$: (a) HD = 50%; hydrogenated on nickel-on-silica at 50 C (5); (b) HD = 45%; hydrogenated on Pd/resin at 40 C. ▨ *trans*; ▧ *cis*; □ *trans* and *cis*.

REFERENCES

1. van der Plank, P., H.J. van Oosten and C. van Dijk, 56:45
2. Lam, C.H., and M.S.F. Lie Ken Jie, J. Chromatogr. 115:559 (1975).
3. Hinze, A.G., U.S. Patent 3,865,853 (1975).
4. van der Plank, P., JAOCS, 49:489 (1972).
5. van der Plank, P., Ibid. 49:327 (1972).

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