Deuteration of Methyl *cis*-9,*cis*-15-Octadecadienoate with Nickel Catalyst

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ABSTRACT

Methyl *cis*-9,*cis*-15-octadecadienoate was partially deuterated with nickel catalyst, and the product was separated into saturate, monoene and diene fractions. Monoenes were separated into *trans* and *cis* fractions, and dienes into *trans,trans*, *cis,trans* and *cis,cis* fractions. Monoene isomers with double bonds at the 9 and 15 positions predominated in both *cis*- and *trans*-monoene fractions. Considerable amounts of isomers with double bonds situated on either side of the original 9 and 15 positions were found in the *trans*-monoene fraction. Diene was extensively isomerized to positional and geometrical isomers, and deuterium was incorporated into these isomers. Double bond migration was greatest in *trans,trans*-dienes and smallest in *cis,cis*-dienes. The amount of deuterium in the dienes was proportional to the extent of isomerization experienced by the dienes.

INTRODUCTION

Reduction of methyl linoleate with nickel catalyst is accompanied by isomerization (1), which leads to the formation of conjugated dienes, geometrical isomers of linoleate and nonconjugatable dienes with double bonds separated by more than one methylene group. A knowledge of the fate of these intermediates will aid our understanding of the mechanism of hydrogenation. Catalytic reduction of conjugated dienes (2,3) and geometrical isomers of linoleate (4) has been investigated. Similar information on nonconjugatable dienes is not available.

Nonconjugatable dienes are also formed during hydrogenation of methyl linolenate with nickel and platinum catalysts (5,6). These dienes, which are less reactive than methyl linoleate (7), tend to accumulate during early stages of reaction. During the later stages of hydrogenation, they are reduced to monoenes. We have employed methyl *cis*-9,*cis*-15-octadecadienoate as a model to study the reduction of nonconjugated dienes. Deuterium was used as a tracer to follow the exchange reaction.

EXPERIMENTAL PROCEDURES

Methyl *cis*-9,*cis*-15-octadecadienoate (8) was reduced with nickel catalyst (Girdler G-49A) at atmospheric pressure and 130 C in a glass manometric apparatus described

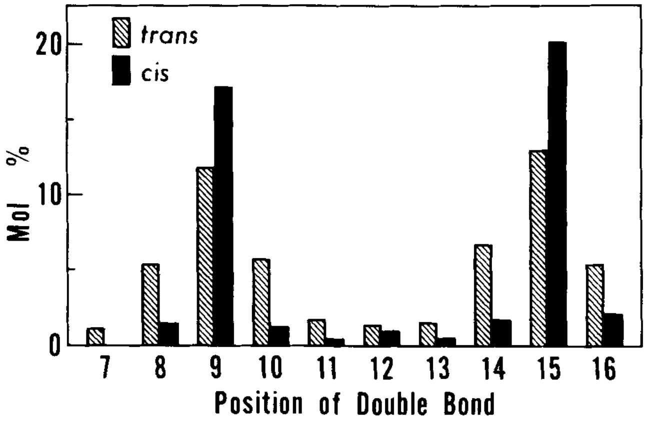

FIG. 1. Double bond distribution in monoenes formed during deuteration of *cis*-9,*cis*-15-octadecadienoate. Product composition: stearate, 9.8%; *trans*-monoene, 16.7%; *cis*-monoene, 14.2%; diene, 59.3%.

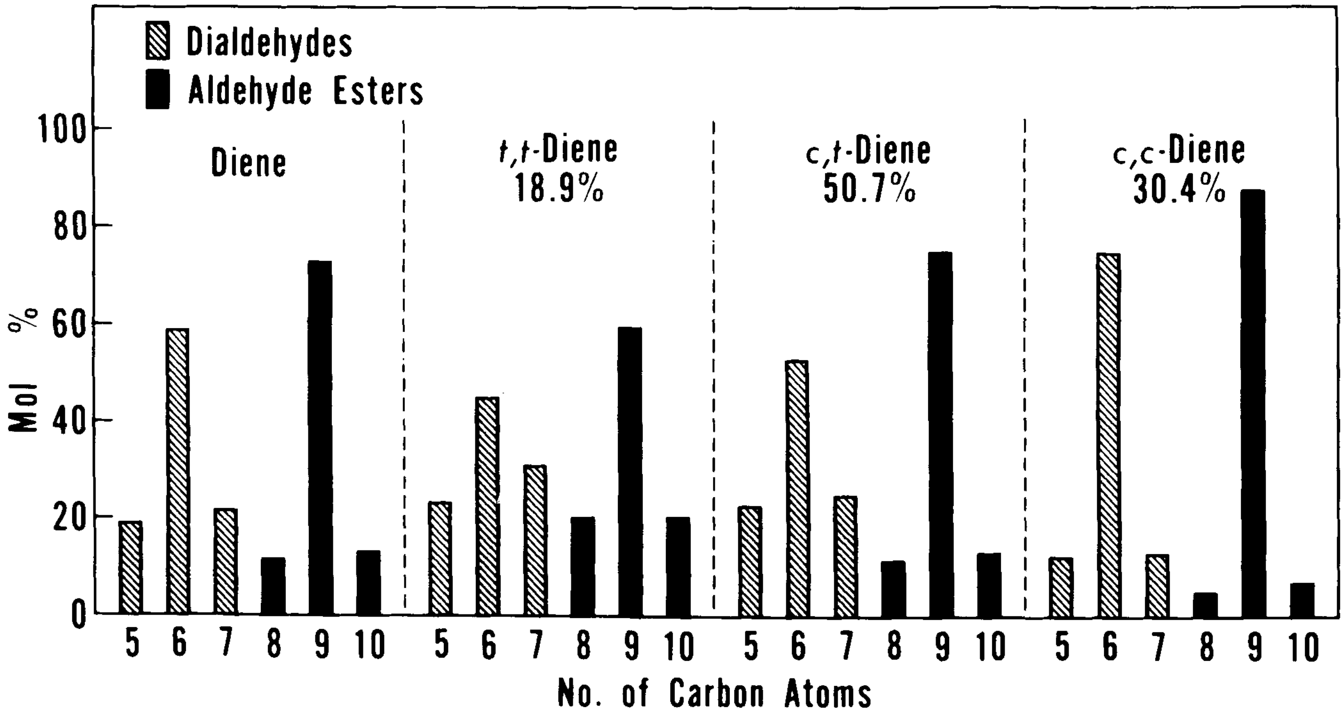

FIG. 2. Composition of aldehyde esters and dialdehydes formed upon ozonolysis of various diene fractions.

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TABLE I

Distribution of Deuterium in Fractions from Nonconjugatable Diene Reduction

No. of deuterium atoms	Monoene		Stearate	Diene	*trans,trans*-Diene	*cis,trans*-Diene	*cis,cis*-Diene
	trans	*cis*					
0	11.6	20.0	4.9	41.4	23.8	37.4	62.0
1	26.2	33.7	12.0	35.0	36.8	39.5	23.2
2	27.4	25.0	17.2	15.1	24.1	14.5	8.8
3	16.9	10.8	16.6	5.3	8.7	5.1	3.1
4	8.5	5.0	13.1	1.9	4.3	2.4	2.2
5	4.2	2.3	9.6	0.8	1.3	0.7	0.5
6	2.3	1.2	7.1	0.3	0.6	0.4	0.2
7	1.3	0.6	5.3	0.2	0.3		
8	0.7	0.3	4.0	0.1	0.2		
Other	0.9	1.1	10.2	—	—	—	—
d_{av}[a]	2.24	1.75	4.24	0.96	1.41	0.99	0.63

[a]Average number of deuterium atoms per molecule.

previously (9). After 0.5 mol deuterium per mole of ester was consumed, the product (gas liquid chromatographic composition: stearate 9.8%, monoene 30.9%, diene 59.3%) was separated into stearate, monoene and diene fractions on a rubber column (10). The monoene fraction was further separated into *cis* (46.1%) and *trans* (53.9%) fractions on a silver-exchanged resin column (11). The diene fraction (IR *trans* % = 55) was similarly resolved into *trans,trans* (18.9%), *cis,trans* (50.7%) and *cis,cis* (30.4%) fractions on a shorter column. Analytical results obtained by reductive ozonolysis of monoene and diene fractions have been plotted in Figures 1 and 2. The distribution of deuterium in the various fractions is given in Table I.

RESULTS AND DISCUSSION

Considerably more stearate is formed during reduction of nonconjugatable diene than of linoleate (1). This is expected from the previous finding (7) that nonconjugatable dienes are only slightly more reactive than monoenes. Monoenes with double bonds at 9 and 15 positions were the predominant isomers in both the *cis* and *trans* fractions (Fig. 1). The *cis*-isomers, which apparently are formed by 1,2-addition to the double bonds in the diene, amount to 38% of the total monoenes. The double bonds in *trans*-monoenes were more scattered than in the *cis*-monoenes. These *trans*-isomers are apparently formed either by reduction of geometrical and positional isomers of diene or by isomerization of monoenes, or both.

Positional isomerization of diene (Fig. 2) is greater with the nonconjugatable diene than with linoleate (1). The double bonds in the nonconjugatable diene moved one position on either side. This positional isomeriation is greatest in the *trans,trans*-diene fraction. From an Ag-resin column analysis, only 30% of the diene had *cis,cis* configuration. Apparently geometrical isomerization is also greater with nonconjugatable diene than with linoleate (1). The percentage *trans* measured by IR absorption is lower than the true value. This discrepancy is apparently caused by olefinic deuterium (12).

Composition of the diene isomers can be calculated from the ozonolysis data in Figure 2 if one assumes that during isomerization only one or the other double bond migrated, but not both. This assumption is valid because dialdehydes containing four and eight carbon atoms are not found in the ozonolysis products. Accordingly the following isomers are possible: $\Delta^{8,15}$, $\Delta^{9,15}$, $\Delta^{10,15}$, $\Delta^{9,16}$ and $\Delta^{9,14}$. The amounts of $\Delta^{8,15}$ and $\Delta^{10,15}$ isomers would correspond to the percentage of aldehyde esters containing eight and ten carbon atoms, respectively. The percentage of $\Delta^{9,15}$ would correspond to the dialdehyde with six carbon atoms, since this isomer is the only one that gives this dialdehyde. The sum of $\%\Delta^{10,15}$ and $\%\Delta^{9,14}$ would equal the percentage of dialdehyde with five carbon atoms. $\Delta^{9,14}$ can be calculated from this relationship, since $\%\Delta^{10,15}$ and %C-5 dialdehyde are known. Similarly $\Delta^{9,16}$ can be calculated from the expression $\%\Delta^{9,16} + \%\Delta^{8,15} = \%$C-7 dialdehyde. The calculated composition of diene isomers in the various fractions is given in Table II.

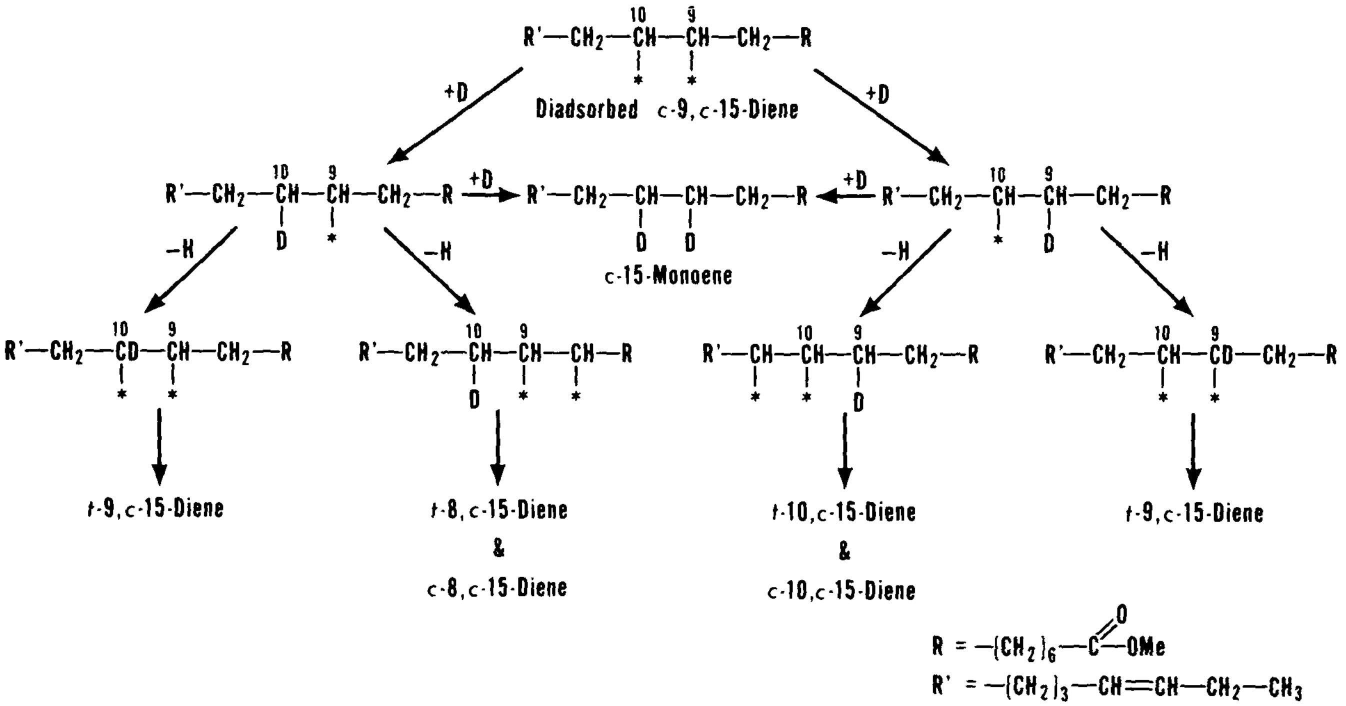
Most migration of double bonds occurred in *trans,trans*-diene fraction. The deuterium content of these diene fractions (Table I) is proportional to the extent of isomerization (Table II). Most deuterium was found in the *trans,trans*-diene fraction that experienced greatest isomerization. The least deuterium was observed in the *cis,cis*-diene fraction that was least isomerized. Apparently isomerization occurs through the half-hydrogenated mechanism. The more alternations that occur between di- and monoadsorbed species (Scheme 1), the more deuterium is incorporated. In the *cis,cis* fraction, 62% of the molecules contained no deuterium, whereas 77% was calculated to have double bonds at the 9 and 15 positions. Therefore some *cis,cis* $\Delta^{9,15}$-diene (2.7% of the starting diene) must contain deuterium, which was probably incorporated through isomerization, e.g., *cis,cis* → *cis,trans* → *cis,cis*.

Considerably more deuterium is incorporated into dienes during reduction of nonconjugatable diene (d_{av} = 0.96) than of linoleate (1). After adding 0.5 mol deuterium, ca. 59% of the remaining diene contained one or more deuterium atoms. This means that at least 59% of the

TABLE II

Calculated Composition of Diene Isomers Formed during Deuteration of Methyl *cis*-9,*cis*-15-Octadecadienoate

Position of double bonds	Diene	*trans,trans*-Diene	*cis,trans*-Diene	*cis,cis*-Diene
8,15	11.8	20.1	11.7	5.0
9,15	59.1	44.6	52.6	76.9
10,15	12.9	20.1	12.9	7.3
9,16	10.0	11.6	13.2	7.8
9,14	6.2	3.6	9.6	4.9



SCHEME 1.

remaining diene was adsorbed on the catalyst surface and exchanged deuterium through the process of isomerization. Through isomerization, up to eight deuterium atoms were incorporated into nonconjugatable diene, which indicates that at least eight altenations between di- and monoadsorbed species occurred before diene was desorbed from the catalyst surface. When deuterium is added to these perdeuterio isomers, the monoenes produced contain up to ten deuterium atoms. The deuterium content of monoenes further increases when they isomerize during reduction to stearate. *trans*-Monoenes, which experienced greater isomerization, contained more deuterium than *cis*-monoenes. Further smearing of deuterium distribution occurs when stearate is formed.

From the deuterium contents of the various fractions, the number of moles of deuterium atoms incorporated per mole of double bond reduced was calculated to be 3.18. This high value (theoretical 2.0) indicated that considerable amounts of hydrogen escaped into the gas phase by hydrogen-deuterium exchange. This type of exchange is much more prevalent during olefin reduction, but is virtually absent during diolefin reduction (13,14). Both isomerization and exchange characteristics of the nonconjugatable diene reduction are similar to those occurring during deuteration of methyl oleate (12). It is thus apparent that nonconjugatable dienes behave like monoenes on the surface of nickel catalyst.

Based on these results, Scheme 1 is proposed to account for the products. Because diene is not strongly adsorbed as indicated by the large amount of deuterium in dienes, it must be chemisorbed by involving either one or the other double bond. Only the reactions involving the 9,10 double bond are shown. Analogous reactions occur with the 15,16 double bond. Adding a deuterium atom to the 9,10 double bond produces two half-hydrogenated species. The addition of another deuterium aton to either half-hydrogenated species forms a Δ^{15} *cis*-monoene, which can undergo further isomerization and addition reactions. Isomerization of diene occurs when half-hydrogenated species revert to diadsorbed species through loss of a hydrogen atom. This hydrogen can be abstracted from the carbon atom on either side of the pivotal site. Removal of hydrogen atom from the same carbon that has added a deuterium atom causes geometrical isomerization. Positional isomerization results if the hydrogen is abstracted from the carbon on the opposite side of the pivotal site. Reiteration of this addition-abstraction sequence to the 15,16 double bond produces *trans,trans*-dienes. Each alternation between mono- and diadsorbed species (addition of a deuterium and abstraction of a hydrogen) incorporates a deuterium into the isomerized diene. From the deuterium distribution of dienes, it appears that several such alternations occur before diene is desorbed from the catalyst surface.

During the reduction of linoleate, conjugated dienes are formed by hydrogen abstraction because the double bonds are separated by one methylene group. These conjugated dienes, which are strongly adsorbed on the catalyst, are selectively reduced to monoene. Hydrogen abstraction with $\Delta^{9,15}$-diene forms only geometrical and positional isomers, which are not strongly adsorbed. Thus, even though isomerization is large with both linoleate and nonconjugatable diene, greater isomerization is observed with the latter than with the former.

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