# Selective Hydrogenation With Copper Catalysts: IV. Reaction of Stearolate, Oleate and Conjugated Esters With Deuterium[1]

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## ABSTRACT

$\beta$-Eleostearate and trans,trans-conjugated diene were reduced with deuterium in the presence of copper chromite. Considerable exchange of hydrogen atoms of the starting material for deuterium atoms was observed. Conjugated double bond systems isomerized (positional and geometric) extensively during hydrogenation. Isomerization and exchange reactions occurred at a faster rate than hydrogen addition reaction. During early stages of the reaction, a large amount of the product formed contained no deuterium. Of the three possible mechanisms of hydrogen addition to $\beta$-eleostearate (1,2; 1,4 and 1,6), no one mechanism could account for all the products formed. Reduction of trans-9,trans-11-octadecadienoate at a higher temperature and pressure (200 C, 500 psi) caused a minimum of exchange and isomerization apparently due to sintering of the catalyst. Monoenes were formed from trans,trans-conjugated diene by both 1,2 and 1,4 addition. Methyl oleate was not reduced, but extensive isomerization occurred. Deuterium was incorporated into isomeric monoenes. Mechanistic schemes are proposed to account for exchange, isomerization and hydrogen addition.

## INTRODUCTION

Even though copper-chromite catalysts have been known for a long time (1-3), they were not investigated for the selective hydrogenation of triglycerides (4). In the past decade, the selectivity of copper-containing catalysts has generated considerable interest as evidenced by the

numerous publications and patents (5-14). Still, the mechanism of hydrogenation with copper catalysts remains unknown although conjugation of the double bonds during hydrogenation was suggested (15). The three previous publications in this series (16-18) indicate that conjugation of double bonds precedes hydrogenation and that extensive isomerization of the conjugated double bond systems occurs. This paper includes some further mechanistic studies based on deuterium as a tracer.

## EXPERIMENTAL PROCEDURES

Preparation of the various conjugated esters and techniques of hydrogenating at 150 C and atmospheric pressure, as well as separation and analysis of the products, have been described (16-18) except that in the present work deuterium replaced hydrogen. Gas liquid chromatographic analyses of methyl esters were carried out with an Aerograph instrument, which was equipped with dual 6 ft X 1/8 in. stainless-steel columns packed with 15% EGSS-X on Gas-Chrom P, and with flame ionization detectors. The columns were held at 190 C with a nitrogen gas flow of 20 ml/min. Peak areas were determined with a disc integrator. Ozonolysis products were analyzed with the same instrument. The column temperature was programmed at 6°/min from 50 to 190 C and held at the higher temperature for the duration of the analysis. Peak areas were calculated by triangulation. High-pressure reductions with deuterium were carried out in a 150 ml magnetically stirred Magna-Dash autoclave provided with cooling jacket and sampling valve. The mixture of ester and copper-chromite catalyst was heated under helium to the temperature of the reaction. Helium was then replaced with 500 psi deuterium. Samples were withdrawn when the calculated amount of pressure drop occurred. At the end of reduction the autoclave was cooled and the product was recovered in the usual manner. The hydrogenated products were separated
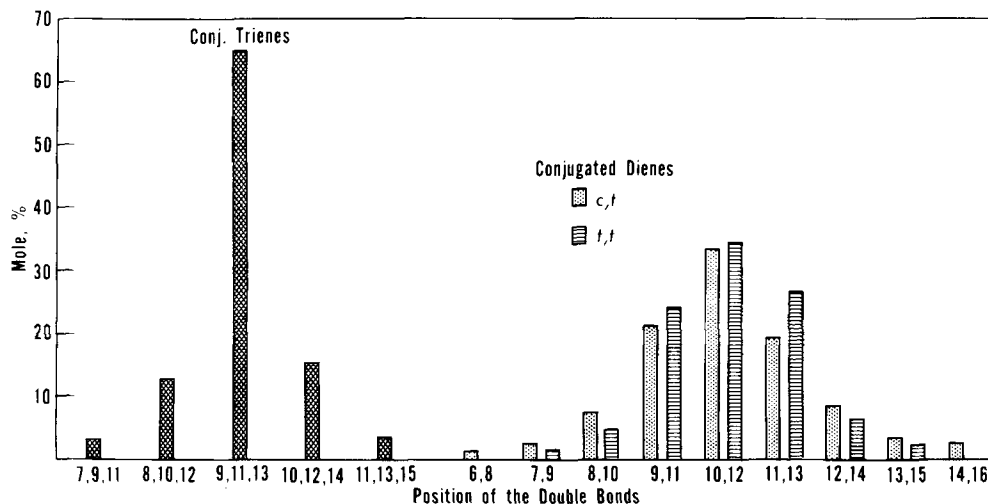


FIG. 1. Double bond distribution in fractions from $\beta$-eleostearate reduction with copper chromite at 150 C and atmospheric deuterium pressure. Final composition: conjugated triene, 95%; trans,trans-conjugated diene, 3.5%; cis,trans-conjugated diene, 1.5%.
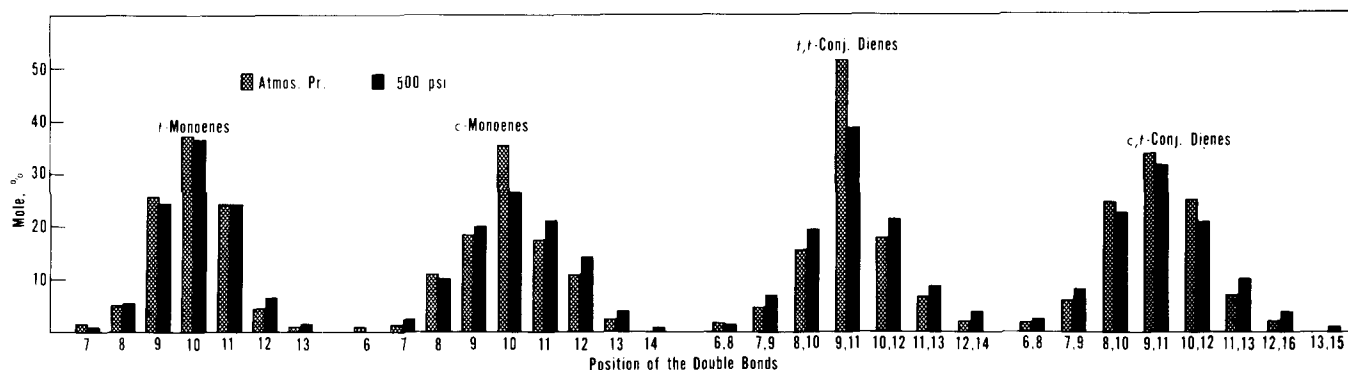
FIG. 2. Double bond distribution in fractions obtained from partial reduction of *trans*-9,*trans*-11-octadecadienoate with copper chromite at 150 C. Final composition for reduction at atmospheric pressure: *trans,trans*-conjugated diene, 64.6%; *cis,trans*-conjugated diene, 27.7%; *trans*-monoene, 5.6%; *cis*-monoene, 2.3%. Composition of the product at 500 psi reduction: *trans,trans*-conjugated diene, 25.6%; *cis,trans*-conjugated diene, 8.5%; *trans*-monoene, 50.7%, *cis*-monoene, 15.2%.

into individual classes, and the position of the double bonds was determined by reductive ozonolysis as described previously (16,18). The isotopic analyses of the separated products were determined with a Nuclide mass spectrometer. The position of the deuterium in some products was determined by NMR spectroscopy.

## RESULTS

### Reactions of Conjugated Triene

At 150 C and atmospheric pressure β-eleostearate was 5% reduced with deuterium in the presence of copper chromite and the distribution of positional isomers in the products is plotted in Figure 1. Evidently, conjugated trienes isomerized extensively even during early stages of hydrogenation. After the triene was reduced 5%, 35% of the triene molecules were isomerized. Thus the initial rate of isomerization is much faster than the rate of hydrogenation. Only conjugated dienes were formed from the reduction of conjugated triene. These conjugated dienes could be formed by (a) 1,2 addition of hydrogen (the term hydrogen is used generically and can be replaced with deuterium) to the end double bonds, (b) 1,6 addition and (c) 1,4 addition followed by rearrangement to form conjugated double bonds. The isomeric distribution of conjugated dienes can be accounted for by mechanisms (a) and (b), although the possibility of all three mechanisms operating simultaneously cannot be discounted.

The distribution of deuterium in the products was measured by a mass spectrometer (Table I). When deuterium is used instead of hydrogen, a new reaction,

triene exchange (defined as exchange of hydrogen atoms or triene for deuterium atoms), becomes evident. At 5% reduction, 7.3% of the triene contained one or more deuterium atoms. Thus the exchange process is slightly faster than the addition reaction. In early stages of reduction, a major part of the conjugated dienes formed (>69%) contained no deuterium even though deuterium was used to reduce. More than 75% of the incorporated deuterium appeared in the conjugated trienes. Evidently the hydrogen atoms of trienes are first exchanged for deuterium atoms and the hydrogen atoms are then added to another molecule of triene to produce conjugated dienes with no deuterium.

### Reactions of Conjugated Diene

*Trans*-9,*trans*-11-octadecadienoate was reduced (7.9% at atmospheric pressure and 65.9% at 500 psi) with deuterium at 150 C in the presence of copper chromite. The distribution of positional isomers in the products is shown in Figure 2. At both pressures, *trans,trans* conjugated diene was isomerized to *cis,trans* conjugated diene. Also, there was extensive isomerization of the double bonds. However, isomerization was somewhat suppressed at higher pressure (compare the diene isomers with those in reference 18 where *trans,trans* conjugated diene was 40% reduced at atmospheric pressure). At 7.9% reduction at atmospheric pressure about 59% of the conjugated dienes were isomerized (geometric and positional). Thus isomerization was much more rapid than hydrogen addition. The double bond distribution in the monoenes can be accounted for by invoking both 1,2 and 1,4 hydrogen addition reaction
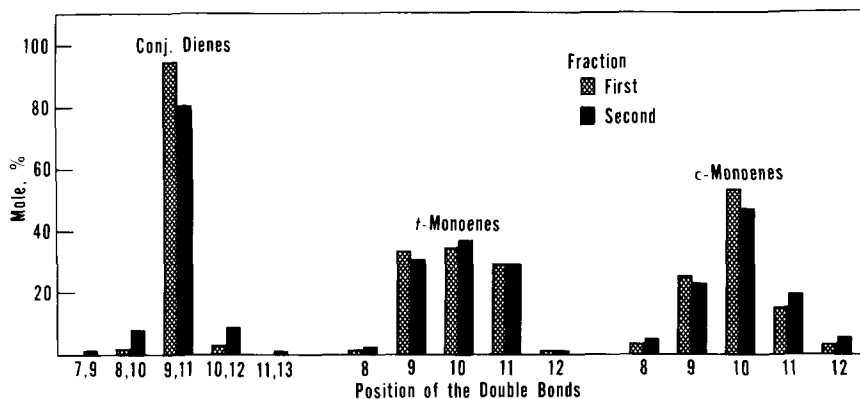


FIG. 3. Double bond distribution in fractions obtained during the reduction of *trans*-9,*trans*-11-octadecadienoate with copper chromite at 200 C and 500 psi deuterium pressure. Composition of first fraction: *trans,trans*-conjugated diene, 82.3%; *cis,trans*-conjugated diene, 2.1%; *trans*-monoene, 14.7%; *cis*-monoene, 0.9%. Second fraction: *trans,trans*-conjugated diene, 18.3%; *cis, trans*-conjugated diene, 3.1%; *trans*-monoene, 72.3%; *cis*-monoene, 6.3%.
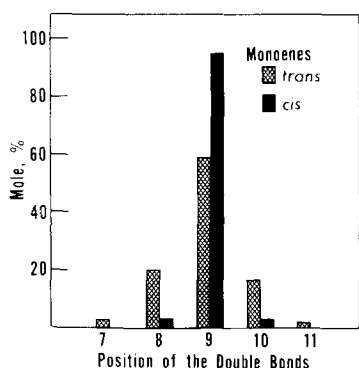
FIG. 4. Double bond distribution of *trans*- and *cis*-monoenes formed during reaction of methyl oleate with copper chromite.

occurring simultaneously. The double bonds in *cis*-monoenes were slightly more scattered than in *trans*-monoenes because *cis*-monoenes are formed from *cis,trans* conjugated dienes which, in turn, resulted from isomerization of the starting material.

Distribution of deuterium in the products is given in Table II. Reduction at atmospheric pressure is accompanied by much diene exchange (defined as exchange of hydrogen atoms of diene for deuterium atoms). At 7.9% reduction about 15% of the unreacted conjugated dienes contained one or more deuterium atoms. Thus the exchange reaction is about twice as fast as the addition reaction. More than 80% of the incorporated deuterium appeared in the conjugated dienes. Apparently hydrogen atoms of the dienes are first exchanged for deuterium atoms and then the hydrogen atoms are added to another diene molecule. Thus more than 65% of the monoenes formed contained no deuterium. There was also considerable diene exchange during high-pressure reduction.

When 500 psi reduction of *trans*-9,*trans*-11-octadecadienoate was carried out at 200 C, surprisingly little isomerization occurred (Fig. 3). At 15.6% reduction (first fraction) about 95% of the unreacted material retained its position of the double bonds and only minor amounts of *cis,trans* conjugated dienes were formed. About 94% of the monoene formed had *trans* configuration. Essentially equal amount of $\Delta 9$-, 10- and 11-*trans*-octadecenoates are formed indicating 1,2 and 1,4 addition. Even at 78.6% reduction (Fig. 3, second fraction), the unreacted conjugated diene isomerized surprisingly little. More than 90% of the monoene formed had *trans* configuration and double bonds are found in 9, 10 and 11 positions in equal amounts. The double bonds in *cis*-monoenes, which represented a minor amount of the product formed, were slightly more scattered than those in *trans*-monoenes. The rather large amount of $\Delta 10$ isomer in the *cis*-fraction was probably formed by 1,4 addition of hydrogen to conjugated diene in

a cisoid form. The other isomers resulted, at least in part, from further isomerization of monoenes. Isomerization of monoenes does occur at the higher temperature as will be seen later. Suppression of isomerization of conjugated dienes at a higher temperature of hydrogenation might seem anomalous. But we have observed that the catalyst turns bright red, an indication that we are dealing with a new form of sintered catalyst or a metallic catalyst. Mass spectral data are shown in Table III. There was little diene exchange initially, but at 78.6% reduction the exchange was considerable. However, the amount of exchange is considerably smaller than the exchange during 150 C hydrogenation (Table II). In both *trans*-monoene fractions, 69% and 61% of the isotopic species contained two deuterium atoms. Thus *trans*-monoenes, which represent more than 90% of the product, are formed in large part by the addition of two deuterium atoms to the double bonds. 1,2 Addition should form a monoene that contains one deuterium on a carbon atom $\alpha$ to the double bond, and one deuterium on a carbon atom $\beta$ to the double bond; whereas 1,4 addition should yield a monoene with both deuteriums in the $\alpha$ position. From the double bond distribution (Fig. 3), it is evident that the ratio of rate of 1,2 addition to 1,4 addition is two. The amount of deuterium in the $\alpha$ position should therefore be twice the amount in the $\beta$ position. NMR of *trans*-monoenes showed 53.5% of the deuterium in the $\alpha$ position and 27.5% in the $\beta$ position for the first fraction (54.8% and 31.7%, respectively, for the second fraction). The NMR data further substantiate that the *trans*-monoenes are formed by direct 1,2 and 1,4 addition of two deuterium atoms to the conjugated diene.

## Reactions of Triple Bonds

Stearolate was reduced (98%) with copper chromite at 150 C and atmospheric deuterium pressure. The product consisted of only *cis*-9-octadecenoate. Mass spectral data are given in Table IV. About 76% of the product contained two deuterium atoms. NMR indicated that all the deuterium was olefinic. Stearolate is, therefore, reduced primarily by *cis*-addition of two deuterium atoms across the triple bond. Under the mild conditions of hydrogenation used, the oleate formed will not isomerize (18). Therefore, oleate molecules containing 0, 1, 3, 4 and 5 deuterium atoms must arise by exchange process (exchange of hydrogen atoms of stearolate for deuterium atoms). Since there were no hydrogen atoms on the carbon atoms of the triple bond, the hydrogen on the $\alpha$-carbon atoms must be involved in the exchange process. These hydrogen atoms then add to other stearolate molecules to produce oleate with no deuterium. Oleate with more than two deuterium atoms is formed when deuterium is added to exchanged stearolate. In a similar experiment stearolate was 80% reduced and mass spectral analysis of the unreacted stearoleate ($D_{av} = 0.70$) showed that stearolate with 1 to 4 deuterium atoms was present in amounts ranging from 1% to 5%.

TABLE I

Distribution of Deuterium in Products Formed From
Reduction (150 C and atmospheric pressure) of $\beta$-Eleostearate

| No. of deuterium atoms | Conjugated triene, % | Trans, trans conjugated diene, % | Cis, trans conjugated diene, % |
|---|---|---|---|
| 0 | 92.7 | 69.1 | 74.8 |
| 1 | 5.5 | 17.7 | 15.9 |
| 2 | 1.1 | 5.9 | 4.1 |
| 3 | 0.5 | 2.8 | 1.8 |
| 4 | 0.1 | 1.7 | 1.2 |
| 5 | 0.1 | 0.9 | 0.6 |
| 6 to 11 | | 0.6   to 0.1 | 0.3   to 0.2 |
| $D_{av}$[a] | 0.10 | 0.63 | 0.49 |

[a]Average number of deuterium atoms per molecule.

TABLE II

Distribution of Deuterium in Products Formed During
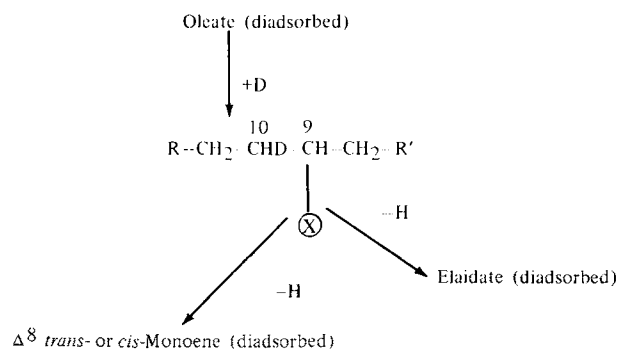Reduction of Trans-9,trans-11-Octadecadienoate at 150 C

| No. of deuterium atoms | Trans, trans conjugated diene, % | | Cis, trans conjugated diene, % | | Trans-monoene, % | | Cis-monoene, % | |
|---|---|---|---|---|---|---|---|---|
| | Atmospheric pressure | 500 Psi | Atmospheric pressure | 500 Psi | Atmospheric pressure | 500 Psi | Atmospheric pressure | 500 Psi |
| 0 | 86.1 | 41.9 | 78.8 | 26.3 | 69.1 | 19.0 | 65.1 | 17.2 |
| 1 | 10.4 | 31.8 | 16.6 | 36.2 | 22.5 | 28.0 | 23.9 | 27.7 |
| 2 | 2.4 | 17.1 | 3.1 | 23.1 | 5.6 | 30.9 | 6.7 | 29.7 |
| 3 | 0.9 | 6.5 | 1.0 | 9.9 | 1.8 | 13.9 | 2.2 | 15.8 |
| 4 | 0.2 | 2.0 | 0.4 | 3.3 | 0.7 | 5.6 | 1.0 | 6.5 |
| 5 | | 0.5 | 0.1 | 0.9 | 0.3 | 1.8 | 0.5 | 2.1 |
| 6 | | 0.1 | | 0.2 | | 0.6 | 0.4 | 0.7 |
| 7 | | | | | | 0.2 | 0.3 | 0.3 |
| 8 | | | | | | 0.1 | | |
| $D_{av}$ | 0.19 | 0.97 | 0.28 | 1.31 | 0.43 | 1.69 | 0.55 | 1.77 |

## Isomerization of Monoene

Methyl oleate was reacted with deuterium (atmospheric pressure) at 200 C in the presence of copper chromite. Only a slight amount of deuterium uptake was observed. After 3 hr, 25% of the oleate was isomerized to trans-monoene. The double bond distribution of trans- and cis-monoenes is shown in Figure 4. Trans-9-octadecenoate was the major isomer formed from oleate. The double bond was also shifted in both directions in trans-monoenes. Trace amounts of all possible isomers were observed. When oleate was reacted under similar conditions with hydrogen instead of deuterium, about 27% of the monoene was isomerized to trans-configuration. Apparently there was no isotopic effect for cis-trans isomerization. However double bond migration showed an isotopic effect since the trans-monoenes formed with hydrogen were more scattered than those formed with deuterium. Similar results were reported for unsaturated hydrocarbons with nicket catalyst (19). Mass spectral data of the monoenes are given in Table V. Trans-monoenes containing 0 to 29 deuterium atoms were formed. About 37.8% and 40.0% of the isotopic species contained 0 and 1 deuterium atom, respectively. Little deuterium was found in cis-monoenes. Methyl stearate did not exchange deuterium under these conditions. When methyl oleate and trans-9,trans-11-octadecadienoate were treated under nitrogen with copper chromite at 200 C for 3 and 1 hr, respectively, no isomerization was observed. Apparently isomerization occurs only in the presence of hydrogen.

## DISCUSSION

Copper-chromite catalyst does not hydrogenate or isomerize monoenes at 150 C and atmospheric pressure (17,18). Even at 200 C hydrogenation was negligible. However, at the higher temperature oleate isomerized apparently by an adsorption-desorption process since no isomerization occurred in the absence of hydrogen. The following mechanism (Horiuti-Polanyi) can be written to account for the isomerization of monoenes.



Addition of one deuterium atoms results in monoadsorbed species in which carbon atom 10 is now free to rotate. Reversal to diadsorbed species could occur by the loss of either hydrogen or deuterium on carbon 10. Loss of

TABLE III

Distribution of Deuterium in Products Formed From
the Reduction (200 C and 500 psi) of
Trans-9,trans-11-Octadecadienoate

| No. of deuterium atoms | Conjugated diene, % | | Trans-monoene, % | | Cis-monoene, % | |
|---|---|---|---|---|---|---|
| | 1[a] | 2 | 1 | 2 | 1 | 2 |
| 0 | 95.1 | 69.6 | 5.1 | 3.2 | 7.6 | 2.7 |
| 1 | 3.7 | 21.6 | 18.3 | 17.4 | 16.0 | 12.9 |
| 2 | 0.5 | 6.1 | 68.9 | 61.3 | 53.5 | 45.5 |
| 3 | 0.4 | 1.6 | 5.9 | 13.3 | 13.5 | 28.7 |
| 4 | 0.3 | 0.7 | 1.2 | 3.0 | 3.0 | 7.0 |
| 5 | | 0.2 | 0.5 | 1.0 | 1.2 | 1.7 |
| 6 | | 0.1 | 0.1 | 0.4 | 0.7 | 0.6 |
| 7 | | | | 0.2 | 0.3 | 0.2 |
| 8 | | | | 0.1 | 0.4 | 0.1 |
| 9 to 16 | | | | | 0.7 to 0.4 | 0.1 |
| $D_{av}$ | 0.07 | 0.43 | 1.82 | 2.02 | 2.38 | 2.42 |

[a]1, 15.6% reduction; 2, 78.6% reduction.

TABLE IV

Distribution of Deuterium in Oleate
Formed From the Reduction of Stearolate With
Copper Chromite at 150 C and Atmospheric Pressure

| No. of deuterium atoms | Oleate, % |
|---|---|
| 0 | 1.6 |
| 1 | 16.6 |
| 2 | 76.1 |
| 3 | 5.0 |
| 4 | 0.2 |
| 5 | 0.5 |
| $D_{av}$ | 1.87 |

TABLE V

Distribution of Deuterium in Trans- and Cis-Monoenes
Formed During Reaction of Oleate and Copper Chromite
in the Presence of Deuterium at 200 C

| No. of deuterium atoms | Trans-monoenes, % | Cis-monoenes, % |
|---|---|---|
| 0 | 37.8 | 92.2 |
| 1 | 40.0 | 5.4 |
| 2 | 5.3 | 1.3 |
| 3 | 2.2 | 0.4 |
| 4 | 1.5 | 0.2 |
| 5 | 1.0 | 0.2 |
| 6 | 0.9 | 0.1 |
| 7 | 0.8 | 0.1 |
| 8 | 0.7 | 0.1 |
| 9 to 29 | 0.7 to 0.3 | 0.0 |
| $D_{av}$ | 2.54 | 0.12 |

hydrogen results in elaidate containing one deuterium atom. This step is responsible for producing a large amount of trans-monoenes with one deuterium atom (Table V). The released hydrogen could then add to another oleate molecule to produce elaidate containing no deuterium. Removal of a hydrogen from carbon 8 results in positional isomerization. If deuterium is first added on the ninth carbon atom instead of the tenth, then removal of hydrogen from the eleventh carbon will move the double bond in the opposite direction. Because isomerization occurred readily without appreciable hydrogenation, the addition of a second hydrogen to monoadsorbed species must be very slow compared to the reversal to diadsorbed species. It is possible to exchange all the hydrogen atoms for deuterium atoms by mere reversal between mono- and diadsorbed species.

Conjugated dienes must not have been strongly adsorbed on the catalyst surface. For if they were, they would not be expected to desorb to any extent until they were reduced to monoenes. The appearance of large amounts of isomeric conjugated dienes (Fig. 2) even during an early period of hydrogenation can only be explained by an adsorption-desorption process. It is unlikely that these dienes are adsorbed by the catalyst at both double bonds for such an adsorbed diene will not readily desorb. The following scheme is offered to explain the reactions of conjugated dienes.



Trans-9,trans-11-conjugated diene (diadsorbed)

ΔI0,I2-Conjugated diene (diadsorbed)
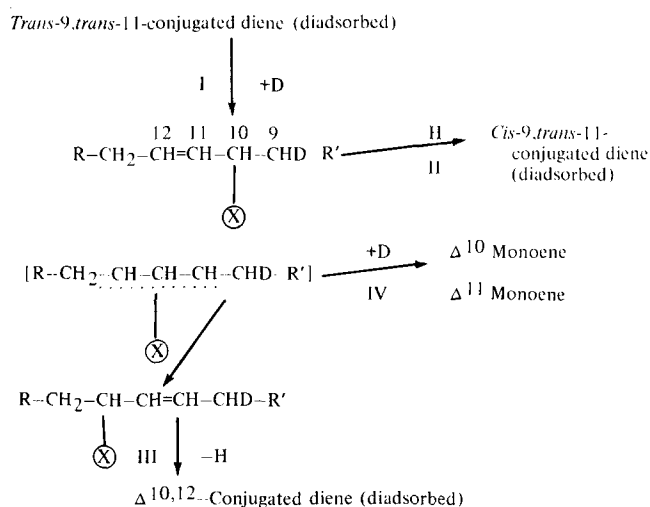
As with the monoenes, the first step is the formation of monoadsorbed species by the addition of deuterium since no reaction occurs in the absence of hydrogen or deuterium. Removal of hydrogen will result in isomerization to cis,trans-conjugated diene (Step 2). This step would explain the large amount of cis-trans-9,11-conjugated diene formed during hydrogenation of trans-9,trans-11-conjugated diene (Fig. 2). Direct addition of hydrogen across a

double bond is not plausible since monoenes or isolated double bonds are not hydrogenated. The π electrons of the 11,12 carbon atoms could be delocalized along 10, 11 and 12 carbon atoms to form π allyl-adsorbed species (20). Addition of another deuterium atom at the 10 or 12 carbon atom will give $\Delta^{10}$ or $\Delta^{11}$ monoene. Positional isomerization could occur through Step 3. If deuterium is added on the tenth carbon atom in Step 1, then no π allyl-adsorbed species could form. However such monoadsorbed species could then form diadsorbed species through Step 2. Similar schemes can be developed by adding deuterium to the 11,12 carbon atoms. Since isomerization occurs faster than addition, reaction Steps 2 and 3 are occurring faster than Step 4. The hydrogen atoms released by Steps 2 and 3 increase the concentration of hydrogen on the catalyst surface. These are then added to another conjugated diene molecule to form monoenes with no deuterium. Addition of hydrogen or deuterium to exchanged diene results in monoenes containing one or more deuterium atoms. During high temperature reduction (200 C and 500 psi), isomerization reactions (Steps 2 and 3) are suppressed and monoenes are formed by the addition of two deuterium atoms.

The mechanism of isomerization and hydrogenation of conjugated trienes could not be ascertained with the little data gathered. Hydrogenation of triple bonds occurs primarily by the cis addition of two hydrogen atoms across the triple bond. The hydrogen atoms on the carbon atoms α to the triple bond in stearolate were easily exchanged with deuterium. Such an exchange process must perforce occur by the dissociative mechanism (for a discussion of different mechanisms see reference 21). This inference gives impetus to speculation whether conjugated dienes exchange by a similar mechanism. Such an exchange mechanism for unsaturated hydrocarbons has not been fully appreciated.

From this series of studies, copper-chromite catalyst shows certain distinct differences in mechanism of hydrogenation from other catalysts. Monoenes or isolated double bonds are not reduced by copper chromite under ordinary conditions of hydrogenation (17). Unlike nickel, palladium and platinum catalysts (22,23 and Koritala et al., unpublished data), copper chromite causes extensive isomerization of the conjugated double bond systems. Considerable exchange of hydrogen atoms of conjugated dienes and trienes for deuterium atoms occurs with copper chromite, whereas no such exchange occurs with nickel, palladium and platinum catalysts (Koritala et al., unpublished data).

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