Hydrogenation.—Kinetic runs were carried out on a 10-mmol scale in solution (cyclohexane, *n*-pentane, or *n*-hexane, 50 ml), and preparative runs were made on a 30-mmol scale with or without solvent. A 150-ml magnetically stirred autoclave was used as previously described.[7] To minimize decomposition of the $Cr(CO)_3$ complex catalysts, it was important to flush the system with nitrogen and to purge the autoclave repeatedly with hydrogen before the heating period. The progress of hydrogenation was followed by glpc of liquid samples taken periodically during each run. Hydrogenation products were generally homogeneous. Occasionally some greenish insoluble material was detected in the product. This material (isolated by filtration) was inactive as a hydrogenation catalyst under our conditions. Methyl benzoate–$Cr(CO)_3$ was recovered by sublimation unchanged from various reaction media and exhibited the same catalytic activity as the initial complex. This result indicates that the $Cr(CO)_3$ complex was in solution and that it was not decomposed during hydrogenation or subsequent treatment.

The complex catalysts were easily decomposed in the final hydrogenation products by treatment with a solution of $FeCl_3$ in 95% ethanol followed by ether extraction.[8] Products of preparative runs were isolated by vacuum distillation after decomposition of the catalyst.

Isomerization experiments were made under the same conditions as the kinetic hydrogenation runs. With dienes the autoclave was pressurized with nitrogen at 50 psi before heating. Control runs were made with helium with essentially the same results. In the absence of catalyst, no isomerization of dienes was observed at 175°.

Separations.—Hydrogenation products of cyclohexadienes and methyl sorbate were separated into monoene and diene components by preparative glpc on a DEGS column (8 ft × 0.25 in.; Chromosorb W, 60–80 mesh; 25% liquid phase). Distilled fatty ester products were separated into monoene and diene fractions by rubber column chromatography.[33]

Analyses.—Hydrocarbon product compositions were determined by glpc on four different columns (20 ft × 0.125 in.; Chromosorb W, 60–80 mesh; 20% liquid phase); tricresyl phosphate (TPC); 1,2,3-tris(2-cyanoethoxy)propane (TCEP); β,β′-oxydipropionitrile; and Carbowax 20M. Components in various hydrocarbon products were identified by the coincidence of their glpc retention times with those of authentic materials on at least two or three different liquid phases. Products containing one main component were further identified by comparing their infrared spectra with that of an authentic material. If necessary, identification was confirmed by mass spectral analysis of pure components.

Methods for fatty ester product analysis by glpc and infrared were the same as those used previously.[4a,17a] Position of the double bond was determined in monoene fractions by reductive ozonolysis and glpc of aldehyde ester cleavage products.[34]

Determination of $Cr(CO)_3$ complexes during hydrogenation was made by infrared analyses. The metal carbonyl stretching bands in the region 1900–2000 cm^{-1} were determined in CCl_4 solution and compared to those of the pure metal carbonyl complexes. Analyses showed that the concentration of benzene–$Cr(CO)_3$ and methyl benzoate–$Cr(CO)_3$ remained essentially constant throughout the hydrogenation of methyl sorbate and conjugated diene fatty esters (165–175°). Cycloheptatriene–$Cr(CO)_3$, however, showed a significant decrease in concentration (*ca.* 50% after 6 hr at 100–125°). In some runs a small increase in the absorption band at 1990 cm^{-1} was observed after hydrogenation (5–10%). This band is characteristic of $Cr(CO)_6$. The product from a preparative run yielded a white crystalline material (after removal of solvent) which was identified as $Cr(CO)_6$ by a sharp band at 1990 cm^{-1}. Various hydrogenation mixtures were examined for evidence of chromium hydride complex. However, no new absorption bands were detected that might be attributable to metal–hydrogen stretching.

Registry No.—1,3-Hexadiene, 592-48-3; 2,4-hexadiene, 592-46-1; 1,4-hexadiene, 592-45-0; 1,5-hexadiene, 592-42-7; **5**, 926-54-5; **6**, 513-81-5; **7**, 926-56-7; **8**, 764-13-6; **10**, 592-57-4; **11**, 628-41-1; **12**, 111-78-4; **13**, 1700-10-3; methyl linoleate (*cis*-9,*cis*-12-dienoate), 112-63-0; methyl *cis*-9,*trans*-11-octadecadienoate, 13058-52-1; methyl *trans*-10,*cis*-12-octadecadienoate, 21870-97-3; methyl *cis*-9,*trans*-11-octadecadienoate, 13058-52-1; methyl *trans*-9,*trans*-11-octadecadienoate, 13038-47-6; methyl *cis*-9,*cis*-15-octadecadienoate, 17309-05-6; methyl benzoate–$Cr(CO)_3$, 12125-87-0; cycloheptatriene–$Cr(CO)_3$, 12125-72-3; benzene–$Cr(CO)_3$, 12082-08-5.

Acknowledgment.—We thank Professor R. B. Bates, University of Arizona, for helpful suggestions in the preparation of this article.

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Homogeneous Hydrogenation of Diolefins Catalyzed by Tricarbonyl Chromium Complexes. II. Deuteration[1]

E. N. FRANKEL, E. SELKE, AND C. A. GLASS

Northern Regional Research Laboratory,[2] Peoria, Illinois 61604

Received April 14, 1969

Deuterium tracer studies provide direct evidence that 1,4 addition is the dominant mechanism of reduction catalyzed by arene–$Cr(CO)_3$. Catalytic deuteration of dienes yields almost exclusively monoenes-d_2 with deuterium located on the α-methylenes. Hydrogen and deuterium addition are predominantly molecular. Although no deuterium is exchanged with hydrogen in conjugated dienes, this exchange occurs at the α-methylenes in methyl linoleate and oleate and is apparently stereoselectively *cis*. With monoenes, positional and geometric isomerization by a 1,3-hydrogen shift is indicated. Key intermediates postulated include $D_2Cr(CO)_3$ and diene–$D_2Cr(CO)_3$ for 1,4 addition, *cis* monoolefin–$Cr(CO)_3$ for deuterium exchange, and π-allyl–$CrH(CO)_3$ for isomerization reactions.

In the preceding paper,[3] studies of the selectivity and kinetics of competitive hydrogenation provided some clues on the nature of the substrate–catalyst intermediate involved in the reduction catalyzed by $Cr(CO)_3$ complexes. In this paper, we report studies in which deuterium was used as a tracer to obtain more definitive evidence of the mechanism of addition and other hydrogen-transfer reactions. ^2H nmr proved to be a most powerful tool in catalytic research which has apparently not been exploited previously in deuteration studies.

(1) Presented at the 156th National Meeting of the American Chemical Society, Division of Organic Chemistry, Atlantic City, N. J., Sept 1968, paper 157.

(2) A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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TABLE I

MASS SPECTRAL ANALYSIS OF DEUTERATED MONOENES

Substrate[a]	Deuterated product	Isotopic distribution,[b] mol % d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_{av}
Methyl sorbate	Methyl 3-hexenoate[c]	2.8	1.3	92.5	2.0	1.9	...	...	1.99
1,3-Cyclohexadiene	Cyclohexene	3.3	...	96.7	...	...	...	...	1.94
1,4-Cyclohexadiene	Cyclohexene	2.4	...	97.6	...	...	...	...	1.95
9,11- + 10,12-Methyl octadecadienoate	Methyl octadecenoate	2.3	3.5	92.5	...	0.9	0.6	0.2	1.96
cis-9,*trans*-11-Methyl octadecadienoate	Methyl octadecenoate	2.9	2.7	92.5	...	1.4	0.4	0.2	1.99
trans-9,*trans*-11-Methyl octadecadienoate	Methyl octadecenoate	3.1	3.2	88.8	...	3.0	0.5	0.7	2.03

[a] Methyl sorbate and cyclohexadienes were deuterated with methyl benzoate–$Cr(CO)_3$ (5 mol %, 160°). All other dienes were deuterated with benzene–$Cr(CO)_3$ (10 mol %, 165°). [b] d_0, d_1, etc. = number of deuterium atoms per mole of ester; d_{av} = average deuterium. [c] Data from ref 4.

Results

Catalytic deuteration of various dienes yielded monoenes-d_2 as the main species (Table I). The small amount of d_1 species and HD in the gas phase (*ca.* 1%) reflect a negligible catalytic H_2–D_2 exchange in reductions with pure D_2.

The major product from methyl sorbate was identified[4] as methyl 2,5-dideuterio-*cis*-3-hexenoate (**4** see part I, Scheme I)[3,5] by ^1H nmr, ^2H nmr, and infrared spectrometry. ^1H nmr of **4** showed decreased intensities of the resonances at τ 7.9 (allyl H on C-5) and 6.9 (α-methylene H on C-2) and other qualitative changes attributable to CHD groups on C-2 and C-5 of **4** (see Experimental Section). The ^2H nmr provides a more direct method than ^1H nmr for locating the deuterium in **4**. The ^2H nmr spectrum of **4** (Figure 1) showed two signals of equal intensities: a doublet at 65.5 cps corresponds to the α-methylene D on C-2 ($J_{gem\,HD}$ = 3 Hz),[6] and a broad multiplet at 81.5 cps is due to the allyl methylene D on C-5.

Infrared spectra of **4** showed two weak absorption bands at 2140 and 2180 cm^{-1} due to C–D stretching vibrations. The peak at 2140 cm^{-1} corresponds to that observed for CHD in the center of the aliphatic chain of methyl 9,10,11,12-tetradeuteriostearate.[8] The other peak at 2180 cm^{-1} is presumably due to CHD (C-2) flanked by the olefinic and carbonyl groups. The absence of CD_2 is evident by the lack of the asymmetric and symmetric stretching vibrations at 2191 and 2102 cm^{-1} reported for methyl 9,9,10,10-tetradeuteriostearate.[8] The *cis* configuration of the double bond in **4** is deduced from the absence of absorption at 970 cm^{-1} due to isolated *trans* unsaturation.[9]

That no catalytic deuterium exchange occurs with hydrogen of methyl sorbate was shown by the absence of deuterated species in the diene fraction after 50% reduction. Especially revealing were the experiments of reduction of methyl sorbate with mixtures of H_2 and D_2. In the product obtained after 20% and after 100% reduction the ratio of d_0 to d_2 species was significantly greater (2:1) than the ratio of H_2 to D_2 in the gas phase (1.3–1.4:1). The kinetic data on the other hand, showed a small inverse isotopic effect in the rates of reduction with either H_2 and D_2 alone ($k_H/k_D \cong 0.9$). Therefore, the formation of product-determining intermediates is not kinetically controlled. Furthermore, the preponderance of d_0 and d_2 species in the product support the formation of dihydride–diene and dideuteride–diene adducts **3a** and **3** (see part I, Scheme I)[3] containing and transferring H_2 and D_2, respectively.

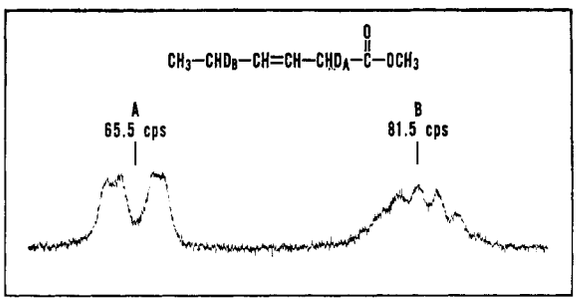

Figure 1.—^2H nmr spectrum of methyl 2,5-dideuterio-3-hexenoate (4, Scheme I) in $CDCl_3$ at 15.4 MHz.

The small amount of d_1 species (5–6%) observed in the product obtained with H_2 + D_2 corresponded to the amount of HD formed in the gas phase (4–6%). A small amount of catalytic H_2–D_2 exchange occurred therefore with methyl benzoate–$Cr(CO)_3$. This exchange increased in the absence of methyl sorbate (12.5% HD after 4 hr and 20% after 7 hr). Therefore, in the absence of a reducible substrate, catalytic H_2–D_2 exchange predominated.

The same cyclohexene-d_2 was obtained from 1,3- and 1,4-cyclohexadiene (Table I). ^2H nmr of this product showed two signals: a doublet at 80–81 cps ($J_{gem\,HD}$ = 2 Hz), corresponding to α-methylene deuterium (–CHD–CH=CH–), and a broad singlet at 86 cps, attributed to β-methylene deuterium (–$CHDCH_2$CH=CH–). From the relative intensity of these signals, one may estimate that 90% of the deuterium is located on the α-methylene carbons and 10% on the β-methylene carbons of cyclohexene-d_2. Therefore, the main path of reduction for both 1,3- and 1,4-cyclohexadiene involves 1,4 addition, with the 1,4-diene conjugating to the 1,3-diene by a 1,3-hydrogen shift before addition. The alternate formation of a 1,4-diolefin–chromium complex is not indicated because the resulting 1,2 addition would produce cyclohexene-d_2 with all the deuterium on the β-methylene positions. The conversion of a 1,4-diolefin complex into a pentadienyl hydride complex is also ruled out because 1,5 addition here would give cyclohexene-d_2 with half the deuterium on the α-methylene and half on the β-methylene positions.

(4) E. N. Frankel, E. Selke, and C. A. Glass, *J. Amer. Chem. Soc.*, **90**, 2446 (1968).

(5) All schemes, compound numbers, and equations are listed in sequence from those in part I.[3]

(6) This coupling does not occur in ^1H nmr because the two protons are equivalent. In hindered systems where geminal coupling can be observed, typical values range from 15–20 cps.[7] Dividing this value by 6 (to convert $J_{H-H\,gem}$ into $J_{H-D\,gem}$ gives 2.5–3 Hz for the expected H–D coupling constant.

(7) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

(8) W. K. Rohwedder, C. R. Scholfield, H. Rakoff, J. Nowakowska; and H. J. Dutton, *Anal. Chem.*, **39**, 820 (1967).

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TABLE II

CATALYTIC DEUTERATION OF METHYL LINOLEATE WITH BENZENE–$Cr(CO)_3$ AND METHYL BENZOATE–$Cr(CO)_3$[a]

	Benzene–$Cr(CO)_3$,[b] % reduction				Methyl benzoate–$Cr(CO)_3$,[c] % reduction		
	53		79		82		94
Analyses	Diene[d]	Monoene[d]	Diene	Monoene	Diene	Monoene	Monoene
Mass spectral, mol %							
d_0	65.5	7.2	35.4	5.4	32.7	9.6	9.6
d_1	0.2	3.3	...	2.7	0.1	2.2	1.2
d_2	25.8	72.6	43.6	69.7	43.5	64.9	60.5
d_3	2.2	...	1.6	0.1	2.3	0.8	...
d_4	4.7	12.8	15.8	17.1	17.2	17.2	20.4
d_5	0.9	1.4	1.8	1.6	2.1	1.2	1.1
d_6	0.7	1.6	0.4	2.4	1.1	2.7	4.9
d_7	...	1.0	0.4	0.6	0.5	0.8	1.2
d_8	...	0.3	0.3	0.3	0.4	0.6	0.7
d_9	...	...	0.1	...	0.3	...	0.3
d_{10}	...	...	0.1	...	...	...	0.3
d_{av}	0.86	2.3	1.8	2.4	1.9	2.4	2.6
^2H nmr, %[e]							
$d_{\alpha\alpha}$	50	...	50	...	50	...	...
d_α	50	90	50	85	50	85	70
Calcd[f] d_α	...	88	...	85	...	83	79
$d_\beta + d_{ins}$	...	10	...	15	...	15	30
Calcd[f] $d_\beta + d_{ins}$	...	12	...	15	...	17	21
Infrared,							
trans, %	6.7	5.9	8.1	5.6	10	5.0	12

[a] Solvent, cyclohexane, 50 ml; initial D_2 pressure, 20 atm. [b] At 165°, 53% reduction at 4 hr, 79% reduction at 8 hr. [c] At 175°, 82% reduction at 1 hr, 94% reduction at 3 hr. [d] Fractions separated by rubber column chromatography. [e] δ_{CDCl_3} 70 cps, $d_{\alpha\alpha}$ C=CCDC=C; δ_{CDCl_3} 80 cps, d_α CDC=C; δ_{CDCl_3} 92 cps, d_β $CDCH_2C{=}C + d_{ins}$ (insulated) $CD(CH_2)_{n>1}C{=}C$. [f] Calculated according to eq 5, 6, and 7 with vinylic D neglected; see text.

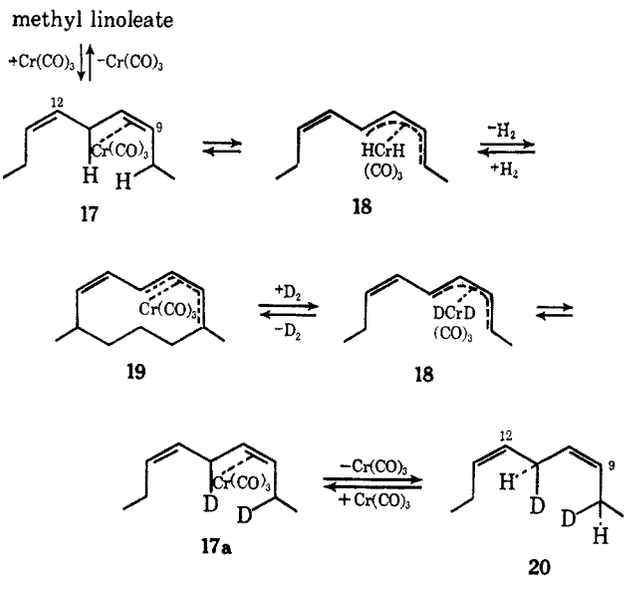
Both methyl *cis,trans*- and *trans,trans*-octadecadienoates yielded methyl octadecenoate-d_2 (Table I). ^2H nmr showed that all the deuterium in the monoenes from the *trans,trans*-diene was on the α-methylene carbons (δ_{CDCl_3} 81 cps). In the monoene from *cis,trans*-dienes, 95% of the deuterium was on the α-methylene carbons (δ_{CDCl_3} 81 cps) and 5% on the β- and insulated methylene carbons [$CHD(CH_2)_nCH{=}CH$, $n \geq 1$, δ_{CDCl_3} 91 cps]. These results provide direct evidence that the dominant mechanism of reduction with both *trans,trans*- and *cis,trans*-1,3-diene fatty esters is by 1,4 addition. There was no evidence of deuterium exchange with hydrogen in the *trans,trans*-diene, as shown by the absence of deuterated species in the diene components after 40 and 90% reduction. Therefore, the conjugate addition step is not reversible.

Methyl linoleate was catalytically deuterated with benzene–$Cr(CO)_3$ and methyl benzoate–$Cr(CO)_3$. Diene and monoene components in the reaction mixtures were analyzed at two levels of reduction (Table II). Dienes of partially reduced methyl linoleate contained significant amounts of deuterated species. Monoenes averaged more than two atoms of deuterium per molecule. Therefore, hydrogen of methyl linoleate undergoes significant exchange with deuterium, in contrast to methyl sorbate and to the conjugated diene fatty esters which do not exchange.

The main deuterated species in the dienes from partially reduced linoleate were d_0, d_2, and d_4; in the monoenes they were d_0, d_2, d_4, and d_6. This evidence clearly indicates selective incorporation of two deuterium atoms at one time in both dienes and monoenes. ^2H nmr analyses showed that the deuterium in the dienes was located half on the $\alpha\alpha$-methylene (methylene between two double bonds) and half on the α-methylene (outside methylenes of the 1,4-diene system). In the monoenes, 70–90% of the deuterium was located on the α-methylenes and 10–30% on the β- or insulated methylene carbons.

These deuterium tracer experiments with methyl linoleate clearly indicate that a dideuteride (dihydride)–chromium carbonyl complex is involved as an intermediate in both exchange and addition steps. To explain the specific labeling of methyl linoleate in the α-methylenes, the formation of a monoolefin–$Cr(CO)_3$ complex (**17**) is postulated (Scheme V). This complex incorporates both α hydrogens (on C-8 and C-11) into its coordination sphere and forms a diene–dihydride complex **18** which may be, in fact, identical with that postu-

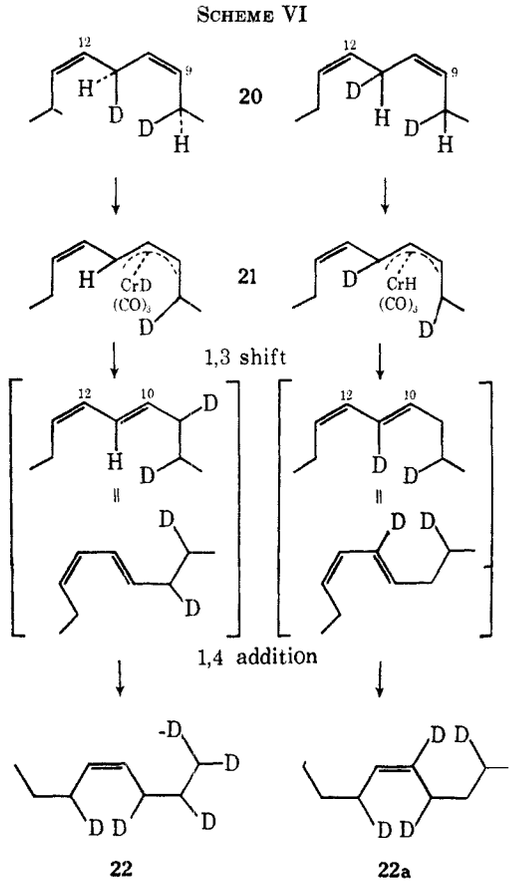
SCHEME V



lated earlier[3] in the reduction of conjugated dienes (*e.g.*, **3**, see part I, Scheme I). Exchange follows by successive elimination of H_2 and addition of D_2. Dissociation of the resulting diene–dideuteride complex **18** and deuterated monene–$Cr(CO)_3$ (**17a**) yields a dideuterated diene **20** specifically labeled in the α-methylene positions. There is equal probability of deuterium exchange occurring with hydrogens on C-11 and C-14 of linoleate. On repetition of the reaction sequence in Scheme V, **20** yields 8,8,11,11- or 8,11,11,14-tetradeuteriolinoleate or 8,11,14-trideuteriolinoleate. This scheme accounts for the deuterium distribution observed in dienes-d_2 and -d_4 (50% $d_{\alpha\alpha}$ and 50% d_α), with lesser amounts of dienes-d_3 and -d_5 but virtually no dienes-d_1.

Conjugation of **20** by 1,3-hydrogen shift *via* the π-allyl complex **21** followed by 1,4 addition yields monoenes-d_4 (**22**) with deuterium located on the α-, β-, and γ-methylenes as well as on the vinyl carbons (Scheme VI). Monoenes-d_4 from the 9,11-diene (produced by a 1,3 shift between hydrogens on C-11 and C-13) would have the same deuterium distribution as **22** and **22a**. Scheme VI can be used also to calculate deuterium distribution in the monoene-d_6 derived from diene-d_4. Small amounts of monoenes-d_5, -d_7, and -d_9 result from reduction of the dienes with two fewer deuteriums; practically no monoene-d_3 is found since there is so little diene-d_1.

SCHEME VI



The average deuterium distribution of monoenes can be calculated according to eq 5, 6, and 7 based on Scheme VI, assuming that **22** and **22a** are formed in equal amounts and that diene-d_0 → monoene-d_2, diene-d_2 → monoene-d_4, and diene-d_4 → monoene-d_6.

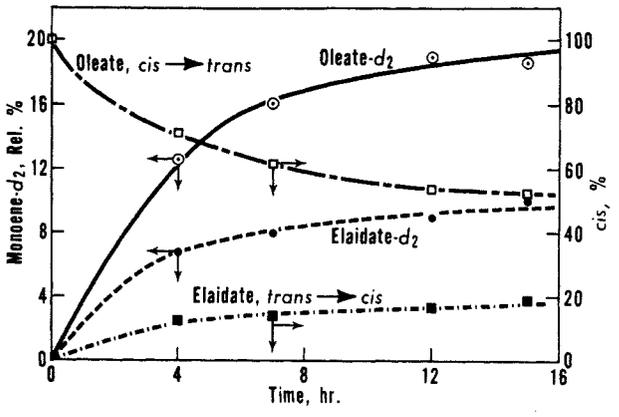


Figure 2.—Catalytic deuteration and isomerization of monoene fatty esters with methyl benzoate–$Cr(CO)_3$ (footnote *a*, Table III).

$$\text{monoene-}d_2 = 100\%\ d_\alpha \quad (5)$$

$$\text{monoene-}d_4 = 50\%\ d_\alpha + 37.5\%\ (d\ + d_\gamma) + 12.5\%\ d_{\text{vinyl}} \quad (6)$$

$$\text{monoene-}d_6 = 33.3\%\ d_\alpha + 50\%\ (d_\beta + d_\gamma) + 16.7\%\ d_{\text{vinyl}} \quad (7)$$

Although ^2H nmr showed little or no resonance corresponding to vinylic deuterium (δ_{CDCl_3} 30 cps), calculations based on the relative concentration of monoenes-d_4 and -d_6 indicate that the intensity of this signal (4–6%) would be below the limit of detection. The contribution of vinylic deuterium was therefore neglected in the calculations. The calculated results in Table II show reasonably good agreement with the experimental values and support the deuterium labeling in Schemes V and VI.

The deuteration experiments have shown that the addition step with conjugated diene fatty esters is not reversible, whereas the exchange step with methyl linoleate, and presumably other *cis,cis*-1,4-dienes, is reversible. In contrast to methyl linoleate, 1,4-cyclohexadiene did not undergo deuterium exchange with hydrogen. This absence of exchange can be attributed to the more rigid and unfavorable conformation of the α-methylene hydrogens in 1,4-cyclohexadiene.

According to the mechanism depicted in Scheme V, the deuterium exchange with hydrogen in methyl linoleate is stereochemically *cis*. The question then arises: Would a *cis*-monoene like methyl oleate ($\Delta^{cis\text{-}9}$) undergo deuterium exchange with hydrogen whereas the corresponding *trans*-monoene, methyl elaidate ($\Delta^{trans\text{-}9}$) would not? Results of experiments designed to answer this question are shown in Table III and Figure 2. This question could not be answered unequivocally because methyl oleate and elaidate were isomerized when treated with methyl benzoate–$Cr(CO)_3$ and D_2. However, the results support the conclusion that the deuterium exchange with hydrogen is stereochemically *cis*. Under the same conditions methyl oleate exchanged deuterium about twice as much as methyl elaidate (Figure 2). Monoenes-d_2 were the main species formed. ^2H nmr showed further that the deuterium in the monoenes from oleate was located predominantly on the α-methylene carbons.

In oleate, the exchange leveled off after 7 hr, presumably because of the isomerization of the double bond from *cis* to *trans* (47% *trans* after 15 hr). With methyl elaidate, less isomerization occurred from *trans* to *cis* (19% *cis* after 15 hr, Figure 2). The small amount of deuterated species observed with methyl

TABLE III

CATALYTIC EXCHANGE OF DEUTERIUM FOR HYDROGEN IN METHYL OLEATE AND ELAIDATE AND THEIR ISOMERIZATION BY METHYL BENZOATE–$Cr(CO)_3$[a]

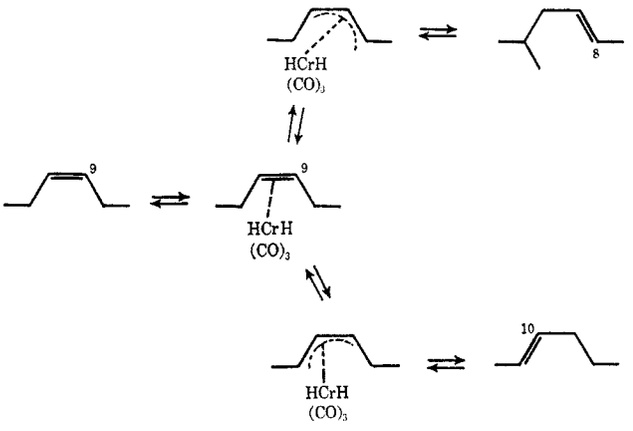
	Methyl oleate				Methyl elaidate			
			15 hr				15 hr	
Analyses	4 hr	7 hr	*cis*[b]	*trans*[b]	4 hr	7 hr	*cis*[c]	*trans*[c]
Mass spectral, mol %								
d_0	83.6	79.6	66.8	75.7	90.2	88.0	79.0	85.7
d_1	0	0	3.1	3.0	0	0.3	2.3	1.3
d_2	12.6	16.2	24.1	16.1	6.8	8.0	15.1	9.0
d_3	1.1	1.5	1.6	1.8	1.0	1.6	1.1	1.1
d_4	1.2	1.6	2.8	2.1	0.8	0.8	1.6	1.5
d_5	0.8	0.6	0.9	0.7	0.5	0.7	0.5	0.7
d_6	0.7	0.5	0.7	0.6	0.7	0.6	0.4	0.7
d_{av}	0.42	0.53	0.79	0.59	0.27	0.31	0.48	0.39
^2H nmr, %[d]								
d_α	90	85	95	30	...	...	95	...
d_{ins}	10	15	5	45	...	...	5	...
d_{vinyl}	0	0	0	25	...	...	0	...
Infrared, *trans*, %	29	62	0	93	88	86	0	95
O_3 cleavage, %[e]								
Δ^8	22	27	2	35	11	14	40	11
Δ^9	61	51	93	14	69	64	10	71
Δ^{10}	17	22	5	51	20	22	50	18

[a] Solvent, cyclohexane, 50 ml; substrate, 9 mmol; catalyst, 1 mmol; temperature, 175°; D_2 pressure, 25 atm. [b] Fractions separated by $AgNO_3$ column chromatography. Yields: 53% *cis*, 47% *trans*. [c] Yields: 19% *cis*, 81% *trans*. [d] δ_{CDCl_3} 80 cps, d_α CDC=C; δ_{CDCl_3} 92 cps, d_{ins} $CD(CH_2)_{n\geq 1}C=C$; δ_{CDCl_3} 30 cps, d_{vinyl} $-CD=C-$. [e] By ozonolysis–glpc.

elaidate can therefore be attributed to exchange occurring after isomerization of the double bond from *trans* to *cis*. According to this interpretation, geometric isomerization and exchange are independent reactions.

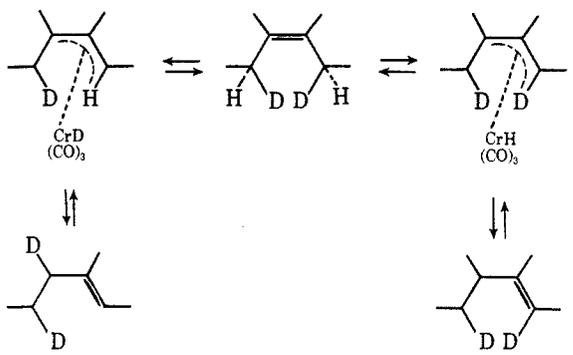
Geometric isomerization of methyl oleate and elaidate was accompanied by positional isomerization of the double bond. Cleavage analysis showed that the Δ^8 and Δ^{10} isomers predominate in the *trans* fraction from isomerized oleate and in the *cis* fraction from isomerized elaidate. Furthermore, ^2H nmr showed that the deuterium is located predominantly on the α-methylenes in the *cis*-monoene fractions. However, in the *trans*-monoene fraction from isomerized oleate, the deuterium was distributed among the α-methylenes (30%), insulated methylenes (45%), and vinylic carbons (25%).

Positional and geometric isomerization of methyl oleate may occur by a 1,3-hydrogen shift through π-allyl-complexed intermediates derived from a *cis*-monoolefin–$Cr(CO)_3$ complex of type **17** (*cf.* Scheme V).



With methyl elaidate, the reverse process would be involved in the formation of $\Delta^{cis\text{-}8}$- and $\Delta^{cis\text{-}10}$-monoenes [π-allyl monohydride–$Cr(CO)_3$ → *cis* monoolefin–$Cr(CO)_3$].

In the isomerization of methyl oleate-d_2, equilibria involving monohydride and monodeuteride allylic intermediates can be assumed (as in Scheme VI).



The *trans*-monoenes have deuterium located on the α- (25%) and β- (50%) methylenes, and on the vinyl carbons (25%). This deuterium distribution agrees well with the observed distribution (Table III) and provides support for the participation of π-allylic intermediates in the isomerization.

Since a *cis*-monoene like methyl oleate can exchange specifically in the α-methylene positions, then the question arises as to whether such exchange also occur in the monoene products obtained from reduction of conjugated dienes. If this exchange does occur, then the monoene products should have an average deuterium content exceeding two atoms per molecule. Since all monoenes from reduced conjugated dienes had a d_{av} close to 2.0, we conclude that no exchange occurred with these products. Also, the extent of isomerization of these monoene products was very small. Therefore, in the presence of diene systems, the exchange and isomerization of monoene products are effectively inhibited. In methyl linoleate, exchange was faster than in

methyl oleate and conjugate addition occurred at a rate substantially greater than isomerization of monoene product.

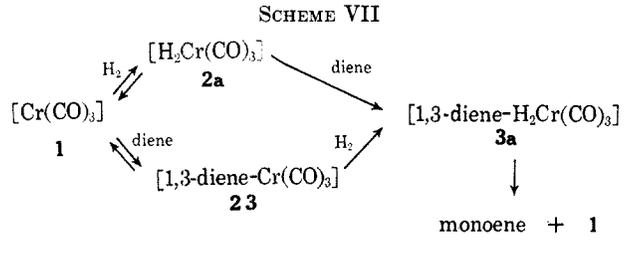
Discussion

The deuteration experiments provide direct evidence that 1,4 addition is the dominant mechanism of reduction catalyzed by the arene–$Cr(CO)_3$ complexes. Hydrogen addition is predominantly molecular, since with D_2 monoene-d_2 is the main product and with $H_2 + D_2$ it is a mixture of monoene-d_0 and monoene-d_2. These results provide compelling evidence for dihydride and dideuteride complex intermediates **3** and **3a** (see part I, Scheme I)[3] involving *cis* 1,4 addition to a cisoid complexed diene. Our results are analogous to those of Wilkinson and coworkers,[10] when simple olefins were reduced with $RhCl(Ph_3P)_3$ in a mixture of $H_2 + D_2$. Their mechanism involves 1,2 addition by *cis*-hydrogen transfer through a $Rh(III)H_2(Ph_3P)_2$ intermediate. The important question arises: Can a dihydride complex add hydrogen by 1,4 addition across a 1,3-diene system and exchange two α hydrogens in *cis*-monoenes (essentially the reverse of the above reaction)? A key factor is very likely the distance between the two *cis* hydrogens on the dihydride complex. It is reasonable to assume that the hydrogen–hydrogen distance in this dihydride complex corresponds to the internuclear distance between α hydrogens in the *cis*-monoene product (3.0 Å in a model) and that other geometric requirements are met for facile 1,4 addition and exchange.

The isotopic discrimination observed with $H_2 + D_2$, which favors the d_0 product over the d_2 product, can be attributed to the relative proportion of either **2a** and **2** ($k_{2a} > k_2$) or of **3a** and **3** ($k_{3a} > k_3$) (see part I, Scheme I).[3] Since a small kinetic isotopic effect was observed ($k_D > k_H$), the formation of product-determining intermediates is not rate determining. Hydride formation reactions (**2** and **2a**) would be expected to be faster than the addition reactions (**3** and **3a**) because the number of vacant coordination sites in **1** is greater than in **2**. Therefore, it seems likely that competition exists between **2a** and **2** rather than between **3a** and **3**.

A mechanistic path alternate to or concurrent with that given in Scheme I (see part I)[3] involves formation of a 1,3-diene complex (**23**) with $Cr(CO)_3$ (**1**) before hydride formation. Competition may thus exist between the diene substrate and hydrogen for the vacant coordination sites of **1** (Scheme VII).

SCHEME VII



The two paths leading to **3a** may not be distinguishable kinetically. However, we have found that methyl benzoate–$Cr(CO)_3$ can effectively activate H_2 catalyzing H_2–D_2 exchange in the absence of the 1,3-diene substrate. Therefore, formation of a hydride complex of type **2a** is indicated. Moreover, the reversible formation of a 1,3-diene–$Cr(CO)_3$ complex (**23**) is not supported by our evidence because it would be expected to yield deuterated 1,3-dienes during reduction. In our system, no such deuterated species were detected in partially reduced conjugated dienes.

The reversible formation of an olefin–$Cr(CO)_3$ complex before addition is indicated with methyl linoleate (Scheme V) because deuterated diene species were obtained during reduction. Olefin complex formation assumes importance also in the deuterium exchange with hydrogen of methyl oleate and in the isomerization reactions observed in the absence of hydrogen.

Experimental Section

Materials.—Deuterium was obtained from Liquid Carbonic, San Carlos, Calif.[11] Mass spectral analysis showed 98.9% D_2 and 1.1% HD. Other materials were as described in the preceding paper.[3]

Deuteration.—The procedure was the same as in the hydrogenation studies.[3] Gas samples were taken in some deuteration experiments and analyzed by mass spectrometry.

Separations.—Deuteration products were separated into monoene and diene components as described.[3] Monoene components from deuteration of methyl oleate and elaidate were separated into *cis* and *trans* isomers by a $AgNO_3$-treated ion-exchange resin column.[12]

Mass spectral analyses of deuterated products were done on a Bendix Model 12 time-of-flight spectrometer at 50 eV with a heated inlet system at 150°. Deuterated products of methyl sorbate (methyl *cis*-3-hexenoate) and cyclohexadienes (cyclohexene) were purified through a glpc instrument connected in tandem to the mass spectrometer. Deuterium analyses were calculated as atoms per molecule in excess of natural abundance. No corrections were made for the presence of HD (1.1%) in the D_2 used. The catalyst complex [methyl benzoate–$Cr(CO)_3$] was identified in the products from reaction with H_2 and D_2 when examined by mass spectrometry without $FeCl_3$ decomposition. No evidence of dihydride or dideuteride species was indicated.

^1H nmr spectra were taken at 60 MHz (Varian A-60) in $CDCl_3$ with tetramethylsilane as internal reference (τ scale). The product from reduction of methyl sorbate was identified as methyl 3-hexenoate (**4a**, Scheme I) by comparing its spectrum with that of an authentic material[9] [triplet at τ 9.0 (methyl, 3 H), multiplet at τ 7.88 (allyl methylene, 2 H), doublet at τ 6.88 (α-methylene, 2 H), singlet at τ 6.30 (methoxy, 3 H), and multiplet at τ 4.40 (vinyl, 2 H)]. The corresponding product from reduction with D_2 (**4**) showed the following resonances: unsymmetrical doublet at τ 9.0 (methyl, 3H, splitting due to adjacent CHD group on C-5), multiplet at τ 7.9 (allyl methylene, 1 H), doublet at τ 6.9 (α-methylene, 1 H), singlet at τ 6.30 (methoxy, 3 H), and poorly resolved doublet at τ 4.4 (vinyl, 2 H, splitting due to adjacent CHD groups on C-2 and C-5).

^2H nmr spectra were taken at 15.4 MHz (Varian HA-100) in $CDCl_3$, also the internal standard (parts per million scale). Assignments of deuterium resonance peaks were made by converting their shifts into the proton τ scale and by using $CHCl_3$–$CDCl_3$ (τ 2.74) as the common internal standard. For example, in Figure 2, the peak at 65.5 cps is converted as follows: $65.5/15.4 = \tau$ 4.25 and $2.74 + 4.25 = \tau$ 6.99 (the corresponding ^1H nmr peak is at τ 6.9 due to α-methylene H on C-2 of **4**). Similarly, for the peak at 81.5 cps, the corresponding proton signal calculates as $81.5/15.4 = \tau$ 5.29 and $2.74 + 5.29 = \tau$ 8.03 (corresponding ^1H nmr peak is at τ 7.9 due to allyl H on C-5 of **4**). Deuterated fatty esters showed four pertinent resonances (Tables II and III): δ 30 cps due to D on vinylic carbon, –CD=C–; δ 70 cps due to D on $\alpha\alpha$-methylene in linoleate, –C=CCDC=C–; δ 80 cps due to D on α-methylene in monoenes and dienes, –CDC=C–;

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(11) The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

(12) E. A. Emken, C. R. Scholfield, and H. J. Dutton, *J. Amer. Oil Chem. Soc.*, **41**, 388 (1964).

and δ 92 cps due to D on β-, γ-, and insulated methylenes [CD-$(CH_2)_n \gtrsim {}_1C{=}C$-], and are not resolved.

Registry No.—Methyl sorbate, 1515-80-6; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; methyl octadeca-10,12-dienoate, 1002-79-5; methyl *cis*-9,*trans*-11-octadecadienoate, 13058-52-1; methyl *trans*-9,*trans*-11-octadecadienoate, 13038-47-6; methyl benzoate-$Cr(CO)_3$, 12125-87-0; benzene-$Cr(CO)_3$, 12082-08-5; methyl linoleate, 112-63-0; methyl oleate, 112-62-9; methyl elaidate, 1937-62-8; **4**, 21899-41-2.

Acknowledgment.—We thank Professor R. B. Bates, University of Arizona, for helpful suggestions in the preparation of this article.

The Effect of Dipolar Aprotic Solvents on the Nucleophilic Addition of Alcohols to Activated Olefins

B. A. FEIT[1] AND Z. BIGON

Department of Chemistry, Tel Aviv University, Tel Aviv, Israel

Received August 26, 1968

The effect of dipolar aprotic solvents on the alkoxide-catalyzed addition of methanol and ethanol to methyl esters and nitriles of acrylic and methacrylic acid was investigated kinetically. The rate equation found was $R = (k_{obsd}\,[\text{olefin}]\,[\text{alkoxide}])/[\text{ROH}]^n$. Rates of addition were relatively very high in solvent mixture poor in alcohol. The order of reaction in alcohol was dependent only on the type of the aprotic solvent used; its absolute value increased with increasing the hydrogen-bonding capability of the aprotic solvent. It is suggested that mainly one and the same nucleophile is involved in the addition reaction, in both pure alcohol and in alcohol dipolar aprotic solvent mixtures poor in alcohol.

The rates of reactions involving nucleophiles or bases have been found to be strongly accelerated in dipolar aprotic solvents as compared to protic solvents. This effect was recently investigated kinetically and synthetically[2-4] mainly with nucleophilic substitutions and with various base-catalyzed reactions such as eliminations,[5] H–D exchange[6] reactions, isomerizations,[7] oxidations,[8] etc. In only a few cases was this effect reported with regard to reactions involving unsaturated compounds. These include nucleophilic additions to olefins[9] and to carbonylic compounds such as esters,[10] ketones,[11] carbon dioxide,[12] and carbon disulfide.[13]

Gradual replacement of a protic solvent by a dipolar aprotic solvent in a mixed protic–dipolar aprotic solvent caused only a slight increase in the rate of nucleophilic substitutions,[14,15] alkaline hydrolysis of esters,[10a,b,d,e] base-catalyzed oxidations,[8] etc. However, in the range of low concentrations of the protic component, a dramatic rate enhancement was observed on further decreasing of its concentration. This behavior was ascribed to a large increase in the reactivity of the nucleophilic species.[2,14] The accepted opinion is that less reactive hydrogen-bonded solvated nucleophiles operate at relatively high concentrations of the protic component, whereas unsolvated and much more reactive nucleophiles operate at low concentrations. Desolvation of the nucleophiles is facilitated by the strong association of dipolar aprotic solvents with hydroxylic solvents.[16-19] According to others, the above-mentioned rate enhancement was due in some cases to a catalytic effect of the dipolar aprotic solvent.[14,15]

The base-catalyzed addition of methanol to acrylonitrile in mixed methanol–dipolar aprotic solvents was previously investigated.[9] The experimental rate equation was

$$R = k\frac{[\text{acrylonitrile}]\,[CH_3O^-]_{total}}{[CH_3OH]^n{}_{total}}$$

This equation accounted for the large rate enhancement which was observed in the presence of low concentration of methanol. The rate constant and the order of reaction in methanol were dependent on the aprotic solvent used.[9] These were higher with the dipolar aprotic solvents (DMF, DMSO) than with apolar aprotic solvents (THF, dioxane).

Negatively charged large transition states are poorly hydrogen bonded owing to dispersion of charge, as compared to small anions. Anions are in general poorly solvated in aprotic solvents, but negatively charged polarizable transition states are solvated by dipolar aprotic solvents to about the same extent as they are in protic solvents. Consequently, bimolecular reactions of anions which pass through large polarizable transition states containing these anions are much faster in dipolar–aprotic than in protic solvents.[20] Based on this assumption concerning the effect of the medium on

(1) To whom correspondence should be addressed: Polymer Research Center, State University College of Forestry, Syracuse, N. Y. 13210.

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