Mechanism of Hydro-Isomerization of Methylene-Interrupted Dienes on Nonmetallic Palladium-on-Resin Catalysts III

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ABSTRACT

A mixture of conjugated dienes, obtained by alkali-isomerization of methyl *cis*-9,*cis*-12-octadecadienoate (*c*9,*c*12) has been hydrogenated on a nonmetallic palladium-on-resin catalyst at 40 C under atmospheric hydrogen pressure in acetone as solvent. The results have been used to quantify the contribution of the conjugation mechanism to the hydrogenation process of *c*9,*c*12. In a 50:50 mixture conjugated dienes are hydrogenated 4.6 times faster than *c*9,*c*12 at 40 C. This diene is hydrogenated very selectively both by straightforward reduction of one of the double bonds and by reduction of conjugated intermediates. The contribution of the former reaction route is more than 50% under the reaction conditions used. It is assumed that the crucial intermediate in the associative mechanism is formed by hydrogen transfer from the metal ion to *c*9,*c*12 resulting in a chelating ring consisting of an ethylene bridge between the π-coordinated double bond and the σ-coordinated bond. This σ,π-complex is responsible for the straightforward, selective hydrogenation of *c*9,*c*12 as well as for the geometric isomerization of this diene.

INTRODUCTION

Previously we reported on some peculiar phenomena observed on nonmetallic palladium-on-resin catalysts (Pd/resin) during the hydrogenation of methyl *cis*-9,*cis*-12-octadecadienoate (*c*9,*c*12; methyl linoleate), its geometric isomers methyl *cis*-9,*trans*-12- and *trans*-9,*trans*-12-octadecadienoate (*c*9,*t*12 and *t*9,*t*12) (1), and a positional isomer, namely methyl *cis*-9,*cis*-13-octadecadienoate (*c*9,*c*13) (2). The hydrogenation of *c*9,*c*12 proceeds with almost infinite selectivity, accompanied by a relatively high activity for the formation of geometric isomers. The ethylene-interrupted diene *c*9,*c*13' is hydrogenated rather slowly, whereas monoenes are reduced with great difficulty.

We have concluded that *c*9,*c*12 is hydrogenated straightforwardly as well as indirectly via conjugated intermediates. To substantiate the conclusion, in the present study we hydrogenated alkali-conjugated methyl linoleate (*c*9,*t*11 + *t*10,*c*12). We further tried to explain the various results on the basis of a reaction scheme in which an ethylene-bridged, coordinated intermediate plays a key part.

EXPERIMENTAL PROCEDURES

Substrates

An equimolar mixture of *c*9,*t*11 and *t*10,*c*12 was prepared by alkali-conjugation of *c*9,*c*12 according to a procedure described by Scholfield and Koritala (3). In addition to 41.4% *t*10,*c*12 and 46.7% *c*9,*t*11, the mixture contained 2.6% *c*9,*c*12, 6.0% monoene (mainly *c*9) and small amounts of other dienes.

Hydrogenation

The preparation of Pd/resin has been described elsewhere (catalyst III, ref. 1). The hydrogenations were carried out with 5 ml ester and 15 ml acetone as solvent at 40 C under atmospheric hydrogen pressure. The conjugated dienes were reduced initially with 120 mg palladium per kg ester; after 48 min an additional amount of 120 mg palladium per kg ester was added to obtain a degree of hydrogenation (HD) of 50%. The same procedure was applied for the hydrogenation of a 50:50 mixture of *c*9,*c*12 and the conjugated dienes. In this case the second amount of catalyst was added after 20 min.

The analysis of the reaction mixtures was carried out as described in the preceding papers (1,2).

RESULTS AND DISCUSSION

Figure 1 shows the trend of the hydrogenations of the conjugated dienes and of their 50:50 mixture with *c*9,*c*12. In both cases the dienes are hydrogenated very selectively. Even at an HD of 35%, only traces of methyl stearate were found. The strong decrease in activity of the catalyst during hydrogenation of active dienes was also observed with other substrates (1,2). The activity was restored by addition of an amount of fresh catalyst.

After the alkali-isomerization, the mixture of conjugated dienes still contained 2.6% of the original ester, *c*9,*c*12. This amount appeared to be very resistant to hydrogenation during reaction of the mixture. At an HD of 34.5%, there was still 2.3% *c*9,*c*12 present in the reaction mixture. This phenomenon, together with the knowledge that hydrogenation of *c*9,*c*12 proceeds partially through conjugated dienes

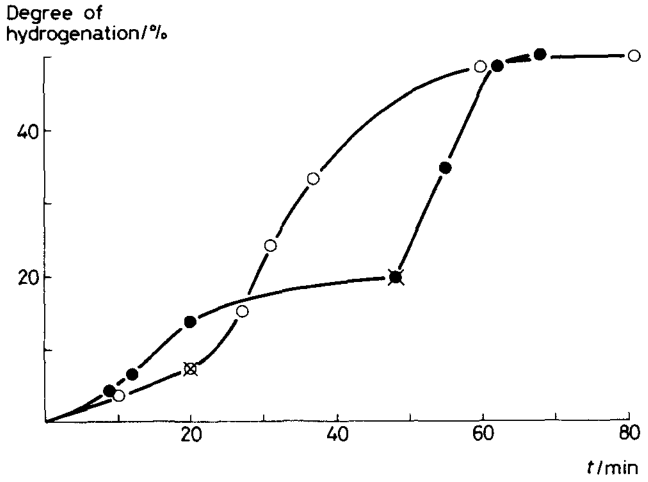

FIG. 1. Degree of hydrogenation as a function of time in the hydrogenation of a mixture of conjugated dienes (*c*9,*t*11 and *t*10,*c*12; (•) and a 50:50 mixture of *c*9,*c*12 and the conjugated dienes (o). The moment of the second addition of catalyst is indicated by x.

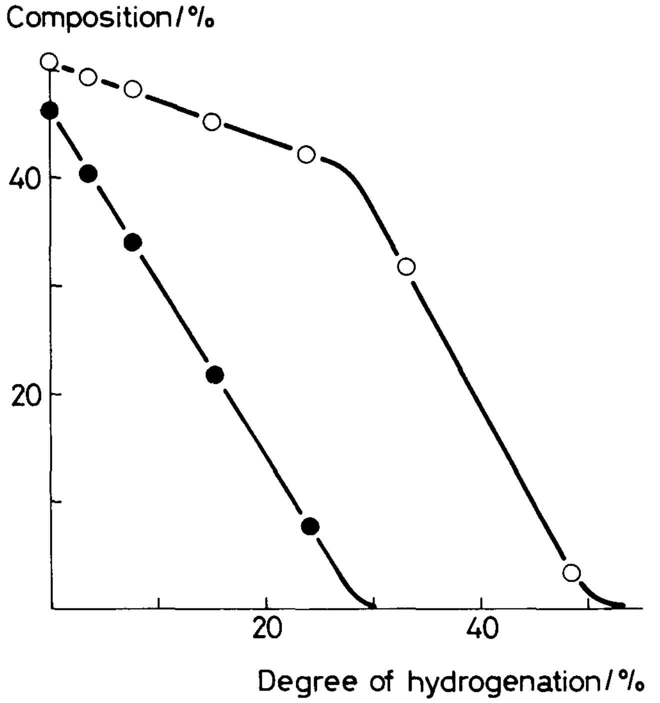

FIG. 2. Substrate composition during hydrogenation of the 50:50 mixture of *c*9,*c*12 and the conjugated dienes (*c*9,*t*11 and *t*10,*c*12). ○ *c*9,*c*12, ● conjugated dienes.

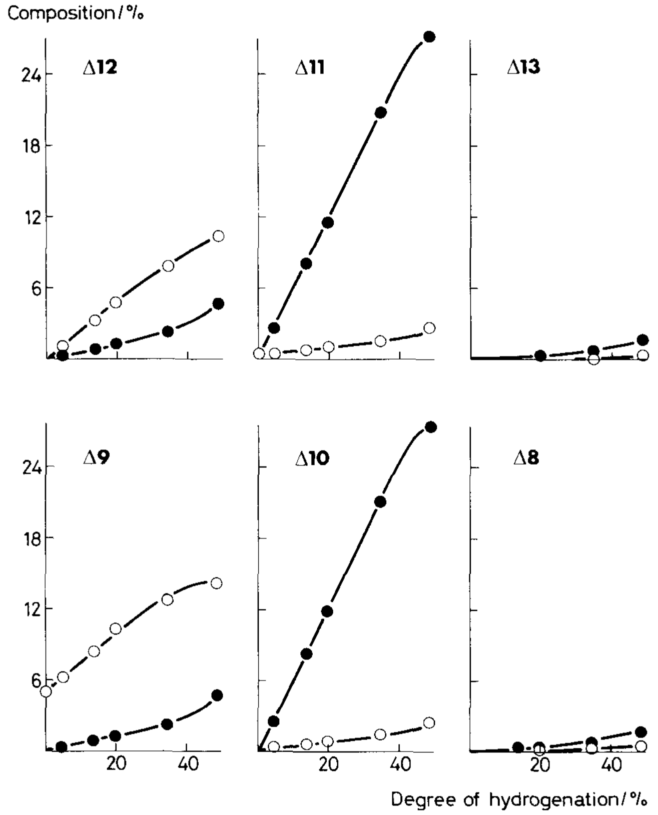

FIG. 3. Monoenes (○; *c*; ●;*t*) obtained from hydrogenation of the mixture of conjugated dienes (*c*9,*t*11 and *t*10,*c*12).

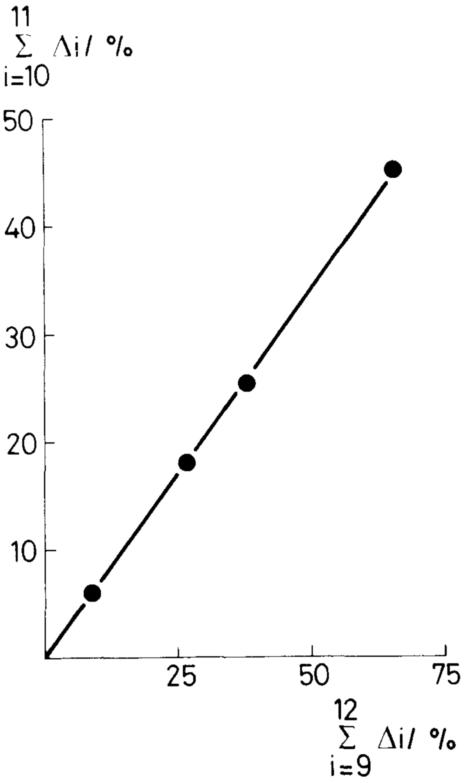

FIG. 4. Sum of the percentages of the 10- and 11-isomers vs. that of the 9- to 12-isomers in the hydrogenation of the mixture of conjugated dienes (*c*9,*t*11 and *t*10,*c*12).

without an appreciable accumulation of these intermediates (1,2), suggests a high selectivity for hydrogenation of conjugated dienes with respect to methylene-interrupted dienes.

To verify this suggestion, we hydrogenated a 50:50 mixture of *c*9,*c*12 and the conjugated dienes. In Figure 2 the amounts of these esters during hydrogenation are given. The curves show that the conjugated dienes are reduced considerably faster (about 4.6 times) than the methylene-interrupted diene.

Next, we consider the monoenes formed by hydrogenation of the mixture of conjugated dienes (*c*9,*t*11 and *t*10,*c*12) (Fig. 3). In Figure 4 the sum of the percentages of the 10- and 11-isomers is plotted vs. that of the 9- to 12-isomers. The resulting straight line indicates that the ratio between the amounts of isomers remains constant. So, the double bond does not migrate in these monoenes during hydrogenation of conjugated intermediates.

The slope of the line in Figure 4, defined as

$$C = \sum_{i=10}^{11} \Delta i / \sum_{i=9}^{12} \Delta i,$$

where Δi = percentage of the positional isomer with the double bond in the ith position, is 0.68. This value shows the contributions of 1,2- and 1,4-addition of hydrogen. C equals to 0.5 at random 1,2-addition and to 1.0 at 1,4-addition of hydrogen to the conjugated dienes. Assuming random 1,2-addition, the value 0.68 corresponds with 64% 1,2-and 36% 1,4-addition.

However, the assumption of a random 1,2-addition may be far from true. For example, Koritala et al. (4) have found a slight preference for hydrogenation of the *cis* double bond in *t*10,*c*12 on palladium-on-coal at 25 C, whereas we have observed that either the *cis* or the *trans* double bond of the same diene is hydrogenated preferentially on homogeneous rhodium catalysts, depending on the type of ligand (to be published). Under identical conditions as applied to the mixture of conjugated dienes, the methylene-interrupted diene *c*9,*c*12 also gives a straight line with a slope of

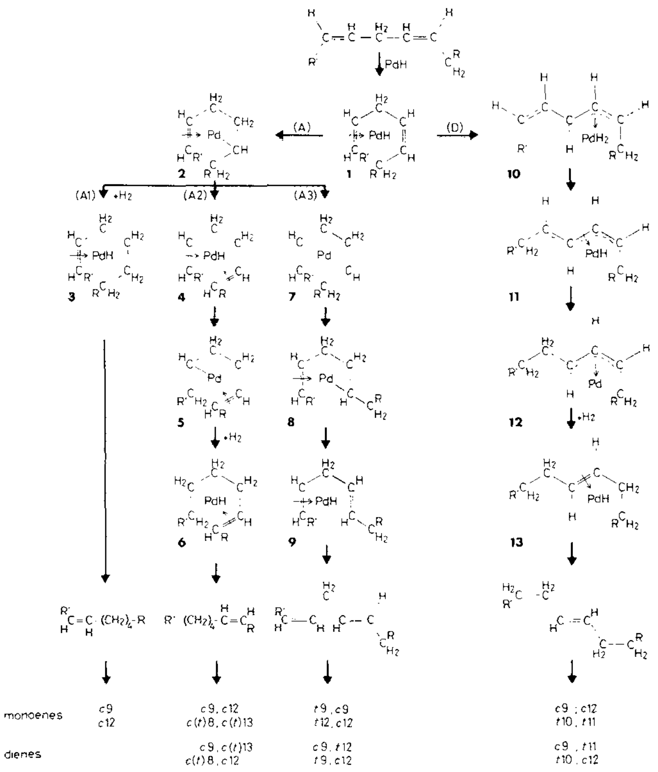

FIG. 5. Reaction scheme for the hydrogenation and isomerization of *c*9,*c*12 (associative mechanism: A; dissociative mechanism: D).

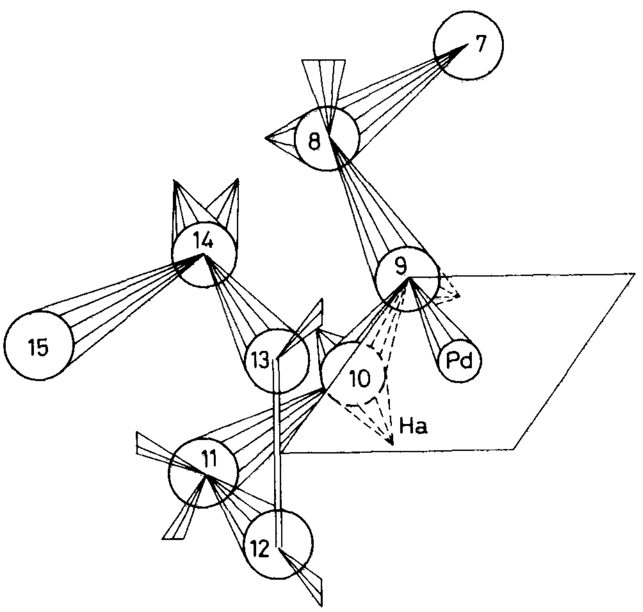

FIG. 6. σ,π-complex obtained from *c*9,*c*12 and Pd-ion after hydrogen (Ha) transfer from palladium to carbon atom 10.

0.29 in a similar plot. From this slope it can be deduced that 43% (100 x 0.29:0.68) of *c*9,*c*12 is hydrogenated through conjugated intermediates. In about the same way, Koritala (5) found 51% for the hydrogenation of *c*9,*c*12 on palladium-on-coal at 25 C.

However, we also observed C-values lower than 0.29. Although we do not know why, the values appeared to depend to some extent on the type of resin used. For example, a value of 0.19 has been found on a catalyst made from commercial Zerolite 325 as support. Despite the low contribution of conjugation in this case (about 28%), *c*9,*c*12 was hydrogenated with almost infinite selectivity. It may be worthwhile to mention that the same catalyst was used for the hydrogenation of *c*9,*c*12 at 92 C. We found a C-value of 0.35 at this temperature, thus nearly a doubling of the value at 40 C due to a strong increase of the contribution of the conjugation mechanism.

So far we have found (see also references 1 and 2), that:

- *c*9,*c*12 is hydrogenated with almost infinite selectivity to the monoene stage for more than 50% by straightforward hydrogenation of one of the double bonds, at least at 40 C;
- the contribution of the conjugation mechanism increases with temperature;
- *c*9,*c*12 isomerizes geometrically to a relatively high degree, whereas it scarcely isomerizes positionally;
- the isomerization rate increases with temperature;
- the hydrogenation of the geometric isomers of *c*9,*c*12 is lower than that of *c*9,*c*12;
- the isomerization of monoenes is strongly suppressed in the presence of methylene-interrupted dienes;
- the hydrogenation of *c*9 proceeds very slowly and is accompanied by a relatively high rate of positional and geometric isomerization;
- *c*9,*c*13 is less active than *c*9,*c*12, but more active than *c*9. This is mainly due to the high isomerization activity of *c*9,*c*13 resulting in the formation of active methylene-interrupted dienes, which are hydrogenated very quickly.

The hydrogenation behavior of *c*9,*c*12 as compared with that of *c*9,*c*13 is interesting in that similar differences were observed in other systems. For example, Nakamura and Otsuka (6) have found that 1,5-cyclooctadiene is inactive, whereas the 1,4-isomer can be hydrogenated selectively to cyclooctene with dicyclopentadienyl dihydridomolybdenum as catalyst. On the other hand, Frankel and Butterfield (7) have been able to isomerize 1,5-cyclooctadiene to conjugated diene with arenetricarbonylchromium, probably via the 1,4-diene as intermediate, which is considerably more active. However, a 1,5-diene system, completely free from angle strain as present in 1,5-hexadiene, did not isomerize at all under identical reaction conditions.

An important question emerges: what is the driving force of the high selectivity of methylene-interrupted diene systems without the intervention of conjugation? Before discussing this question, it may be worthwhile to note some pertinent data from the literature:

- π,π complexes of methylene-interrupted diene systems with metals have not been found so far because a considerable degree of angle strain is introduced when the orbitals of metal and alkene are well overlapped (8). However, molecules, in which this angle strain is already present, complex easily with metals. For instance, bicyclo [2,2,1] heptadiene occurs as a ligand in some stable rhodium complexes (9);
- π,π-complexes are easily formed when the double bonds of the diene are separated by more than one methylene group (8);
- σ,π-complexes require at least two methylene groups between the π- and σ-coordinated bond (8);
- 3 electron π-allyl (-*c*-*c*-*c*-) and 5 electron π-dienyl (-*c*-*c*-*c*-*c*-*c*-) complexes are well known (8).

On the basis of these data, selective hydrogenation

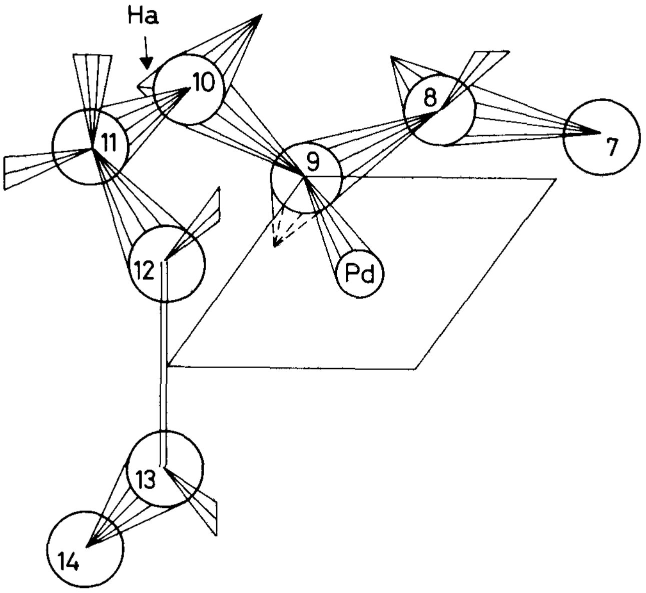

FIG. 7. σ,π-complex obtained from the σ,π-complex given in Fig. 6 after desorption, rotation and readsorption of the 12-double bond.

of a methylene-interrupted diene via conjugation is easy to understand: dissociative adsorption results in a 5 electron π-dienyl complex, from which a conjugated diene is formed (intermediates 10 and 11, Fig. 5) . A typical monoene distribution is found when mainly this mechanism operates (Fig. 3). However, the double-bond distributions in the monoene fractions obtained from *c*9,*c*12 on Pd/resin deviate strongly from this pattern, because (at 40 C) less than 50% of the diene is hydrogenated through conjugated intermediates.

The other reaction route, namely straightforward hydrogenation, is hard to understand when it is preceded by a dissociative adsorption step. In that case we must assume that the migrating double bond is hydrogenated preferentially. So far, we have no indication that this occurs. Moreover, the relatively high degree of geometric isomerization of *c*9,*c*12, especially at 92 C, does not fit the dissociative (or conjugation) mechanism at all.

For this reason we assume that straightforward hydrogenation of one of the double bonds in methylene-interrupted dienes proceeds via the associative mechanism (Fig. 5, route A). In this mechanism, the chemical activity of the methylene group does not play any role. Nevertheless, the selectivity strongly decreases when the double bonds are separated further from each other as in *c*9,*c*13.

The planar representation of the σ,π-complexes (intermediates 2, 5 and 8 in Fig. 5) does not offer sufficient information on the differences in the hydrogenation behavior of methylene- and ethylene-interrupted dienes. Therefore, we designed stereopictures of the intermediates in question on the basis of Stuart and Dreyding models; Figure 6 represents the σ,π-complex obtained from *c*9,*c*12. In connection with this complex, it is of interest to note that Bogdanović et al. (10) isolated a π-cycloocten-4-yl-1-nickel complex, the structure of which was proved to correspond with that given in Fig. 6.

In this complex only the hydrogen atom transferred from Pd can be considered for removal, which leads to the formation of the original product, *c*9,*c*12. The hydrogen atoms bound to carbon atom 8 are sterically hindered by the hydrogen atoms of carbon atom 14; a possible vacant site is, as it were, shielded by this methylene group. Moreover, severe angle strain will be introduced in the transition state for the removal of one of the hydrogen atoms of carbon atom 8. This explains why the positional isomers *t*8,*c*12 or *c*9,*t*13 are rather difficult to form.

The other positional isomers, *c*8,*c*12 and *c*9,*c*13, cannot be formed at all via the complex given in Fig. 6. This is due to sterical energy arising from the repulsion of the seventh methylene group by the fourteenth one in that state, which is necessary for the formation of the ethylene-interrupted *cis,cis*-dienes. Thus, the contribution of route A_2 in Fig. 5 will be very small.

The hydrogen atom bound to the same carbon as the transferred hydrogen atom (Fig. 6) cannot be removed from this position. The complex should be reorganized completely via desorption, rotation, and readsorption of the double bond to bring this hydrogen atom in a favorable position for abstraction by the metal ion (Fig. 7), finally resulting in a methylene-interrupted *cis,trans*-diene. Positional isomerization via this σ,π-complex is difficult for the same reasons as mentioned for the other complex (Fig. 6). Thus, we may conclude that geometric isomerization dominates over positional isomerization, which is in agreement with the experimental facts.

We have shown that *c*9,*c*13 is difficult to form from an ethylene-bridged σ,π-complex. This implies that, according to the principle of microscopic reversibility, that complex is hardly formed from *c*9,*c*13. However, as has been observed, this means loss of activity and selectivity.

More information on the structure of the σ,π-complex is required to draw more exact and less speculative conclusions. Despite this shortcoming the phenomena described in this paper and the preceding ones (1,2) are fairly well understandable on the basis of the reaction scheme discussed.

ACKNOWLEDGMENT

Thanks are due to Mr. C. van Dijk for the hydrogenation experiments.

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[Received March 27, 1978]