Nonmetallic Palladium-on-Resin: A Very Active and Selective Catalyst for the Hydrogenation of Diunsaturated Fatty Acid Esters I

P. VAN DER PLANK, H.J. VAN OOSTEN, and L. VAN DIJK, Unilever Research Vlaardingen, The Netherlands

ABSTRACT

Methyl cis-9,cis-12-octadecadienoate (methyl linoleate; $c9,c12$) and the corresponding $cis,trans$ and $trans,trans$ geometric isomers ($c9,t12$ and $t9,t12$) were hydrogenated at 40 C and atmospheric hydrogen pressure in acetone as solvent, with nonmetallic palladium-on-resin catalyst. These catalysts were prepared by impregnation of cationic exchange resins with an aqueous solution of palladium dichloride. The methylene-interrupted dienes were hydrogenated to the monoene stage with almost infinite selectivity, especially with $c9,c12$, whereas $t9,t12$ was hydrogenated somewhat less selectively. The latter isomer was reduced considerably more slowly than the first, whereas $c9,t12$ occupied an intermediate position. The hydrogenation proceeded for an important part via a straightforward reduction of one of the double bonds, though conjugation prior to hydrogenation also occurred. The methylene-interrupted dienes isomerized to a high degree geometrically during hydrogenation, but they scarcely isomerized positionally, resulting in small amounts of inactive ethylene-interrupted dienes.

INTRODUCTION

Nonmetallic palladium has been described as a catalyst for the hydrogenation of polyunsaturated fatty acid esters, either unsupported (1) or supported as an immobilized homogeneous catalyst (2). However, the selectivities of these hydrogenations were lower than those obtained with copper catalysts, which reduce methylene-interrupted diunsaturated fatty acid esters to the monoene stage with almost infinite selectivity (3, 4). We now report on nonmetallic palladium catalysts supported on resin which hydrogenate methylene-interrupted diunsaturated fatty acid esters with the same selectivity as copper catalysts, but under milder conditions and with considerably less isomerization.

EXPERIMENTAL PROCEDURES

Preparation of the Catalyst

Catalyst I. 10 g commercial Zerolite 325 (a strongly acidic cation exchange resin based on a sulfonated polystyrene matrix crosslinked with divinylbenzene) was treated with 100 ml of a 5% aqueous sodium hydroxide solution at 100 C for 4 hr. After filtration, the resin was impregnated with 170 mg palladium dichloride at 20 C for 20 hr. in an aqueous medium. Subsequently, the resin was filtered off, washed with water, and dried under vacuum, after which it was ready for use (palladium content: 1.02%).

Catalyst II. 110 mg $AgNO_3$ and 100 ml H_2SO_4 were heated at 90 C under vacuum for 45 min. To the resulting mixture (Ag_2SO_4/H_2SO_4), 10 g copolymer of divinylbenzene (14%) and acrylic acid (86%) was added at 80 C. After stirring at 100 C for 6 hr, the mixture was kept at ambient temperature for 16 hr. Subsequently, the mixture was poured into 50% sulfuric acid, filtered, poured into distilled water and filtered again. The black-brown powder was washed with sodium hydroxide (2 mol/1),, hydrochloric acid (2 mol/1), again sodium hydroxide (2 mol/1), and at last with water. The residue was dispersed in water at pH 9.3 and impregnated with 170 mg palladium dichloride at 20 C for 20 hr. After washing with water and acetone, the catalyst was dried under vacuum (palladium content: 1.02%).

Catalyst III. 31 g copolymer of divinylbenzene (14%) and methacrylic acid (86%) were impregnated with 850 mg palladium dichloride, dissolved in 500 ml water, at 20 C for 20 hr. The catalyst was washed with water and acetone and dried under vacuum (palladium content: 1.6%).

In this study, we used cationic exchange resins as

TABLE I

Reaction conditions of the hydrogenations of
methyl octadecadienoates[a]

Ester	Catalyst	Reactor	Amount of catalyst/ (mg Pd/kg ester)	Time of catalyst addition t/min
$c9,c12$[b]	I	A	60	0
$c9,c12/c9$ (93.2:6.8)	II	A	40	0
$c9,c12$	III	B	40	0
$c9,t12$	III	B	100	0
			+100	21
			+100	37
$t9,t12$	III	B	100	0
			+200	33
$c9,c12/t9,t12$ (50:50)	III	B	100	0
			+200	28

[a]Reactor A: 350 ml; 40 ml ester + 160 ml acetone. Reactor B: 40 ml; 5 ml ester + 15 ml acetone. Temperature: 40 C. Hydrogen pressure: 101 kPa ($\approx$ 1 atm).
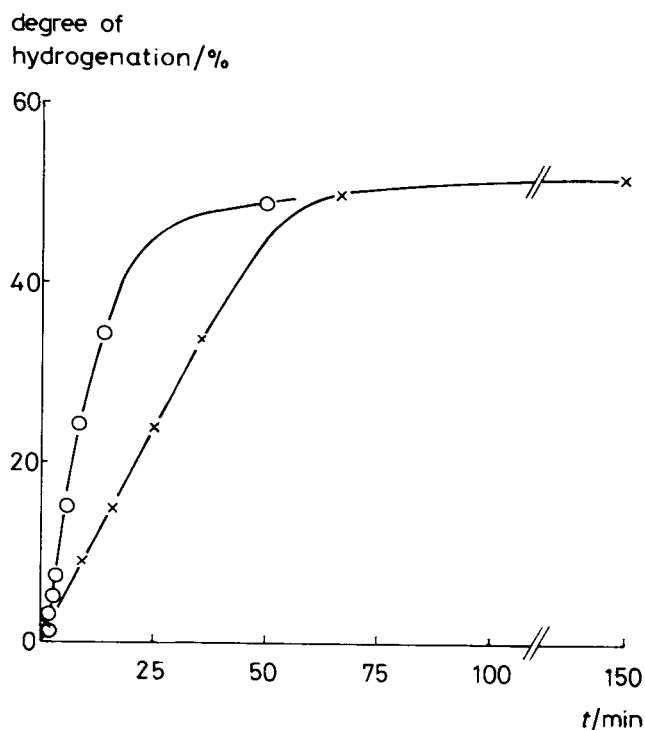[b]Also carried out at 92 C in pentanol.

degree of
hydrogenation/%

FIG. 1. Degree of hydrogenation as a function of time in the hydrogenation of $c9,c12$ at 40(x) and 92 C (o) in reactor A.

composition/%

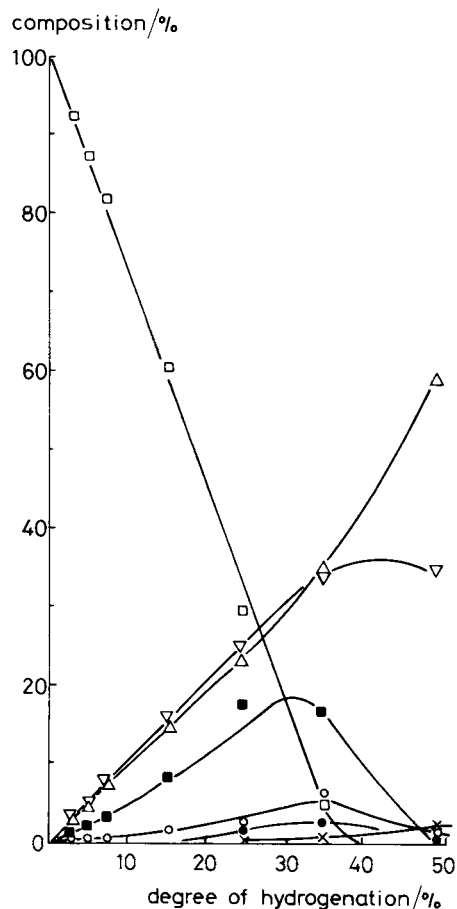FIG. 2. Product composition during hydrogenation of $c9,c12$ at 92 C in reactor A. △ *trans*-monoene; □ $c9,c12$; ○ $t9,t12$; ▽ *cis*-monoene; ■ $c9,t12$ and $t9,c12$; ● $c9,t13$ and $t8,c12$; × $t9,t13$ and $t8,t12$. Since the percentages of methyl stearate were very low, they have been omitted in the figure. However, the sample at an HD of 49.5% contained 2.1% methyl stearate.

supports. However, Hinze (5) has shown that anionic exchange resins behave in the same way.

Substrates

The following substrates were hydrogenated: methyl *cis*-9,*cis*-12-octadecadienoate ($c9,c12$; methyl linoleate), methyl *cis*-9,*trans*-12-octadecadienoate ($c9,t12$), methyl *trans*-9,*trans*-12-octadecadienoate ($t9,t12$) and a mixture of $c9,c12$ and $t9,t12$ (50:50). In one experiment $c9,c12$ was hydrogenated in the presence of 6.8% methyl *cis*-9-octadecenoate ($c9$; methyl oleate).

$C9,c12$ was isolated from the methyl esters of safflower oil by urea crystallization followed by distillation (b.p. 146-148 C/40 Pa; purity 98.5%). $T9,t12$ was prepared from linoleic acid by geometric isomerization with sulfur dioxide at 200 C, followed by distillation, crystallization from acetone and from light petroleum. Finally the t,t acid was methylated and distilled (b.p. 142 C/53 Pa; purity 100%). $C9,t12$ was synthesized according to the procedure described by Gaudemaris and Arnaud (6). The final product was obtained after distillation and recrystallization from acetone (b.p. 152 C/95 Pa; purity 99.6%).

Prior to hydrogenation, the esters were purified by chromatography over alumina with hexane as eluent.

Hydrogenations

The reactions were carried out in acetone as solvent under atmospheric ($\simeq$ 101 kPa) hydrogen pressure and at 40 C either in reactor A(content: 350 ml) or in reactor B (content: 40 ml). Both reactors were provided with a stirrer, a septum through which samples were taken by means of an injection needle, and a gas buret to measure the hydrogen consumption. Substrate, solvent, and catalyst were mixed under air, after which the air was replaced by hydrogen. Hydrogenation was initiated by starting the stirrer of the reactor.

In Table I the various reaction conditions used in this study are given. In several experiments the catalytic activity decreased to below an acceptable level, so that fresh amounts of catalyst (indicated by a + sign) were added to maintain a reasonable reaction rate. One experiment was carried out at 92 C. In this case pentanol was used as solvent.

Analysis

The samples were separated into saturated, mono- and diunsaturated fractions by gel permeation chromatography on Lipidex 5000 (Packard) using a mixture of water, methanol and chloroform (10:85:15, v/v/v) as eluent. The mono- and diunsaturated fractions were further separated into geometric isomers by argentation TLC. GLC on DEGS and capillary GLC on Apiezon L were used for identification and quantification of these weighed fractions. GLC analysis of the oxidative degradation products obtained via ozonolysis (7) gave the double-bond distribution in the monounsaturated fractions.

RESULTS AND DISCUSSION

Fig. 1 shows the degree of hydrogenation (HD), defined as (hydrogen uptake/hydrogen uptake after complete hydrogenation) x 100, as a function of time in the hydrogenation of $c9,c12$ at 40 and 92 C on catalyst I. Fig. 2 gives the detailed product composition during hydrogenation at 92 C. The hdrogenation at 40 C showed a similar product distribution, though the formation of diene isomers was less prounced. At 40 C a maximum of about 9% $c9,t12$ and $t9,c12$ was found, whereas these dienes accumulated to about 20% at 92 C. Figures 1 and 2 show that the methylene-
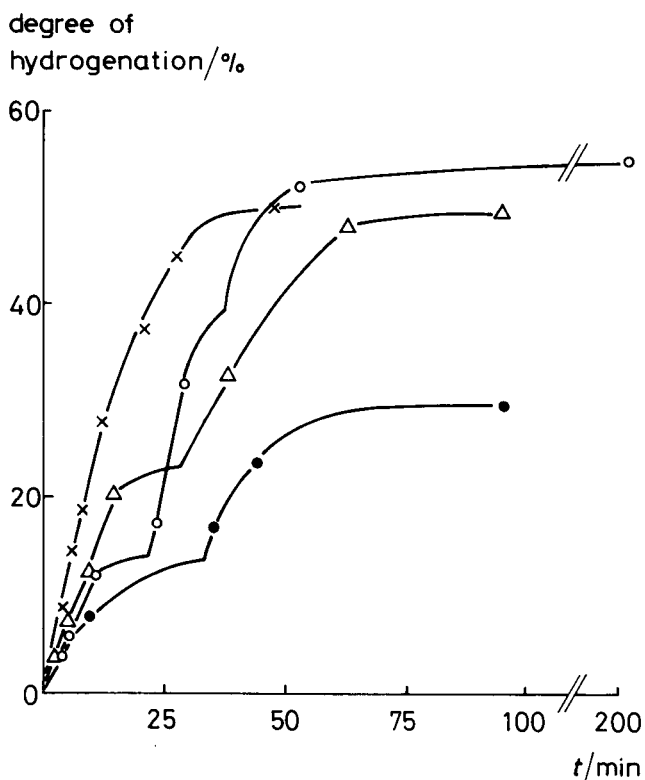
degree of
hydrogenation/%

FIG. 3. Degree of hydrogenation as a function of time in the hydrogenation of $c9,c12$ (x), $c9,t12$ (o), $t9,t12$ (●) and $c9,c12/t9,t12$ (50:50) (△) in reactor B. The course of the curves is also based on the amount of hydrogen consumed, which was measured continuously.

composition/%

FIG. 4. Product composition during hydrogenation of a 50:50 mixture of $c9,c12$ and $t9,t12$. △ *trans*-monoene; o $t9,t12$; □ $c9,t12$ and $t9,c12$; x $t8,t12$ and $t9,t13$; ∇ *cis*-monoene; ● $c9,c12$; ■ $c8,t12$; $t9,c13$; $c9,t13$; $t8,c12$; ▲ saturated.

interrupted dienes were hydrogenated very selectively to the monoene stage and that the monoenes formed were hardly hydrogenated, because after 50% HD the hydrogenation rate nearly drops to zero. The high selectivity for $c9,c12$ hydrogenation is also observed on catalyst III, as can be concluded from Fig. 3.

Another point of interest is the accumulation of $c9,t12$ and $t9,c12$ to concentrations beyond the equilibrium value with respect to $c9,c12$. Apparently, these dienes were reduced relatively slowly until the concentration of $c9,c12$ had reached a rather low level. This suggests preferential hydrogenation of $c9,c12$ which was supported by the results of hydrogenation of $c9,t12$ and $t9,t12$ (Fig. 3) and those of a mixture of $c9,c12$ and $t9,t12$ (50:50; Figs. 4 and 5). The *cis,trans* diene was hydrogenated more slowly than the *cis,cis* diene, whereas the former isomer was considerably more active than $t9,t12$. In the 50:50 mixture, the *cis,cis* isomer was hydrogenated preferentially over the *trans,trans* one (Fig. 4). In the hydrogenations of $c9,t12$ and $t9,t12$, the activity of catalyst III strongly decreased after some time for unknown reasons. Similar phenomena were observed on the other catalysts. However, the hydrogenation of the mixture of $c9,c12$ and $t9,t12$ showed unambiguously that poisons which might be present in the esters do not interfere with the hydrogenation process because the course of the product composition is not influenced by the addition of fresh catalyst (Fig. 4). After an HD of about 25%, only 8% $c9,c12$ was present in the reaction mixture. The initial hydrogenation rate was not restored after addition of fresh catalyst (twice as much as the starting amount, Fig. 3).

Figures 6 and 7 show the product composition in the hydrogenation of $t9,t12$ and $c9,t12$, respectively.
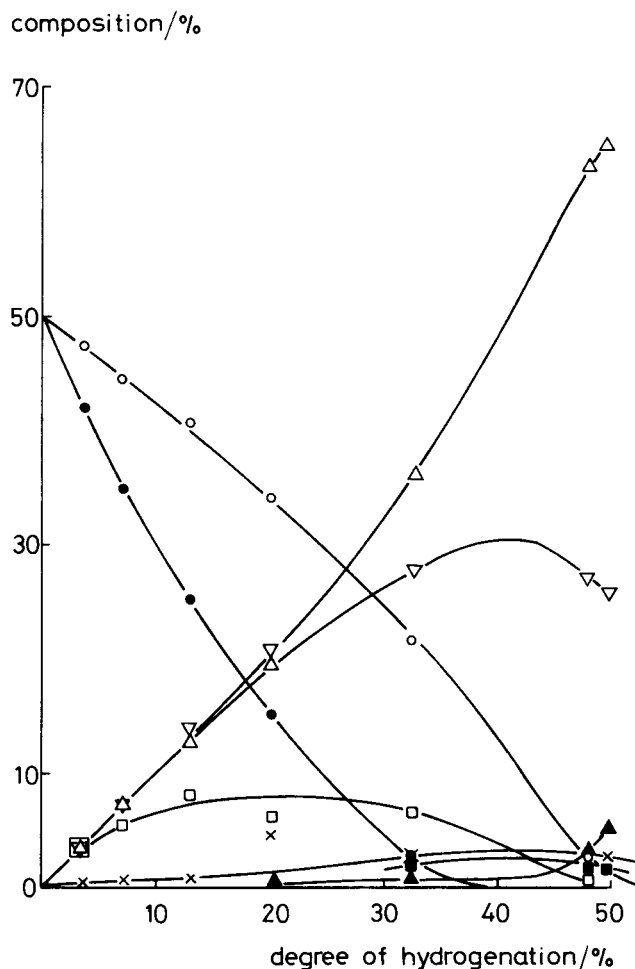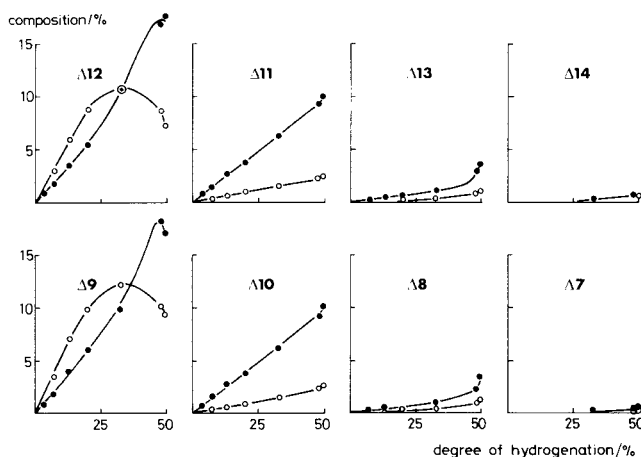

FIG. 5. Monoenes (o *cis*; ● *trans*) obtained from hydrogenation of a 50:50 mixture of $c9,c12$ and $t9,t12$.

The *trans,trans* diene was very inactive; after a reaction time of 1.5 hr, an HD of only 30% was obtained (Fig. 6). Moreover, the hydrogenation process proceeded somewhat less selectively than with the other isomers.

The product distributions (Figs. 2,4,6 and 7) and the detailed monoene compositions (Figs. 5, 8-10) show that the dienes were isomerized geometrically to
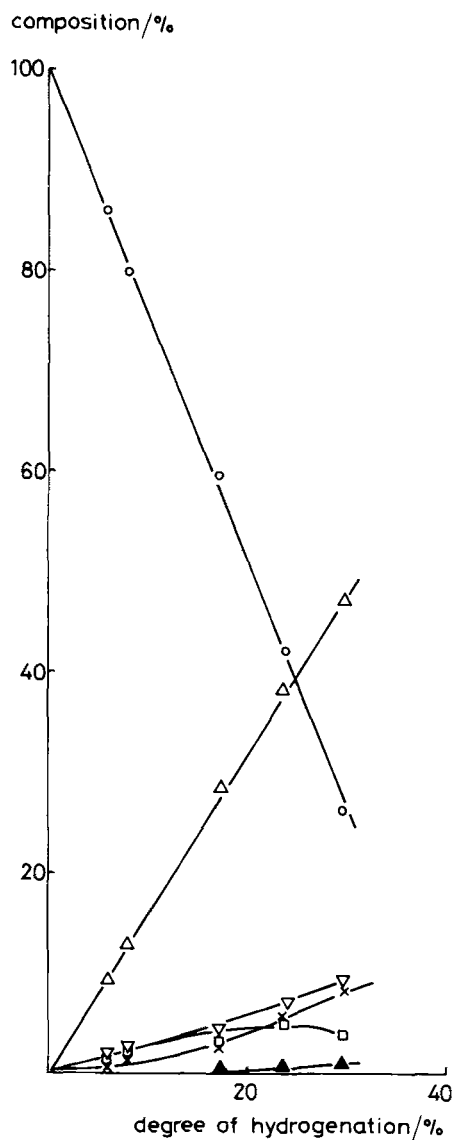
composition/%

FIG. 6. Product composition during hydrogenation of[1] *t9,t* 12. △ *trans*-monoene; ○ *t9,t*12; x *t8,t*12;*t9,t*13; unidentified isomers; △ *cis*-monoene; □ *c9,t*12 and *t9,c*12; ▲ saturated.

composition/%

degree of hydrogenation/%
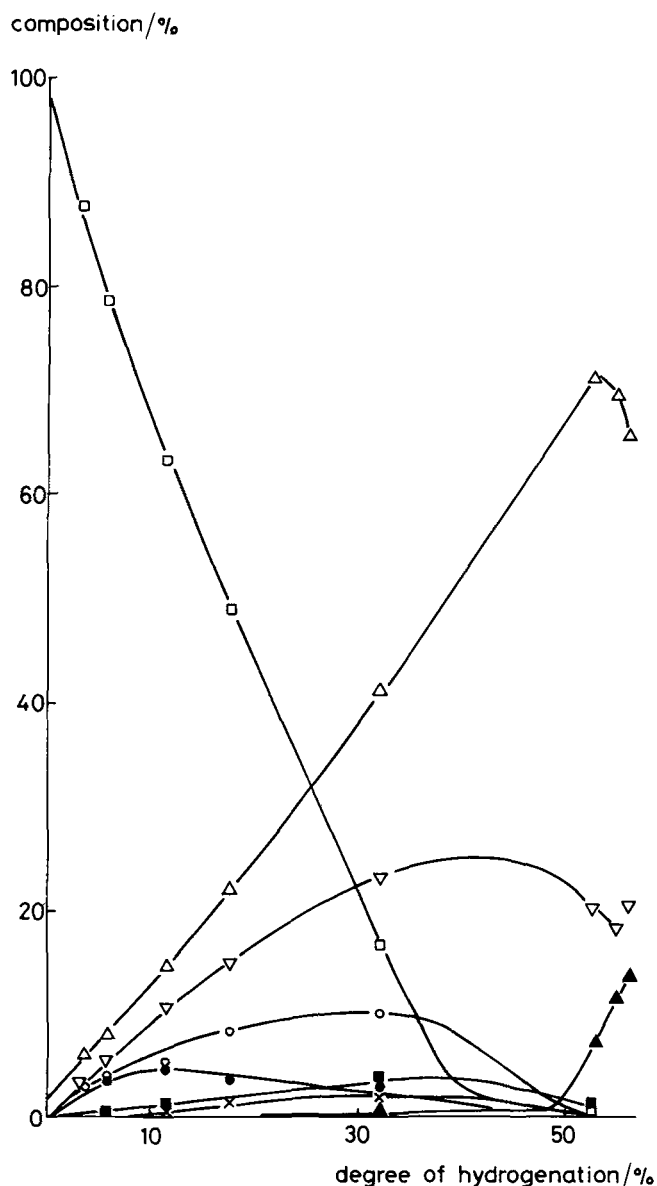
FIG. 7. Product composition during hydrogenation of *c9,t*12. △ *trans*-monoene; ○ *t9,t*12; □ *c9,t*12; x *t8,t*12 (and *t9,t*13); ▽ *cis*-monoene; ● *c9,c*12; ■ *c8,t*12 and *c9,t*13; ▲ saturated

a high degree, but scarcely positionally, irrespective of the formation of reactive conjugated intermediates. This positional isomerization was limited to migration of one of the double bonds over one carbon-carbon distance and resulted in the formation of inactive ethylene-interrupted dienes. The conjugated intermediates, though not formed in detectable amounts, contributed for an important part to the hydrogenation process, as will be elucidated in another paper.

The monoenes formed did not isomerize in the presence of active diene, as can be concluded from the monoene compositions obtained from the mixtures of *c9,c*12 and *t9,t*12 (50:50; Fig. 5) and of *c9,c*12 and *c9* (93.2:6.8; Fig. 10). In the latter, the *c9* and *c*12 curves run parallel until an HD of about 35%, implying that the original amount of 6.8% *c9* did not react in anyway. A high degree of monoene isomerization was observed at an HD higher than 40%. Thus the monoenes obtained at HDs lower than 40% were primary hydrogenation products of dienes and originated from small amounts of positionally isomeric dienes. The 10- and 11-isomers stem from conjugated intermediates which could only be detected (less than

1%) at the beginning of the hydrogenation process.

The nonmetallic palladium-on-resin catalysts are, as regards selectivity, almost similar to copper catalysts. Both types of catalyst hydrogenate methylene-interrupted dienes with almost infinite selectivity. However, the nonmetallic palladium catalyst hydrogenates these dienes for an important part via a straightforward reduction of one of the double bonds as can be concluded from the monoene distributions observed. Copper catalysts hydrogenate the dienes exclusively via conjugated intermediates (8) and, prior to hydrogenation, considerably isomerize conjugated dienes. Dienes, hydrogenated with a copper catalyst, give a wider double-bond distribution in the monoene fraction (9) than dienes reduced with nonmetallic palladium-on-resin.

Differences in hydrogenation behavior of geometric isomers of *c9,c*12 were also observed by Scholfield and Snyder et al (10, 11). They found the same sequence in hydrogenation rate on platinum and nickel catalysts, though the differences were less spectacular.
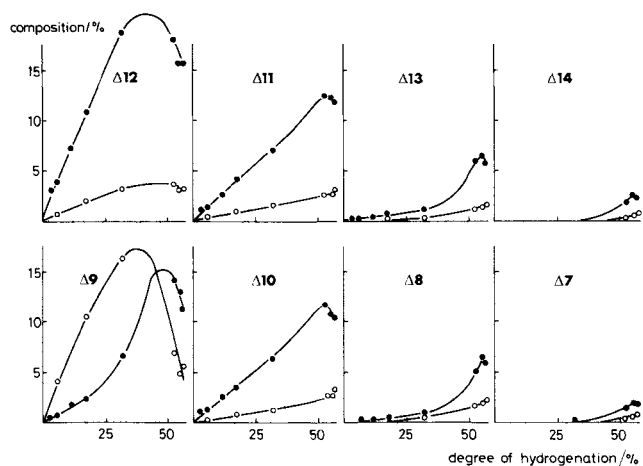
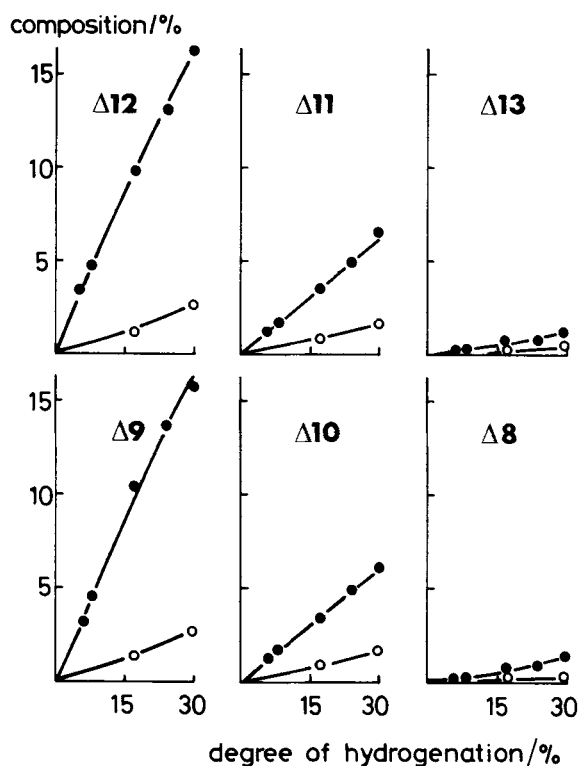FIG. 8. Monoenes (o   cis;   •   trans) obtained from hydrogenation of c9,t12.

FIG. 9. Monoenes (o   cis;   •   trans) obtained from hydrogenation of t9,t12.

FIG. 10. Monoenes (o   cis;   •   trans) obtained from hydrogenation of a mixture of c̈9,c12 and c9   (93.2:6.8).

of the double bonds in the original diene.

The inactivation of the palladium catalyst during hydrogenation is attributed to reduction of active palladium ions, the valence state of which is not precisely known, to inactive metallic palladium as could be concluded from electron spectroscopy measurements. So in our case, palladium ions are responsible for the catalytic activity in contrast to nonmetallic palladium-on-resin described by Sabadie   et al. (12). They found evidence that in their systems investigated (for example, hydrogenation of cyclohexene at 25 C) metallic palladium was the active species. Their observations agree to some extent with ours. Their catalysts needed a rather long induction period to convert inactive palladium ions into finely dispersed, active metallic palladium for the hydrogenation of a monoene like cyclohexene. Our catalysts in the nonmetallic form are also incapable of hydrogenating monoenes, as can be concluded from this paper.

For example, the initial ratio between the hydrogenation rates of t9,t12 and c9,c12, which can be derived from Fig. 4, is 0.3, whereas Snyder et al (10) found values of 0.4 and 0.6 for a mixture of the same composition when hydrogenated with platinum-on-carbon at 50 C and with nickel-on-silica at 140 C, respectively. Scholfield (11) found that t9,t12 was hydrogenated less selectively than c9,c12.

Scholfield further established that relatively more c10 and c11 was formed from t9,t12 than from c9,c12; the ratios t10/c10 and t11/c11 originating from t9,t12 are lower than those originating from c9,c12. In agreement with this phenomenon, t11/c11 is lower than t10/c10 on hydrogenation of c9,t12 with a nickel catalyst. With nonmetallic palladium-on-resin as catalyst, the trans/cis ratio between the geometric isomers with the double bond on the 10 and 11 position appeared to be independent of HD and geometry
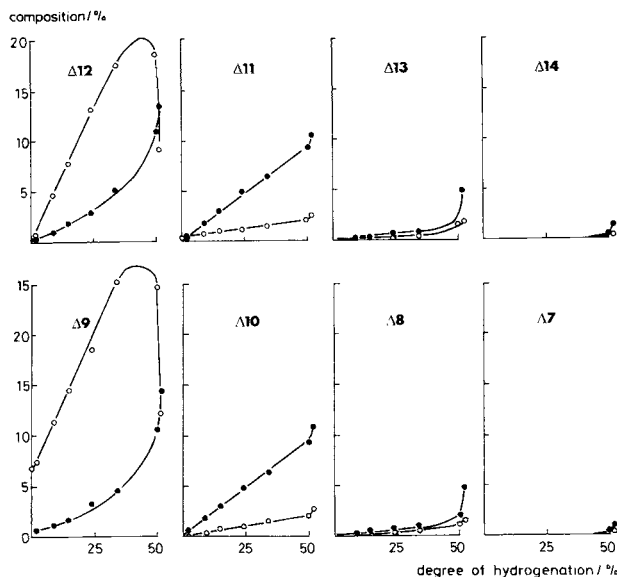
REFERENCES

1. Itatani, H., and J.C. Bailar, Jr., JAOCS, 44:147 (1967).
2. Bruner, H., and J.C. Bailar, Jr., Inorg. Chem., 12:1465 (1973).
3. Popescu, O., S. Koritala, and H.J. Dutton, JAOCS, 46:97 (1969).
4. Koritala, S., E. Selke, and H.J. Dutton, Ibid. 50:310 (1973).
5. Hinze, A.G., U.S. Patent 3,865,853 (1975).
6. Gaudemaris, M. de, and P. Arnaud, Bull. Soc. Chim. Fr. 315 (1962).
7. Van der Plank, P., JAOCS, 49:489 (1972).
8. Koritala, S., and C.R. Scholfield, Ibid. 47:262 (1970).
9. Koritala, S., E. Selke, and H.J. Dutton, Ibid. 50:310 (1973).
10. Snyder, J.M., C.R. Scholfield, T.L. Mounts, R.O. Butterfield, and H.J. Dutton, Ibid. 52:244 (1975).
11. Scholfield, C.R., Ibid. 49:583 (1972).
12. Sabadie, J., G. Descotes, and J.E. Germain, Bull. Soc. Chim. Fr. 1855 (1975).

[Received March 27, 1978]