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## CONTRIBUTIONS TO THE STUDY OF METAL-CATALYSED REDUCTION. HYDROGENATION OF METHYL *CIS*-9-OCTADECENOATE

By

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### Abstracts

Methyl *cis*-octadecenoate and methyl 9,10-dideutero-*cis*-9-octadecenoate have been reduced with deuterium and with hydrogen over Adams catalyst. The reductions were carried out either in dioxan or acetic acid or acetic acid-*d*, at room temperature, and under normal pressure.

Three deuterations of the non-deuterated ethylenic ester in dioxan show that the hydrogen redistribution and the deuterium distribution depend upon the concentration of the catalyst. A low concentration (5% of the sample weight) of catalyst promotes the light isotope redistribution, while a high concentration (10%) favours the heavy isotope distribution.

Hydrogenation of the dideuterated ethylenic ester in dioxan exhibits the exchange of deuterium (in the carbon chain) for hydrogen and the redistribution of deuterium. Deuteration of this olefin reveals the hydrogen redistribution which is as extensive as the deuterium redistribution in the preceding hydrogenation.

Reduction of the non-deuterated ethylenic ester carried out with deuterium gas in acetic acid and with hydrogen in acetic acid-*d* shows the apparent hydrogen-deuterium exchange. This seems to occur partly before the reduction between  $H^+$  or  $D^+$  of solvents and  $D_2$  or  $H_2$  of the reductants, and partly during the reduction between  $H^+$  or  $D^+$  and  $\underset{*}{H}$ ,  $\underset{*}{H}_2$  or  $\underset{*}{D}$ ,  $\underset{*}{D}_2$ . The  $H_2$ - $D_2$  exchange is also due to the phenomena involving the successive adsorption and desorption of the olefin, the C=C migration, etc., during the reduction.

### Introduction

It is well known that the metal-catalysed hydrogenation of olefins may be accompanied by *cis-trans* isomerization, double-bond migration and exchange reactions.<sup>1-4)</sup> It has been recognized for some time that hydrogen redistribution\*\*) may occur during this reduction.<sup>4-9)</sup> The hydrogenation of ethylenic hydrocarbons has generally been extensively studied but as yet there is no general agreement as to the mechanisms of the elementary reactions cited

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\*\*) In the sense of WAGNER *et al.*<sup>6,8)</sup>

above.

A detailed understanding of the elementary reactions involved in catalytic hydrogenation would be useful in the study of the catalytic hydrogenolysis of halogen-substituted compounds\*), in which some of these elementary reactions doubtlessly participate.

It has been shown that with the aid of a suitable mass spectrometer it is possible to obtain mass spectra of methyl esters of saturated<sup>12)</sup> and ethylenic<sup>13)</sup> long-chain carboxylic acids, in which relatively high parent peaks due to the ionized unfragmented molecules are present. These allow a direct determination of molecular weights of the compounds studied.

The present investigation has been made on the platinum-catalysed deuteration or hydrogenation of some normal long-chain olefinic and halogen-substituted methyl esters.<sup>10,11)</sup> The reductions were carried out either in neutral or ionic media, at room temperature, and under normal pressure.

This paper presents some observations concerning: 1) carbon-carbon double-bond migration, hydrogen-deuterium exchange reactions, and hydrogen redistribution; and 2) the addition reaction, and exchange between reducing gas (deuterium or hydrogen) and acidic solvent (acetic acid or acetic acid-*d*).

## Experimental \*\*)

### Apparatus

A modified macro-scale hydrogenation apparatus, constructed as described by PARRETTE<sup>15)</sup>, was employed. All stopcocks were lubricated with Dow-Corning silicone grease. The deuterium gas storage bottle and buret were filled with pure paraffin oil. The reaction vessel was connected to the gas buret by means of vacuum rubber tubing, which was washed with chloroform and ethanol before use. A water pump was used to evacuate air in the reaction vessel and the connecting lines before all reductions. To avoid the contamination of water vapour from the pump, the system was separated from the latter by a tower loosely packed with dry calcium chloride. A Microid flask shaker was used for shaking the reaction vessel which consisted

\*) A study on hydrogenolysis is to be published.

\*\*\*) Boiling points uncorrected. The melting points were taken in capillary tubes using calibrated Anschütz type thermometers completely immersed in a well-stirred bath of liquid paraffin, except in the cases marked "Kofler block". The molecular refractions were computed from the Lorenz-Lorentz equation:

$$R_D = \frac{(n_D^0)^2 - 1}{(n_D^0)^2 + 2} \cdot \frac{M}{d_4^0}$$

The values in brackets were calculated from the bond refractions of VOGEL *et al*<sup>14)</sup>.

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of a 100-ml interchangeable round-bottomed glass flask fitted with an adaptor with a stopcock.

### Materials

Deuterium gas was prepared by electrolysis of 99.73 per cent deuterium oxide (Norsk-Hydro) with nickel electrodes. The electrolyte was made by dissolving anhydrous sodium carbonate in the heavy water to give a 5% solution. The deuterium gas was dried by passage through a dry-ice trap before being collected in the storage bottle described above.

Commercial electrolytic hydrogen was used. It was transferred from a tank into a gas storage bottle and kept over distilled water.

Adams catalyst ( $\text{PtO}_2$ ,  $\text{H}_2\text{O}$ ) was purchased from Baker Platinum Ltd., or prepared in our laboratory, from platinum residues.<sup>16)</sup>

Lindlar catalyst ( $\text{Pd-Pb}$ ,  $\text{CaCO}_3$ ) utilized in the reduction of carbon-carbon triple bonds to double bonds<sup>17-20)</sup> was prepared in the laboratory. Quinoline, p. a. (E. Merck), which is a necessary poison for this catalyst, was used without further purification.

Anhydrous sodium carbonate, p. a. (E. Merck), was ground fine and then kept in an oven for 2 hours at about  $200^\circ$ .

Dioxan, p. a. (May and Baker), was distilled over sodium sand and kept over sodium wire.

Methanol, p. a. (E. Merck), used for crystallization was distilled.

Acetic acid, p. a. (E. Merck), was distilled, and the fraction with b. p.  $115^\circ$ ,  $n_D^{20}$  1.3741 was used.

Acetic acid-*d* was prepared from the equivalent amounts of freshly distilled acetic anhydride, 10.210 g, and deuterium oxide, 2.003 g, with a trace of sulphuric trioxide, as follows. In a round-bottomed flask equipped with a reflux condenser fitted with a calcium chloride drying tube, the mixture was left at room temperature overnight; then it was cautiously heated at about  $100^\circ$  (oil bath) for 2 hours, and distilled under normal pressure. The fraction, 10.115 g, with b. p.  $113^\circ$ ,  $n_D^{23}$  1.3720,  $d_4^{23}$  1.062,  $R_D$  13.06 [12.90] was utilized.

Methyl *cis*-9-octadecenoate (oleate): *a*) commercial product from Mann Research Laboratories,  $n_D^{20}$  1.4512; *b*) sample from the collection of Professor E. STENHAGEN,  $n_D^{20}$  1.4515; and *c*) prepared from olive-oil acids. This preparation was performed<sup>21,22)</sup> by treatment of 1 part of olive-oil acids, 50 g, with 3 parts of urea, 150 g, and 200 ml of methanol; after cooling at about  $0^\circ$ , the urea complexes of the fatty acids were separated by filtration on a Büchner funnel and washed with chloroform. The complexes were then destroyed with water, and the recovered acids (the endocytetes) were again

treated with the urea as before; the process was repeated twice. Finally the recovered acids, 25 g, were converted into methyl esters, and the crude compounds obtained were treated with urea in the same manner as the free acids. The mixture of covered esters was distilled under reduced pressure, using a short fractionating column filled with glass rings. The methyl *cis*-9-octadecenoate, 20 g, was isolated in the fraction with b. p.  $_{3}$  169°,  $n_D^{20}$  1.4511,  $n_D^{25}$  1.4492,  $d_4^{28}$  0.867,  $R_D$  91.50 [91.48].

Methyl octadecanoate (stearate), a sample from the collection of Professor E. STENHAGEN, was successively recrystallized from methanol and light petroleum to yield white plates, melting at 38.5–39.0° and remelting at 38.2–38.8°.

Methyl 9-octadecynoate (stearolate) was synthesized by dehydrohalogenation of methyl 9, 10-dibromoöctadecanoate with alcoholic potassium hydroxide.<sup>23)</sup> In the first step the synthesis gave 9-octadecynoic acid with m. p. 46.1–46.5°, which was then esterified with diazomethane. The acetylenic ester was obtained as a colorless liquid with the following physical data:  $n_D^{24}$  1.4543,  $d_4^{24}$  0.886,  $R_D$  90.05 [90.20]. Gas-liquid chromatographic analysis showed that the ester was isolated in a pure state.

Methyl 9, 10-dideutero-*cis*-9-octadecenoate was synthesized by partial deuteration of methyl 9-octadecynoate over Lindlar catalyst, as follows. The catalyst, 1 g, was weighed in a round-bottomed flask equipped with an adapter and a stopcock, and 15 ml of dry dioxan and 0.4 g of quinoline were added. The system was evacuated, filled with deuterium gas and shaken for 2 hours. The latter procedure was repeated six times. Then, the methyl 9-octadecynoate, 1.796 g, dissolved in 2 ml of dioxan, was introduced to the reaction vessel. After evacuation the system was connected to the deuterium buret and shaken until absorption stopped (about 3 hours) at room temperature and under normal pressure. After removal of catalyst and solvent the residue was dissolved in light petroleum, washed twice with dilute HCl to remove quinoline, then with NaHCO<sub>3</sub> solution and water, and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent *in vacuo*, a colorless liquid, 1.655 g, was obtained with the following physical data:  $n_D^{23}$  1.4504,  $d_4^{23}$  0.878,  $R_D$  91.40 [91.48]. This compound was submitted to GLC analysis (run at 243°, with silicone grease as stationary phase). The chromatogram consisted of a high peak followed by another of very low intensity, corresponding to the olefinic and acetylenic methyl esters, respectively. No saturated ester was detected. The olefinic ester, separated by GLC and collected (about 0.5 mg) in a glass capillary tubing, was submitted to mass spectrometric analysis\*); the high-mass end of the spectrum showed clearly

\*) The mass spectrometer and the general procedure utilized have been described by RYHAGE<sup>25)</sup>. The intake system was kept at 200°, and the energy of the electrons was 70 eV.

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that a single molecule-ion peak at  $m/e$  298 —followed by its isotope peak at  $m/e$  at 299 due to the natural content of  $^{13}\text{C}$ — corresponds to the addition of 2 deuterium atoms to the acetylenic bond of the starting ester. In addition, a chemical hydrogenation of the olefinic ester with hydrazine<sup>26,28)</sup> gave methyl 9, 10-dideuterooctadecanoate which has been used in the study of the determination of ethylenic bond positions by mass spectrometry.<sup>26-28)</sup> The olefinic compound is therefore methyl 9, 10-dideutero-*cis*-9-octadecenoate, which has been reported by KHAN<sup>29)</sup> and KHAN *et al.*<sup>30)</sup> These authors prepared the olefinic ester in a manner similar to that described here with the exception that deuterized Raney nickel was used as catalyst. The infrared spectrum of the olefinic ester indicated that an absorption band at  $4.46\mu$  is due to C—D stretching vibrations. A band at  $6.15\mu$ , which is due to C=C stretching, is relatively strong in comparison with that at  $6.10\mu$  in the spectrum of methyl *cis*-9-octadecenoate<sup>31,32)</sup>; the factor which increases the intensity of this absorption band is probably an isotope effect. No appearance of absorption bands in the region  $10\text{--}11\mu$  indicates the absence of the *trans* form\*), in accordance with earlier reports.<sup>29,30)</sup> The experiment of reduction mentioned above, using Lindlar lead-palladium catalyst, followed by certain physical analyses, permits the conclusion that the catalyst leads to selective reduction of the carbon-carbon triple bond to a double bond with *cis* configuration, and gives no unspecific exchange of hydrogen for deuterium (the reducing gas).

**General procedure for the catalytic reduction and the separation of the products**

Adams platinum oxide —1–10 per cent of the amount of the sample weight— and solvent were first placed in the reaction vessel, the latter fitted to the adaptor, and the system evacuated, filled with deuterium or hydrogen gas and shaken for about 15 minutes. Then the olefinic ester, dissolved in the same solvent, was introduced into the reaction vessel. After evacuation, the system was connected to the deuterium or hydrogen gas buret and shaken until absorption stopped (as small amounts of olefinic ester were submitted to the reduction, the reaction was ordinarily accomplished in a few minutes but the shaking was continued for about 1–6 hours). The reduction was carried out at normal pressure and at room temperature. The catalyst was separated from the medium by filtration (paper), washed with ether, and the filtrate was evaporated *in vacuo*. The crude product obtained was crystallized

\*) The *trans* configuration generally exhibits a strong absorption band at  $10.36\mu$ <sup>31,32)</sup> which is due to a C—H deformation about a *trans* C=C bond, but it is not yet demon-

strated how this band is displaced in the case of  $\begin{array}{c} \text{D} \\ | \\ -\text{C}=\text{C}- \\ | \\ \text{D} \end{array}$ .

TABLE 1. Summary of experiments on catalytic reduction of methyl 9,10-dideutero-*cis*-9-octadecenoate and its non-deuterated analogue

Expt. No.	Starting products									Final saturated esters		
	Olefinic esters				Adams catalyst		Reduc-tants	Solvents		mg	No.	M. p. °C
		mg	mmole	mg	%*)			ml				
1	Methyl <i>cis</i> -9-octadecenoate	<i>b</i> **)	148	0.5	7	5	D <sub>2</sub>	Dioxan	6	121	I	38.3-38.8 38.1-38.5
2	<i>idem</i>	<i>b</i>	444	1,5	44	10	D <sub>2</sub>	Dioxan	5	400	II	38.5-38.8 38.1-38.4
3	<i>idem</i>	<i>c</i>	2013	6.7	201	10	D <sub>2</sub>	Dioxan	15	1720	III	37.9-38.6 37.8-38.0
4	<i>idem</i>	<i>a</i>	150	0.5	1.5	1	D <sub>2</sub>	AcOH	3	115	IV	38.4-38.8 37.9-38.3
5	<i>idem</i>	<i>a</i>	150	0.5	1.5	1	D <sub>2</sub>	AcOD	3	130	V	38.6-39.9 38.0-38.2
6	<i>idem</i>	<i>a</i>	150	0.5	1.5	1	H <sub>2</sub>	AcOD	3	117	VI	38.6-39.0 38.0-38.4
7	Me 9,10-dideutero- <i>cis</i> -octadecenoate		154	0.5	1.6	1	H <sub>2</sub>	Dioxan	3	135	VII	38.0-38.7 37.6-38.2
8	<i>idem</i>		58	0.2	5.8	10	D <sub>2</sub>	Dioxan	2	46	VIII	38.1-38.5 37.7-38.1

\*) Percentage of the sample weight.

\*\*\*) Origin of the compound is described in the paragraph on methyl *cis*-9-octadecenoate.

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twice from methanol, and the pure end compound isolated in the usual manner and dried under vacuum.

All experiments on catalytic reduction of methyl *cis*-9-octadecenoate are summarized in the table 1.

**Attempted hydrogen-deuterium exchange on methyl octadecanoate**

Two experiments were executed separately as follows.

Mixture *a*: 149 mg (0.5 mmole) of methyl octadecanoate, 7.5 mg (0.03 mmole) of Adams catalyst—corresponding to 5 per cent of the ester weight—and 6 ml of dioxan.

Mixture *b*: 149 mg (0.5 mmole) of methyl octadecanoate, 1.5 mg (0.006 mmole) of Adams catalyst—corresponding to 1 per cent of the ester weight—and 3 ml acetic acid-*d*.

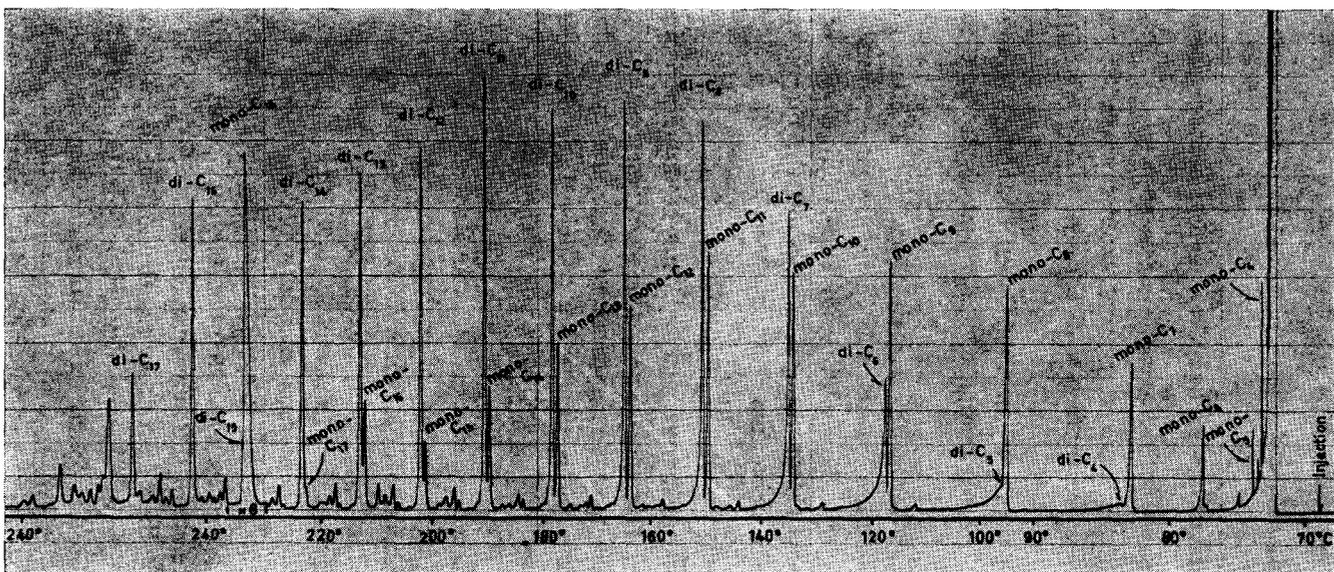
Both mixtures were shaken with deuterium gas for 2 hours at room temperature. The resulting esters were isolated in the same manner as the analogues described above. The dioxan utilized in experiment *a* was recovered.

Mass spectrometric analysis of the end esters and the dioxan indicated that none of these possessed deuterium.

**Mass spectrometric analysis**

All saturated esters prepared were analysed, first by gas-liquid chromatography, then by mass spectrometry. The mass spectrometric analyses were carried out, in part with a mass spectrometer of Dempster type which has been described by RYHAGE<sup>25)</sup>, and in part with a combined gas chromatograph-mass spectrometer designed and constructed by STENHAGEN.<sup>33)</sup> With the latter apparatus the GLC analysis and the MS analysis may be carried out successively in one combined operation. It was conveniently utilized for analysing the mixture of methyl esters of carboxylic acids, which were the result of an oxidative degradation of a partly deuterated methyl octadecanoate (see the next paragraph). In both spectrometers the ionizing voltage utilized was 70 eV and the inlet system was maintained at 200°.

As the displacements of deuterium and/or hydrogen atoms<sup>34-37)</sup> and/or other molecular rearrangements<sup>28,38-41)</sup> may occur during ionic dissociation in the mass spectrometer, it is not easy to determine the position of all deuterium atoms in the partly deuterated saturated fatty esters studied in the present work by comparing directly their mass spectra with those of the non-deuterated analogues. Even with the well-known deuterium labelled methyl octadecanoates<sup>28)</sup>, it has been found that some molecular rearrangements considerably disturb the determination of the position of the labelled atoms.<sup>28)</sup> Mass spectrometry was therefore used, in the present case, only for determining



**Fig. 1.** Gas liquid chromatogram of methyl esters prepared from acids formed by permanganate oxidation of catalytically deuterated methyl *cis*-9-octadecenoate (specimen III, table 1). The positions of the esters of monoacids and diacids are marked. Conditions: glass capillary column (length 53 m, diameter 0.35 mm) coated with M-307 methyl silicone rubber gum SE-30; nitrogen pressure 16 p.s.i.; flame ionization detector; temperature programmed from 70 ° to 90° at a rate of 1°C/min, and from 90° to 240° at a rate of 2.5°C/min.

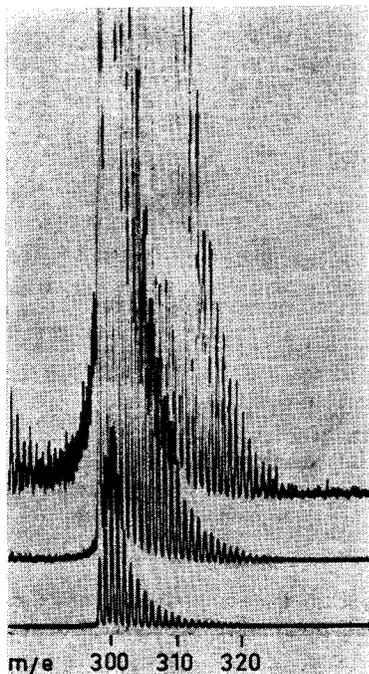
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the deuterated species by means of their molecule-ion peaks.

For accurate interpretation the height of the molecule-ion peaks was corrected by subtracting the contribution due to the natural abundance (1.1 per cent) of carbon-13, from that of the next lowest molecular weight.<sup>28,42)</sup>

**Oxidative degradation of the carbon chain and analysis of the end product**

Since the exact location of the deuterium atoms in the carbon chain of the partly deuterated methyl octadecanoates by a "direct" mass spectrometric analysis had presented considerable difficulty<sup>28)</sup>, it has been necessary, for unequivocal solution, to resort to chemical degradation and identification of the resulting products. The degradation has been performed by oxidative cleavage with potassium permanganate in acetic acid.<sup>43,44)</sup> Thus, a small amount (0.5 g) of the catalytically deuterated methyl *cis*-9-octadecenoate (specimen III, table 1) was oxidized to yield two homologous series of normal mono- and dicarboxylic acids; the corresponding methyl esters were successively analysed by gas-liquid chromatography and mass spectrometry.



**Fig. 2.** High-mass end of mass spectrum of catalytically deuterated methyl *cis*-9-octadecenoate (III).

The chromatogram reproduced in figure 1 shows that about 60 per cent of the catalytically deuterated olefinic ester was affected by the oxidative degradation. Acetic and propionic acids should exist among the series of monocarboxylic acids, but in the chromatogram the peaks corresponding to methyl esters of these lower homologues are covered by solvent peak. The fact that heptadecanoic acid is found in a very small amount among the products is inexplicable, as long as the mechanism of the oxidative degradation of aliphatic methyl esters is not understood.

Table 2 summarizes the non-deuterated and deuterated species in methyl esters of C<sub>5</sub>-C<sub>16</sub>-carboxylic acids determined by mass spectrometric analysis. A certain number of deuterium atoms which were distributed along the carbon chain of the catalytically deuterated ethylenic ester may be localized in this way. According to the high-mass end of the mass spectrum of

TABLE 2. Result of mass spectrometric analysis of the series of methyl esters of n-monocarboxylic acids obtained from oxidative degradation of catalytically deuterated methyl *cis*-octadecenoate (III)

Carbon chain <sup>†)</sup>	Acids	Methyl esters Analogues of varying deuterium content (%)									
		d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	d <sub>4</sub>	d <sub>5</sub>	d <sub>6</sub>	d <sub>7</sub>	d <sub>8</sub>	
C-2	C <sub>17</sub>	**									
C-3	C <sub>16</sub>	5	25	37	18	7	3	2	1	1	
C-4	C <sub>15</sub>	5	25	37	18	7	3	2	1	1	
C-5	C <sub>14</sub>	5	25	37	18	7	3	2	1	1	
C-6	C <sub>13</sub>	5	25	37	18	7	3	2	1	1	
C-7	C <sub>12</sub>	5	25	37	18	7	3	2	1	1	
C-8	C <sub>11</sub>	5	25	37	18	7	3	2	1	1	
C-9	C <sub>10</sub>	18	58	19	4	1					
C-10	C <sub>9</sub>	83	12	3	2						
C-11	C <sub>8</sub>	89	6	3	2						
C-12	C <sub>7</sub>	90	5	3	2						
C-13	C <sub>6</sub>	90		10							
C-14	C <sub>5</sub>	95	5								
C-15	C <sub>4</sub>	±									
C-16	C <sub>3</sub>	±									
C-17	C <sub>2</sub>	±									
C-18	C <sub>1</sub>	*									

†) C-1 belonging to carboxyl group.

\*\* Not analysed. \* HCOOH formed is easily oxidized (by MnO<sub>4</sub><sup>-</sup>) to CO<sub>2</sub>.

± Compound unseparated by GLC, which was made under following conditions: aluminium column (length 2m, diameter 0.4 cm) packed with Gas-Chrom Z (80-100 mesh) and 6 per cent Dow-Corning silicone grease; helium flow 40 ml/min; flame ionisation detector; temperature programmed from 80° to 215° at a rate of 4°C/min.

the ester, reproduced in figure 2, the compound studied consists of a mixture of methyl octadecanoates possessing from none to 29 deuterium atoms. The dimethyl n-dicarboxylates have also been analysed by mass spectrometry, but their spectra are less helpful than those of the methyl carboxylates since the process of formation of dicarboxylic acids during the oxidative degradation reaction is not yet understood.

## Discussion of the results

### Notes on previous work

The migration of carbon-carbon double bonds during catalytic hydrogenation of unsaturated fatty acids and esters has been demonstrated by several investigators. MOORE isolated certain isomers from partially hydrogenated ethyl *cis*-9-octadecenoate (oleate) over nickel at 140–240°, and found that shifting of the double bond from the original 9 position to the 10 and 11 positions had occurred.<sup>45)</sup> HILDITCH and VIDYARTHI found that partial hydrogenation of methyl and ethyl *cis*-9-octadecenoates, over a supported nickel catalyst at 114–220°, gave positional isomers with the ethylenic bond in the 8 and 10 positions.<sup>46)</sup> WATERMAN *et al.* determined the extent of the migration of the ethylenic bond in methyl esters of *cis*-6-, *cis*-9- and *trans*-9-octadecenoic acids and of *cis*-9, *cis*-12-octadecadienoic acid, on partial hydrogenation at 170–180° with a supported nickel catalyst<sup>47,48)</sup>; the authors obtained positional isomers, from each of these respective unsaturated esters, with the ethylenic bond in positions 5 and 7, 7 through 12 (from both starting *cis*- and *trans*-9 isomers), and 8 through 12. ALLEN and KIESS demonstrated that during hydrogenation of *cis*-9- and *trans*-9-octadecenoic acids and the corresponding methyl esters, over nickel catalyst at 150° and 200°, large amounts of positional isomers were formed with the ethylenic bond in the 7 through 11 positions.<sup>49)</sup> These authors have also shown that during hydrogenation of methyl *cis*-9, *cis*-12-octadecadienoate, at 220° with poor hydrogen dispersion, methyl octadecenoates with a double bond at the 10 or 11 position were produced.<sup>50)</sup> BLEKKINGH, JANSSEN and KEPPLER determined the extent of the migration of the ethylenic bond in methyl *cis*-9-octadecenoate on hydrogenation at 20–25° with platinum catalyst and at 100° with palladium or nickel catalyst<sup>51)</sup>; they showed that the ethylenic bond was localized in positions 7 through 14 in the series of positional isomers obtained. Investigation on the effect of the operating conditions on the migration of carbon-carbon double bonds has been carried out by COUSINS, GUICE and FEUGE<sup>52)</sup>, using methyl *cis*-9, *cis*-12-octadecadienoate. The operating conditions varied with temperature (110–200°), rate of hydrogen dispersion, type of catalyst (nickel, sulphur-poisoned nickel, palladium, and platinum), and catalyst concentration (0.1, 0.2, and 0.4 per cent). The pattern of distribution of the ethylenic bond was found in position 10, and the concentration in the other positions—6 through 14—decreased as the distance from the position 10 increased; the distribution curve tended to be symmetrical, and approximately the same number of double bonds was found on each side of position 10.

Exchange reactions between deuterium gas and hydrogen in methyl *cis*-

9-octadecenoate taking place during reduction over platinum catalyst at 170° were reported by BAXENDALE and WARHURST.<sup>53)</sup> These authors obtained both saturated and ethylenic esters containing deuterium, and assumed that the saturated product did not contain more than two deuterium atoms per molecule. They have suggested that exchange reactions between deuterium and hydrogen were due to the half-hydrogenated states postulated for the so-called *associative mechanism*.<sup>54,55)</sup>

The hydrogen redistribution during catalytic deuteration of olefins was reported by several investigators. TURKEVICH, SCHISLER and IRSA<sup>5)</sup> have determined, by means of mass spectrometry, the rates of different ethylenes ( $C_2H_3D$ ,  $C_2H_2D_2$ , etc.) and different ethanes ( $C_2H_6$ ,  $C_2H_5D$ , etc.) in the reaction of ethylene with deuterium over nickel catalyst, at 90°. The initial rate of formation of different ethylenes and ethanes was found to decrease regularly with increasing deuterium substitution and the ethane formed was predominantly  $C_2H_6$ . In a study on the mechanism of catalytic hydrogenation of olefins, using an analytical mass spectrometer, WAGNER *et al.*<sup>6,8)</sup> found that the product resulting from the reaction between *cis*-2-butene and a large excess of deuterium, over nickel catalyst at -78°, contained all isotopic species from  $C_4H_{10}$  to  $C_4D_{10}$  with an essentially random distribution of the deuterium atoms among the hydrogen positions. It is suggested<sup>6,8)</sup> that at low temperatures both alkane formation and the redistribution of hydrogen atoms among chemisorbed hydrocarbon species occur largely by elementary reactions in which a hydrogen atom is transferred from one chemisorbed hydrocarbon fragment to another rather than by reactions involving chemisorbed hydrogen atoms directly. At higher temperatures (50°), exchange reactions involving chemisorbed hydrogen become more prominent. On the basis of these observations and the results obtained by other investigators, these authors have proposed a mechanism for exchange and hydrogenation, which provide for competition among a number of elementary reactions. MARKHAM, WALL and LAIDLER<sup>7)</sup> have also proposed a mechanism applied to the deuteration of ethylene, which could explain the phenomena reported by WAGNER *et al.*<sup>6,8)</sup>

#### Results of the present investigation

The results of mass spectrometric analysis obtained here on catalytically deuterated methyl *cis*-9-octadecenoate show that the reduction involved not only the addition of deuterium to the carbon-carbon double bond but also the distribution of deuterium and the redistribution of hydrogen.

When the reduction is performed with deuterium gas in acetic acid, or with hydrogen in acetic acid-*d*, hydrogen-deuterium exchange was very apparent (see tables 1 and 3, and figure 3). The exchange reaction seems to occur

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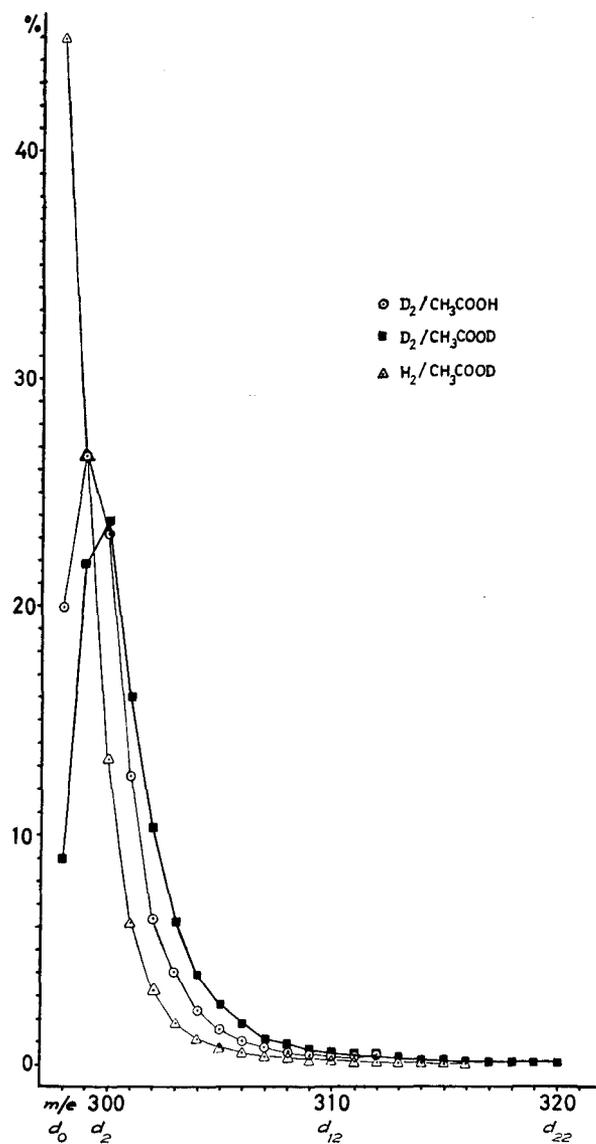


Fig. 3. Product distributions from the reactions of methyl *cis*-9-octadecenoate with deuterium and with hydrogen over Adams platinum catalyst in acetic acid and in acetic acid-*d*, established according to mass spectrometric analysis (see table 3).

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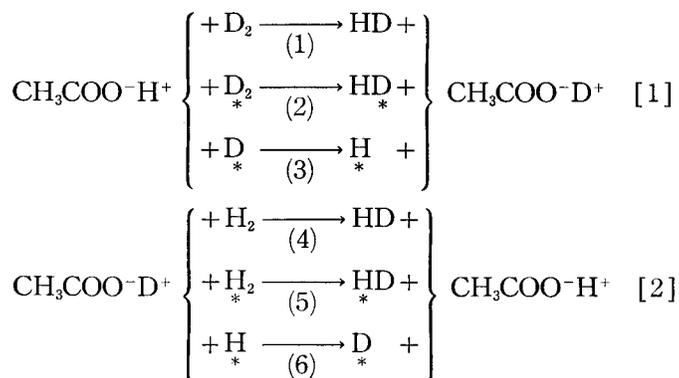
TABLE 3. Result of mass spectrometric analysis of catalytically reduced methyl 9,10-dideutero-*cis*-9-octadecenoate and its non-deuterated analogue

<i>m/e</i>		Analogues of varying deuterium content (%) of compounds <sup>†</sup>							
		I	II	III	IV	V	VI	VII	VIII
298	d <sub>0</sub>	13.11▲	1.60▲	8.08▲	19.91▲●	9.02▲	44.87	3.98	1.18▲
299	d <sub>1</sub>	25.80	9.96	19.06	26.60	21.82	26.33●	7.57	3.34
300	d <sub>2</sub>	23.58	23.86	20.37	23.14	23.76	13.22	71.18	16.72
301	d <sub>3</sub>	14.53	19.13	14.17	12.48	15.98	6.23	11.90■	26.03
302	d <sub>4</sub>	11.79	11.72	14.07	6.35	10.24	3.20	4.19	20.13
303	d <sub>5</sub>	4.41	7.69	4.88	4.02	6.19	1.80	0.64	11.88
304	d <sub>6</sub>	2.49	4.99	4.64	2.35	3.91	1.11	0.32	7.11
305	d <sub>7</sub>	1.69	3.44	4.37	1.49	2.62	0.74	0.23	4.50
306	d <sub>8</sub>	0.99	2.45	2.05	0.98	1.77	0.49		2.95
307	d <sub>9</sub>	0.62	1.87	1.87	0.74	1.13	0.36		1.80
308	d <sub>10</sub>	0.39	1.55	1.49	0.53	0.89	0.28		1.30
309	d <sub>11</sub>	0.26	1.35	1.25	0.41	0.62	0.21		0.81
310	d <sub>12</sub>	0.20	1.18	0.95	0.35	0.45	0.18		0.62
311	d <sub>13</sub>	0.13	1.06	0.50	0.27	0.37	0.14		0.41
312	d <sub>14</sub>		0.96	0.50	0.37	0.27	0.13		0.30
313	d <sub>15</sub>		0.85	0.40		0.23	0.11		0.23
314	d <sub>16</sub>		0.78	0.25		0.15	0.09		0.20
315	d <sub>17</sub>		0.70	0.25		0.14	0.07		0.16
316	d <sub>18</sub>		0.61	0.19		0.12	0.03		0.11
317	d <sub>19</sub>		0.55	0.16		0.09	0.04		0.07
318	d <sub>20</sub>		0.49	0.11		0.10			0.07
319	d <sub>21</sub>		0.42	0.10		0.07			0.04
320	d <sub>22</sub>		0.36	0.08		0.06			0.04
321	d <sub>23</sub>		0.32	0.05					
322	d <sub>24</sub>		0.30	0.04					
323	d <sub>25</sub>		0.28	0.03					
324	d <sub>26</sub>		0.28	0.03					
325	d <sub>27</sub>		0.26	0.03					
326	d <sub>28</sub>		0.26	0.01					
327	d <sub>29</sub>		0.23	0.01					
328	d <sub>30</sub>		0.21	0.01					
329	d <sub>31</sub>		0.17						
330	d <sub>32</sub>		0.12						

<sup>†</sup>) Certain analogues are formed due to hydrogen redistribution (▲), or deuterium redistribution (■). The existence of certain analogues exhibits the exchange between reductant and acidic solvent (●).

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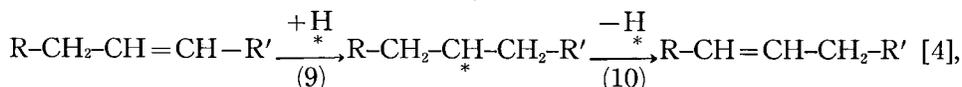
partly before the reduction between the acidic hydrogen or deuterium of the solvent and deuterium or hydrogen of the reductant, and partly during the reduction between the acidic ions and the chemisorbed deuterium or hydrogen<sup>†)</sup>:



Exchange is also due to the phenomena involving the successive adsorption [reaction path (7)] and desorption [reaction path (8)] of the olefin



the carbon-carbon double bond migration



etc., during the reduction, according to the *associative mechanism*<sup>54-58)</sup> or the *dissociative mechanism*<sup>59-62)</sup> of the hydrogenation.<sup>1-4,63)</sup> Thus, hydrogen redistribution and deuterium distribution phenomena (especially interesting for the case of compound VI) exhibited during the reductions of methyl *cis*-9-octadecenoate in the acetic acids could be explained by a series of reactions described in table 4. The distribution of deuterium along the carbon chain of the saturated ester (IV, V and VI) may be interpreted by referring to the phenomena outlined by reaction schemes [3] and [4].

Reduction of methyl 9,10-dideutero-*cis*-9-octadecenoate carried out with hydrogen in dioxan (see tables 1 and 3) clearly reveals the exchange of heavy isotope (in the carbon chain) for light isotope and the redistribution of deuterium<sup>††)</sup>. This exchange is probably due to several successive reactions, for

†) Catalytic sites on the metallic surface are indicated by asterisks. To simplify the diagrams, the bonds of hydrogen and deuterium atoms and radicals attached to the surface sites are omitted.

††) In the sense of WAGNER *et al.*<sup>6,8)</sup>

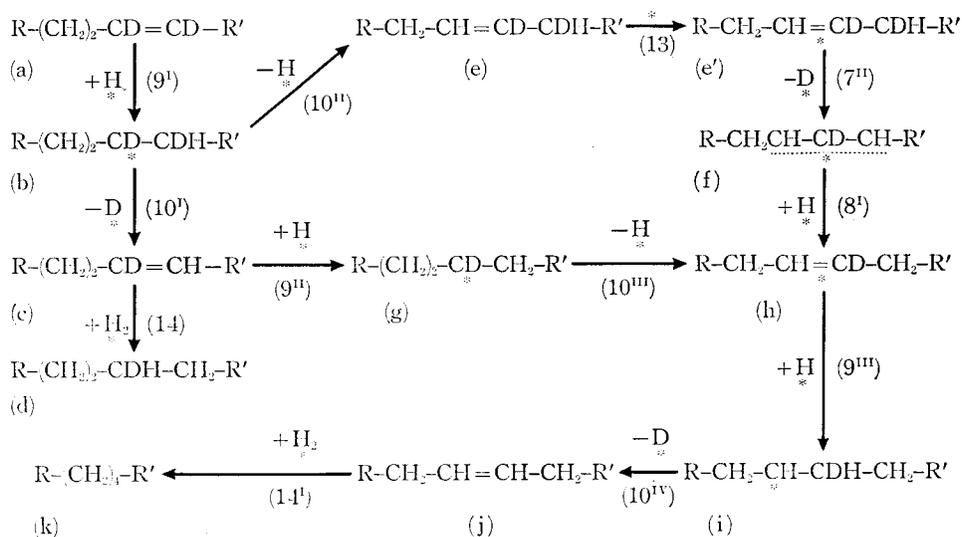
TABLE 4. Outline of reactions responsible for hydrogen redistribution and deuterium distribution phenomena (max. 2 isotopic atoms)

Compound species	Reaction types	Examples of compounds <sup>†</sup>
d <sub>0</sub> (C <sub>19</sub> H <sub>38</sub> O <sub>2</sub> )	$2 \text{CH}_3\text{COO}^- \text{H}^+ + \text{HD} \xrightarrow{(11)} \text{H}_2 + \text{CH}_3\text{COO}^- \text{H}^+ + \text{CH}_3\text{COO}^- \text{D}^+$	IV
	$2 \text{CH}_3\text{COO}^- \text{H}^+ + \text{D}_2 \xrightarrow{(2I)} \text{H}_2 + 2 \text{CH}_3\text{COO}^- \text{D}^+$	
	$2 \text{R-CH}_2\text{-CH}=\text{CH-R}' \xrightarrow{(7I)} 2 \text{H} + 2 \text{R-CH-CH-CH-R}'$	IV, V, VI
d <sub>1</sub> (C <sub>19</sub> H <sub>37</sub> D <sub>1</sub> O <sub>2</sub> )	$\text{CH}_3\text{COO}^- \text{H}^+ + \text{D}_2 \xrightarrow{(2)} \text{HD} + \text{CH}_3\text{COO}^- \text{D}^+$	IV
	$\text{CH}_3\text{COO}^- \text{D}^+ + \text{H}_2 \xrightarrow{(5)} \text{HD} + \text{CH}_3\text{COO}^- \text{H}^+$	VI
	$\text{R-CH}_2\text{-CH}=\text{CH-R}' \xrightarrow{(7)} \text{H} + \text{R-CH-CH-CH-R}'$	V
	$\text{CH}_3\text{COO}^- \text{D}^+ + \text{H} \xrightarrow{(6)} \text{D}_2 + \text{CH}_3\text{COO}^- \text{H}^+$	
	$\text{CH}_3\text{COO}^- \text{H}^+ + \text{D}_2 \xrightarrow{(2)} \text{HD} + \text{CH}_3\text{COO}^- \text{D}^+$	
d <sub>2</sub> (C <sub>19</sub> H <sub>36</sub> D <sub>2</sub> O <sub>2</sub> )	$2 \text{CH}_3\text{COO}^- \text{D}^+ + \text{HD} \xrightarrow{(12)} \text{D}_2 + \text{CH}_3\text{COO}^- \text{H}^+ + \text{CH}_3\text{COO}^- \text{D}^+$	VI
	$2 \text{CH}_3\text{COO}^- \text{D}^+ + \text{H}_2 \xrightarrow{(5I)} \text{D}_2 + 2 \text{CH}_3\text{COO}^- \text{H}^+$	

<sup>†</sup> Compounds reduced under different conditions (see table 1): IV (D<sub>2</sub>/AcOH), V (D<sub>2</sub>/AcOD), VI (H<sub>2</sub>/AcOD).

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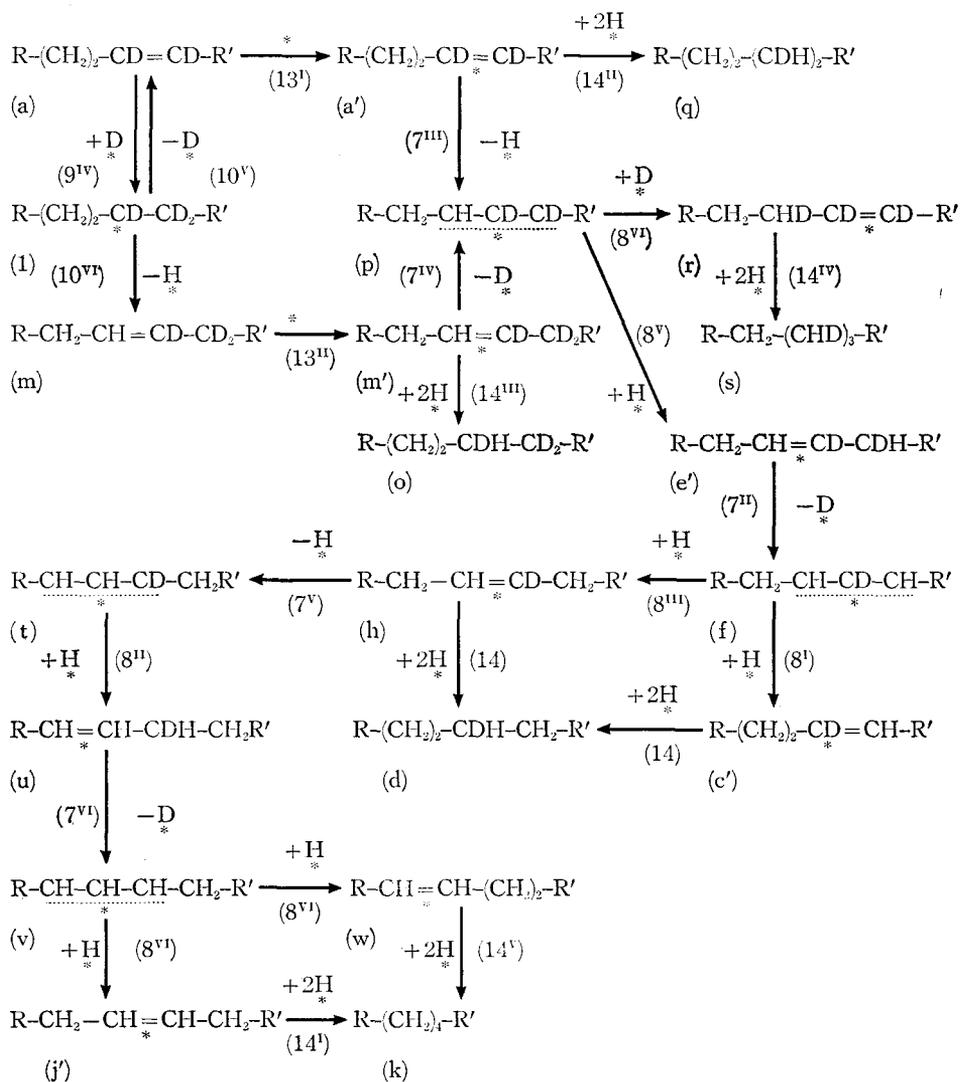
example the following:



This series of steps resulted in a methyl monodeuteroöctadecanoate [type (d)] and a non-deuterated analogue [type (k)]. The redistribution of the heavy isotope may be understood by referring to the phenomena involving the successive adsorption and desorption of the olefin and the ethylenic bond shift, which are illustrated by reaction schemes [3] and [4]. The chemisorbed deuterium may have originated from several reactions, of which three are taken as examples; these are designated by the pathways (10<sup>I</sup>), (7<sup>II</sup>) and (10<sup>IV</sup>). When the dideuterated ethylenic ester is reduced with deuterium in dioxan (see tables 1 and 3) it results in a series of methyl octadecanoates possessing from 0 to 22 deuterium atoms. The hydrogen redistribution in this deuteration is as extensive as the deuterium redistribution in the preceding hydrogenation. One of several alternative series of reactions responsible for the light isotope redistribution is given below. Thus the trideutero-, dideutero- and monodeutero-octadecanoic acid methyl esters [types (o) and (s), (q), and (d) respectively] and the non-deuterated analogue [type (k)] were formed.

As viewed, the hydrogen redistribution in the above reduction is not similar to the other redistribution which occurred during the deuteration of methyl *cis*-9-octadecenoate in dioxan (see tables 1 and 3). Since this ethylenic ester does not possess deuterium in its molecules, the hydrogen redistribution could succeed more easily with this compound than with the dideuterated analogue. The result of three deuteration of the non-deuterated

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ethylenic ester in dioxan shows that a low concentration of catalyst promotes the light isotope redistribution, while a high concentration favours the heavy isotope distribution. Thus, the hydrogen redistribution and the deuterium distribution, in the present cases, depend upon the concentration of the catalyst.

It may be noted that the unsaturated site of the ethylenic esters in the presence of the catalyst provides a starting point for the adsorption, and then the distribution and/or the redistribution of hydrogen isotopes, in connexion

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with other phenomena, can occur on the adsorbed species. On the other hand, the saturated carbon chain of the methyl octadecanoate, under the same conditions, does not become an adsorbed species and therefore none of these reactions takes place. This is confirmed by the unsuccessful hydrogen-deuterium exchange attempted on methyl octadecanoate (see Experimental part). It may also be noted that the water in the composition of Adams catalyst ( $\text{PtO}_2$ ,  $\text{H}_2\text{O}$ ) is a source of hydrogen contamination in the deuterations discussed above. The fact that two experiments (nos. 2 and 3, table 1) carried out under similar conditions do not give similar results (see table 3) is probably due to variations in the catalytic characteristics of Adams platinum catalyst, which has a tendency to clump during reaction.

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