4,4-dinitro-2-pentenoate, 21824-03-3; *trans*-ethyl β-(2,2-dinitropropoxy)acrylate, 21824-04-4; *cis*-ethyl β-(2,2-dinitropropoxy)acrylate, 21824-05-5.

Acknowledgment.—We wish to thank Mr. K. Inouye for the elemental analyses and Mr. L. A. Maucieri for the nmr analyses.

Homogeneous Hydrogenation of Diolefins Catalyzed by Tricarbonyl Chromium Complexes. I. Stereoselective 1,4 Addition of Hydrogen[1]

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Arene–Cr(CO)$_3$ complexes catalyze selectively the homogeneous hydrogenation of conjugated dienes by 1,4 addition to give predominantly *cis* monoenes. With 1,4-dienes, conjugation to the 1,3-dienes precedes addition. With *cis*-1,3-dienes, isomerization by a 1,5-hydrogen shift during hydrogenation is indicated. Reduction rates are decreased by methyl substituents on C-1 and C-4 of the 1,3-diene system. Although 1,5-hexadiene is not reduced or isomerized, 1,5-cyclooctadiene is readily isomerized to 1,4- and 1,3-dienes and reduced to cyclooctene. Kinetic studies with computer simulation techniques show that, in a mixture, 1,3-cyclohexadiene is reduced twice as fast as 1,4-cyclohexadiene with methyl benzoate–Cr(CO)$_3$. A mixture of conjugated methyl linoleate (9,11- and 10,12-octadecadiene) is reduced 22 times faster than methyl linoleate (9,12-diene). The arene–Cr(CO)$_3$ catalysts are highly stereoselective for *trans,trans*-conjugated dienes (relative rates: *cis,cis*, 1.0; *cis,trans*, 8.0; and *trans,trans*, 25). The mechanism advanced for conjugate addition involves H$_2$Cr(CO)$_3$ and its 1,3-diene adduct, which undergoes 1,4-hydrogen insertion across a cisoid 1,3-diene system.

Several organometallic and metal coordination compounds are now recognized for their catalytic activity in addition and transfer reactions of hydrogen with mono- and polyolefins in solution.[3] Iron pentacarbonyl is an effective homogeneous catalyst for the hydrogenation[4] and isomerization[5] of olefinic compounds. It forms stable and isolable π complexes with diene and triene fatty esters.[6,7] These complexes are useful reaction intermediates in studies of homogeneous catalysis.[8]

Our previous work has shown that olefin–Fe(CO)$_3$ complexes catalyze the hydrogenation of methyl sorbate (*trans*-2,*trans*-4-hexadienoate) to a mixture of methyl 2,3,4-hexenoate, as well as to methyl hexanoate.[9] By contrast, arene–Cr(CO)$_3$ complexes catalyze selectively the hydrogenation of methyl sorbate to methyl 3-hexenoate in yields of 90–99%.[10] Changing substituents in both substituted complexes, butadiene–Fe(CO)$_3$ and arene–Cr(CO)$_3$, modifies the order of catalytic activity, but the selectivity remains essentially the same. The order of catalytic activity of various carbonyl complexes of Cr, Mo, and W was related to thermal stability of the complexes during hydrogenation.[11] With mesitylene–M(CO)$_3$ complexes, for example, activity varied in the order Mo > W > Cr, and selectivity in the order Cr > Mo > W.

In a preliminary communication,[12] we have shown by deuterium tracer studies that the reduction of methyl sorbate catalyzed by methyl benzoate–Cr(CO)$_3$ proceeds by 1,4 addition. A catalytic mechanism was postulated (Scheme I) in which the active complex intermediates included chromium tricarbonyl (**1**), its dideuteride (**2**) as well as its dihydride (**2a**), and the dideuteride chromium tricarbonyl diene adduct (**3**) as well as its corresponding dihydride (**3a**). This paper reports details of this catalytic reaction with various diolefins. The kinetics of competitive hydrogenation and catalytic isomerization were also examined to elucidate the mechanism further.

Results and Discussion

Diene Hydrocarbons.—Generally, methyl benzoate–Cr(CO)$_3$ was used in this work because its activity and thermal stability were high under the conditions of hydrogenation (160–175°). Although benzene–Cr(CO)$_3$ is less active than methyl benzoate–Cr(CO)$_3$, cycloheptatriene–Cr(CO)$_3$ is more active, but its thermal lability limits its use to lower temperatures (100–125°). Data in Table I are from hydrogenation with methyl benzoate–Cr(CO)$_3$ and hexadiene isomers. Conjugated hexadienes were most rapidly and completely reduced at 160° to the 1,4-addition monoenes as main products. On the other hand, under the same conditions, 1,4-hexadiene was very slowly reduced. Raising the temperature from 160 to 175° resulted in 77% reduction to a mixture of 2- and 3-hexenes as main products. Since

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[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.

[3] For reviews, see (a) H. W. Sternberg and I. Wender, International Conference of Coordination Chemistry, London, April 1959, Special Publication No. 13, The Chemical Society, London, 1959, p 35; (b) J. Halpern, Advances in Chemistry Series, No. 70, American Chemical Society, Washington, D. C., p 1; (c) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Logos Press, London, 1966, pp 248–271; (d) J. C. Bailar, Jr., and H. Itatani, *J. Amer. Chem. Soc.*, **89**, 1592 (1967), and references cited therein.

[4] (a) E. N. Frankel, H. M. Peters, E. P. Jones, and H. J. Dutton, *J. Amer. Oil Chem. Soc.*, **41**, 186 (1964); (b) A. Misonou, I. Ogata, and F. Funami, *Yukagaku*, **13**, 21 (1964).

[5] (a) J. E. Arnet and R. Pettit, *J. Amer. Chem. Soc.*, **83**, 2954 (1961); (b) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962); (c) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964); (d) M. Orchin, *Advan. Catal.*, **16**, 1 (1966).

[6] (a) E. N. Frankel, E. A. Emken, H. M. Peters, V. L. Davison, and R. O. Butterfield, *J. Org. Chem.*, **29**, 3292 (1964); (b) I. Ogata and A. Misonou, *Yukagaku*, **13**, 308 (1964); *Bull. Chem. Soc. Jap.*, **37**, 439 (1964).

[7] E. N. Frankel, E. A. Emken, and V. L. Davison, *J. Org. Chem.*, **30**, 2739 (1965).

[8] E. N. Frankel, T. L. Mounts, R. O. Butterfield, and H. J. Dutton, ref 3b, p 177.

[9] E. N. Frankel, N. Maoz, A. Rejoan, and M. Cais, Abstracts, Third International Symposium on Organometallic Chemistry, Munich, West Germany, Aug–Sept 1967, p 210.

[10] E. N. Frankel and M. Cais, unpublished work, 1967; M. Cais, E. N. Frankel, and A. Rejoan, *Tetrahedron Lett.*, 1919 (1968).

[11] E. N. Frankel and F. L. Little, *J. Amer. Oil Chem. Soc.*, **46**, 256 (1969).

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

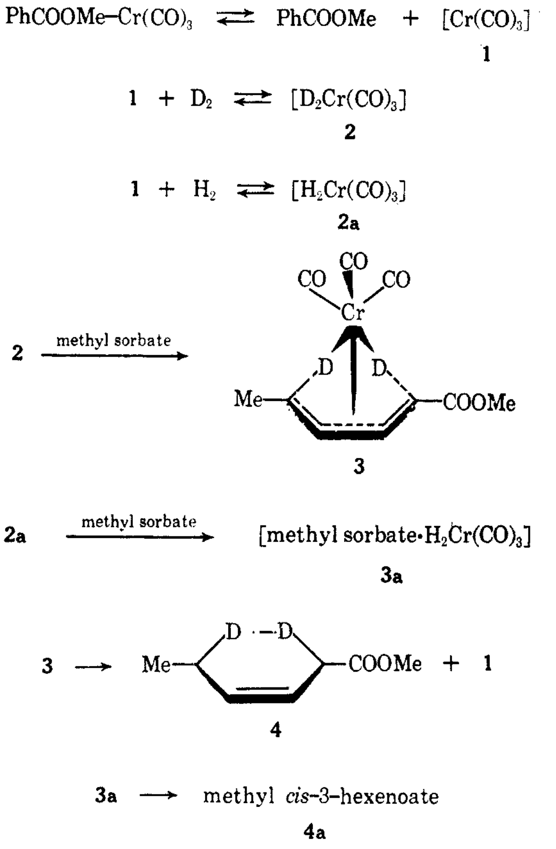
TABLE I

CATALYTIC HYDROGENATION OF HEXADIENE ISOMERS WITH METHYL BENZOATE–$Cr(CO)_3$ (0.5 MMOL)[a]

				Glpc analysis, % at *t*			
				Hexenes			
Hexadienes, 9.5 mmol	Temp, °C	*k*,[b] hr^{-1}	Time (*t*), hr	1-	2-	3-	Hexadiene
1,3 (*cis* and *trans*)	160	0.90[c]	6	6	66 (*cis*) 10 (*trans*)	18 (*cis* and *trans*)	0
2,4 (*cis,trans* and *trans,trans*)[d]	160	2.1	2		10 (*cis*)	90 (*cis*)	0
1,4 (*cis* and *trans*)[e]	160	0.008	6		2 (*cis*)	3 (*cis* and *trans*)	95
	175	0.22[c]	6		18 (*cis*) 19 (*trans*)	40 (*cis* and *trans*)[f]	23[g]
1,5	175	0.004	6	1	1		98

[a] Solvent, *n*-pentane, 50 ml; initial H_2 pressure, 30 atm. [b] Decrease in diene. [c] Rates determined after an induction period of 30–60 min. [d] 48% *cis,trans* and 52% *trans,trans*. [e] 28% *cis* and 72% *trans*. [f] Approximately 38% *cis* and 2% *trans*. [g] Includes approximately 1% 1,3-diene and 3% 2,4-diene.

SCHEME I

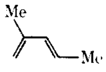
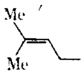
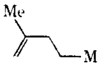
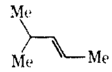
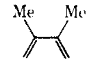
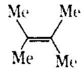
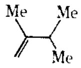
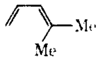
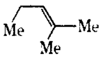
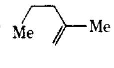
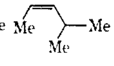
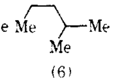
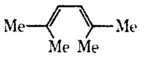
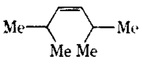


small amounts of 1,3- and 2,4-hexadienes were detected in the product, probably isomerization of 1,4-dienes into a mixture of 1,3- and 2,4-dienes preceded hydrogenation. Conjugation as an intermediate step in the reduction of 1,4-hexadiene is further supported by the absence of hydrogenation of hexenes and by the results of isomerization. 1,5-Hexadiene was unreactive and only 2% reduction occurred at 175°. Apparently, the catalyst cannot promote conjugation of the 1,5-diene, and this step is necessary for reduction of acyclic nonconjugated diolefins.

Various branched 1,3-dienes were examined to determine whether the mode of hydrogen addition is affected by the substituent (Table II). 2-Methyl-1,*trans*-3-pentadiene (**5**) and 2,3-dimethyl-1,3-butadiene (**6**) were readily reduced to the corresponding 1,4-addition monoenes as main products. As anticipated, methyl substituents on C-2 and C-3 of the diene system did not interfere with 1,4 reduction. Methyl substituents on C-1 and C-4, however, seriously inhibited reduction, as shown by the relative unreactivity of 2,5-dimethyl-2,4-hexadiene (**8**) even at 175°. 4-Methyl-1,3-pentadiene (**7**) was readily hydrogenated to 2-methyl-2-pentene as the major product. If 1,4 addition is the main path of reduction, then this product can be accounted for by the isomerization between **7** and **9** through a 1,5-hydrogen shift preceding hydrogenation (Scheme II). There is a precedent[13] for such a reversible thermal isomerization of *cis*-1,3-dienes by a 1,5 shift.

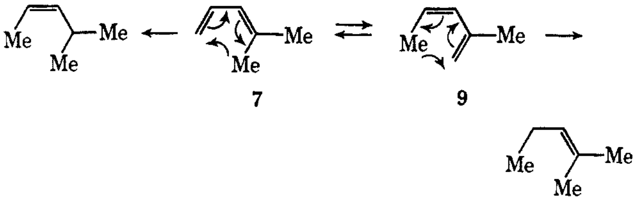
TABLE II

CATALYTIC HYDROGENATION OF METHYL-SUBSTITUTED DIENES WITH METHYL BENZOATE–$Cr(CO)_3$ (0.5 MMOL)[a]

Dienes, 9.5 mmol	*k*,[b] hr^{-1}	Glpc analysis			
		Products (% at 6 hr)			
 **5**	0.69	 (75)	 (17)	 (8)	
 **6**	0.64	 (82)	 (18)		
 **7**	1.1	 (66)	 (14)	 (14)	 (6)
 **8**	0.007	 (5)			
	0.10[c]	(45)			

[a] Solvent, *n*-pentane, 50 ml; temperature, 160°; initial H_2 pressure, 30 atm. [b] Decrease in diene. [c] At 175°.

SCHEME II



The *cis* configuration of the main monoene products from acyclic dienes (Tables I and II) is consistent with an intermediate 1,3-diene–catalyst complex assuming a cisoid conformation of type **3** (Scheme I). Furthermore, the catalyst does not effectively promote the *cis* to *trans* isomerization of the monoene products.[11] Further studies indicate that the minor monoene products from acyclic dienes (Table I) are attributable to isomer-

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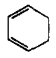
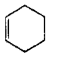
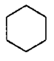
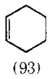
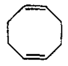
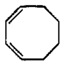
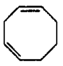
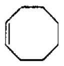
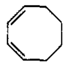
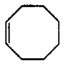
[13] J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, **84**, 2775 (1962).

ization of the diene substrates before reduction and not to 1,2 addition of hydrogen.

Both 1,3- and 1,4-cyclohexadiene were readily reduced to cyclohexene as the main product (Table III).

TABLE III

CATALYTIC HYDROGENATION OF CYCLIC DIENES WITH METHYL BENZOATE–CR(CO)$_3$ (0.5 MMOL)[a]

Dienes, 9.5 mmol	k,[b] hr^{-1}	Glpc analysis—Products (% at 6 hr)		
 10	0.50	 (98)	 (2)	
 11	0.42	 (93)		
 12	0.090	 (64)	 (1)	 (35)
	0.19[c]	(28)[c]	(2)[c]	(70)[c]
 13	0.05	 (25)		

[a] Solvent, n-hexane, 50 ml; temperature 160°; initial H_2 pressure, 30 atm. [b] Decrease in diene. [c] At 170°.

If isomerization of **11** to **10** occurs rapidly before hydrogenation, the forced cisoid conformation of **10** would account for the relative ease with which **11** was reduced. With 1,5-cyclooctadiene (**12**), the thermodynamically stable 1,3-diene[5a,14] (**13**) was the main product at 160°, whereas cyclooctene was the main product at 170°. The stability of **13** is further indicated by its relative resistance to reduction. The ease of hydrogenation of **10** compared with **13** may be related to a more favorable conformation in **10** for diene complex formation with the catalyst.

The activity of methyl benzoate-Cr(CO)$_3$ in catalyzing isomerization of olefins was studied to check how this reaction may influence product composition in the hydrogenation experiments. On the one hand, no isomerization of 2- and 3-hexene (*cis* and *trans*) was detected with methyl benzoate–Cr(CO)$_3$ under the conditions of hydrogenation at 170°. On the other hand, 1-hexene is isomerized slowly to a mixture of the 2- and 3-hexenes (*cis* and *trans*) and reached 11% at 160° and 23% at 175° after 6 hr. Therefore, an equilibrium favoring strongly 2- and 3-hexene would be indicated. No reduction of any of these hexene isomers was observed under the hydrogenation conditions at 175°.

Several dienes were isomerized to varying degrees when heated with methyl benzoate-Cr(CO)$_3$ under nitrogen (Table IV). An equilibrium favoring the 2,4-diene (*cis,trans*) is indicated in the isomerization of conjugated hexadienes. Under the conditions used, conjugation of 1,4-hexadiene to a mixture of 2,4- and 1,3-diene was confirmed and no change was observed with 1,5-hexadiene. Isomerization of **7** to **9** occurred to a small degree under nitrogen. This result supports Scheme II, suggested as applicable under hydrogenation conditions. 1,4-Cyclohexadiene was readily isomerized to the corresponding 1,3-diene at 160°. With 1,5-cyclooctadiene, it was necessary to raise the temperature to 175° to obtain significant isomerization to the 1,3-diene. 1,3-Cyclohexa- and -octadienes were isomerized only slightly. Consequently, an equilibrium favoring the 1,3-dienes is indicated. The presence of benzene and benzene–Cr(CO)$_3$ in the products from 1,3- and 1,4-cyclohexadiene shows that disproportionation takes place as a side reaction. The minor amounts of cyclohexene and of reduction products from other dienes can be attributed to disproportionation. These experiments show that catalytic isomerization of dienes occurring under hydrogenation conditions probably contributes to some of the minor products of acyclic dienes (Table I).

TABLE IV

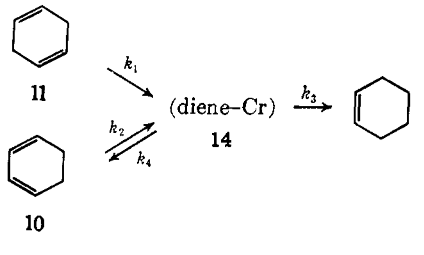
CATALYTIC ISOMERIZATION OF DIENES WITH METHYL BENZOATE–Cr(CO)$_3$ UNDER NITROGEN[a]

Dienes, 9.5 mmol	Products	Glpc analysis, % at 6 hr 160°	175°
1,3-Hexadiene (*cis* and *trans*)	2,4-Diene (*cis,trans*)	12	18
	Hexene (2- + 3-)	0	3
2,4-Hexadiene[b]	1,3-Diene	. .	8
	Hexene (2- + 3-)	. .	1
1,4-Hexadiene[c]	2,4-Diene	. .	38[d]
	1,3-Diene	. .	8
	Hexene (2- + 3-)	. .	1
1,5-Hexadiene	None	. .	. .
4-Methyl-1,3-pentadiene (**7**)	2-Methyl-1,3-diene (**9**)	3	4
	Unidentified (?)	3	6
1,3-Cyclohexadiene	1,4-Diene	3	. .
	Cyclohexene	7	. .
	Benzene[e]	2	. .
1,4-Cyclohexadiene	1,3-Diene	58	. .
	Cyclohexene	4	. .
	Benzene[e]	1	. .
1,5-Cyclooctadiene	1,4-Diene	3	14
	1,3-Diene	8	71
1,3-Cyclooctadiene	1,4-Diene	. .	1
	Cyclooctene	. .	1

[a] Conditions: 0.5 mmol of catalyst, 50 ml of n-pentane, initial N_2 pressure 50 psi. [b] 48% *cis,trans* and 52% *trans,trans*. [c] 28% *cis* and 72% *trans*. [d] 33% *cis,trans*, 2% *trans,trans*, and 3% *cis,cis*. [e] Benzene–Cr(CO)$_3$ was identified in the product by infrared (λ 1912 and 1985 cm^{-1}).

Kinetics of competitive hydrogenation was studied by simulating the data with a digital computer.[15] An equal mixture of 1,3- and 1,4-cyclohexadiene was reduced with methyl benzoate–Cr(CO)$_3$. The data in Figure 1 were simulated according to Scheme III involving a common diene-chromium carbonyl intermediate **14**. The relative rates estimated by a steady-state approximation are $k_1 = 1.0$, $k_2 = 2.4$, and $k_4 =$

SCHEME III



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[14] D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *J. Amer. Chem. Soc.*, **85**, 1553 (1963).

[15] R. O. Butterfield, *J. Amer. Oil Chem. Soc.*, **46**, 429 (1969).

TABLE V

CATALYTIC HYDROGENATION OF OCTADECADIENOIC FATTY ESTERS WITH CHROMIUM TRICARBONYL CATALYSTS UNDER 30 ATM OF HYDROGEN PRESSURE

Substrates, 9 mmol	$Cr(CO)_3$ complexes, 1 mmol	Temp, °C	Time, hr	Glpc analysis, % Monoene	Diene	Infrared, *trans*,[b] %
Methyl linoleate (*cis*-9,*cis*-12-dienoate)	Methyl benzoate	175	3	94.8	5.2	12.4
	Benzene	165	8	79.0	21.0	6.1
Alkali-conjugated linoleate (*cis*-9,*trans*-11-, and *trans*-10,*cis*-12-dienoate)	Methyl benzoate	175	1.5	97.0	3.0	10.1
	Benzene	165	4	98.8	1.2	8.8
	Cycloheptatriene	125	1	98.0	2.0	14.5
Methyl *cis*-9,*trans*-11-octadecadienoate	Methyl benzoate	175	1.5	97.9	2.1	14.8
	Benzene	165	4	100	0	7.9
	Cycloheptatriene	125	3.5	95	5	8.9
Methyl *trans*-9,*trans*-11-octadecadienoate	Methyl benzoate	175	1	97.8	2.2	7.4
	Benzene	165	2	100	0	9.1
	Cycloheptatriene	125	1	95.4	3.4	7.7
Methyl *cis*-9,*cis*-15-octadecadienoate	Methyl benzoate	175	7	1.6	98.4[c]	34.5

[a] Solvent, cyclohexane (50 ml). [b] Expressed as methyl elaidate (*trans*-9-octadecenoate). [c] Diene peak was partially resolved into three isomeric components.

0.1 k_3. In a mixture, **10** was reduced about twice as fast as **11**. However, when each of these dienes was reduced alone, **10** reacted only 1.2 times faster than **11** (Table III). Therefore, in a mixture there is competition for the coordination sites of the chromium carbonyl complex catalyst. Reduction of the 1,3-diene is favored over conjugation of the 1,4-diene, which is assumed to occur in the conversion of **11** to **14**.

Diene Fatty Esters.—Hydrogenation of 1,3- and 1,4-diene fatty esters catalyzed by three $Cr(CO)_3$ complexes gave monoenes in conversion yields of 94–100% (Table V). Although the 1,4-diene (methyl linoleate) was readily hydrogenated with methyl benzoate–$Cr(CO)_3$, the 1,6-diene fatty ester ($\Delta^{cis\text{-}9,cis\text{-}15}$) was reduced only about 2% after 7 hr. These $Cr(CO)_3$ complexes can apparently catalyze conjugation of the 1,4-diene but not of the 1,6-diene fatty ester, and, as previously observed, conjugation is required for hydrogenation to take place with these catalysts.

Monoene products from the 1,3-and 1,4-dienes were predominantly *cis* in configuration (85–94% *cis*). These $Cr(CO)_3$ catalysts are unique in yielding *cis*-monoenes as main products.[16] In contrast, the 1,6-diene fatty ester was extensively isomerized from the *cis* to the *trans* form. Methyl benzoate–$Cr(CO)_3$ can therefore catalyze isomerization of isolated double bonds in the absence of reactive dienes (1,3 and 1,4). This conclusion is further supported by the isomerization experiments with pure methyl oleate (*cis*-9-octadecenoate).

The double-bond distribution in monoene products from the 1,3- and 1,4-diene fatty esters is given in Figure 2. Methyl *trans*-9,*trans*-11-octadecadienoate yielded essentially only the 1,4-addition product Δ^{10}-monoene (92%), whereas the corresponding *cis*,*trans*-diene gave a mixture mainly of Δ^9- and Δ^{10}-monoenes (83%) (Figure 2a). The deuteration experiments described below show that both *cis*,*trans*- and *trans*,*trans*-dienes are reduced predominantly by 1,4 addition. Therefore, the observation that two main monoene isomers (Δ^9 and Δ^{10}) are formed from the *cis*,*trans*-9,11-diene (**15**) can be explained by assuming that it is isomerized to the 8,10-diene (**16**) by a 1,5-hydrogen shift followed by 1,4 addition of the H_2 (Scheme IV). This path is the same as suggested previously for **7** and **9** (Scheme II).

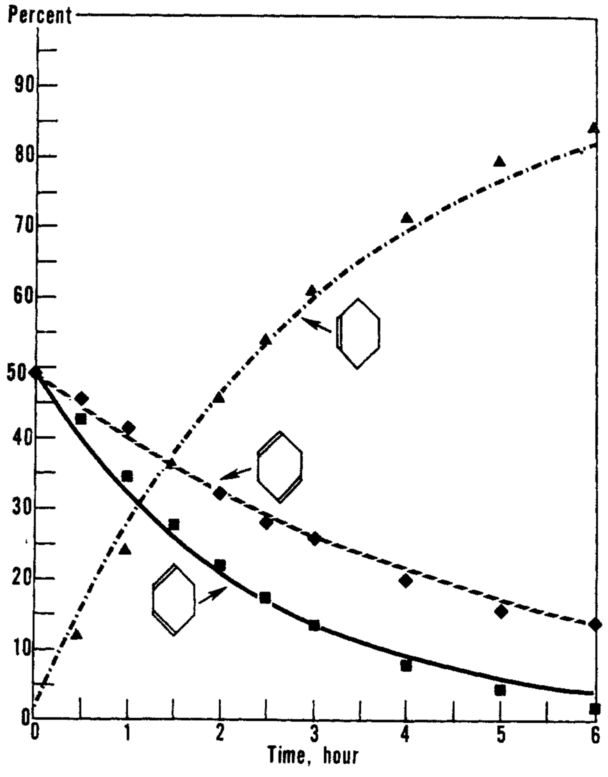

Figure 1.—Catalytic hydrogenation of an equal mixture of 1,4- and 1,3-cyclohexadiene (9.5 mmol) with methyl benzoate–$Cr(CO)_3$ (0.5 mmol) in *n*-hexane solution (50 ml) under 30 atm of H_2 pressure at 160°. The curves were plotted with a digital computer to fit the data according to Scheme III.

In each monoene from methyl linoleate and alkali-conjugated methyl linoleate (mixture of mainly *cis*,-*trans*-9,11- and -10,12-octadecadienoates), the double bond was about equally distributed between the C_9, C_{10}, C_{11}, and C_{12} positions (Figure 2b). Methyl linoleate is apparently conjugated into a mixture similar to that of alkali-conjugated linoleate. A common conjugated diene intermediate would seem to be involved in the hy-

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(16) All other homogeneous catalysts that have been examined[4a,6a,7,17] so far for hydrogenation of unsaturated fatty esters have produced a much larger proportion of *trans* isomers at corresponding levels of conversion.

(17) (a) E. N. Frankel, E. P. Jones, V. L. Davison, E. A. Emken, and H. J. Dutton, *J. Amer. Oil Chem. Soc.*, **42**, 130 (1965); (b) E. A. Emken, E. N. Frankel, and R. O. Butterfield, *ibid.*, **43**, 14 (1966); (c) J. C. Bailar, Jr., and H. Itatani, *ibid.*, **43**, 337 (1966); (d) E. N. Frankel, E. A. Emken, H. Itatani, and J. C. Bailar, Jr., *J. Org. Chem.*, **32**, 1447 (1967).

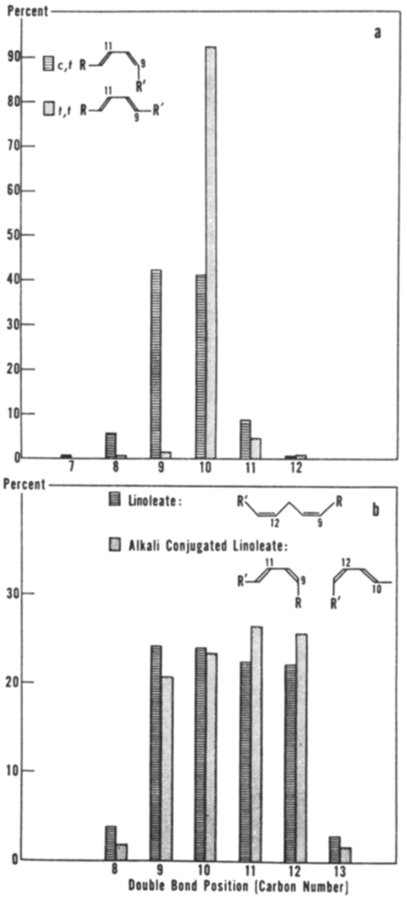
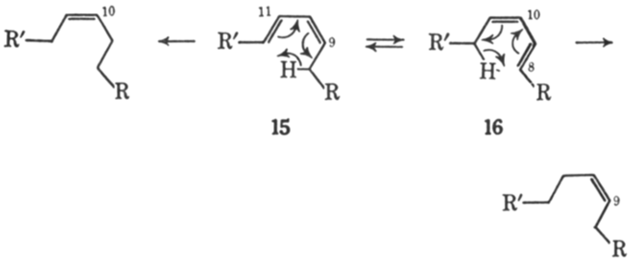


Figure 2.—Double-bond distribution in monoenes: (a) methyl 9,11 octadecadienoates hydrogenated with benzene–$Cr(CO)_3$ (Table V); (b) diene fatty esters hydrogenated with methyl benzoate–$Cr(CO)_3$ (Table V).

SCHEME IV



drogenation of these dienoic fatty esters to account for the formation of the same isomeric monoene products.

Kinetics of competitive hydrogenation were studied with a mixture of methyl linoleate and alkali-conjugated methyl linoleate. Scheme III was used to simulate the data in Figure 3. The relative rates calculated according to this scheme are k_1 (1,4) = 1.0 and k_2 (1,3) = 22. The calculated ratio (k_4/k_3) for the dissociation of the intermediate (diene–Cr) complex to its reduction is 0.3. The data could be equally well simulated with a scheme in which no dissociation of the (diene–Cr) complex occurs (k_4 = 0). In this event, the relative constants were calculated as k_1 = 1 and k_2 = 16. A scheme involving no dissociation of the (diene–Cr) complex is consistent with the results from deuteration studies.

Since methyl linoleate was reduced much more slowly than its conjugated diene isomers, it seems likely that conjugation of 1,4- to 1,3-dienes is a rate-determining step in their reduction. The ratio of relative rates (k_2/k_1) for competitive hydrogenation of 1,3- and 1,4-diene fatty esters was much higher than that of 1,3- and 1,4-cyclohexadienes. This difference can then be related to the ease of conjugation of 1,4-cyclohexadiene compared to that of methyl linoleate. The common intermediate diene fatty ester–chromium carbonyl complex postulated from the kinetic data would be expected to be short-lived and difficult to isolate. However, it may be assumed to involve a mixture of *cis,-trans*-conjugated dienes consistent with the observed composition of the monoene products (Figure 2b).

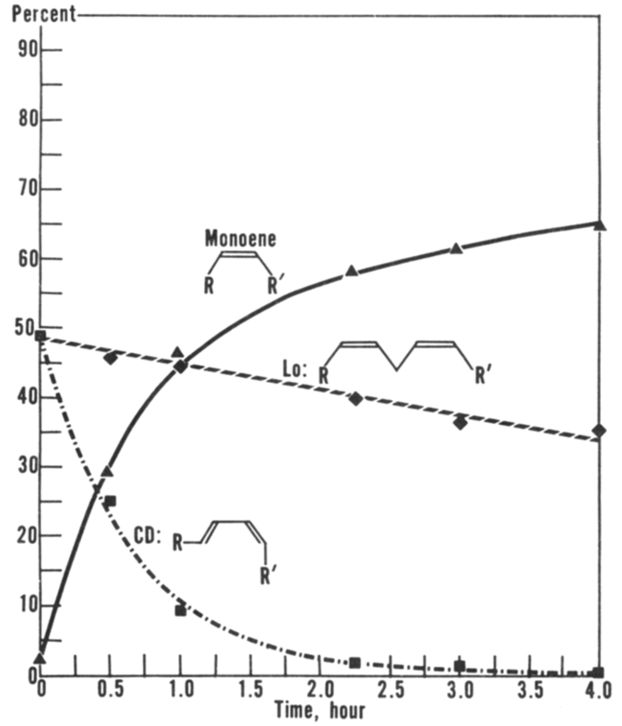


Figure 3.—Catalytic hydrogenation of an equal mixture of methyl linoleate (Lo) and conjugated diene (CD: 9,11- and 10,12-octadecadienoate) (9.5 mmol) with methyl benzoate–$Cr(CO)_3$ (0.5 mmol) in cyclohexane solution (50 ml) under 30 atm of H_2 pressure at 165°. Curves were computer plotted according to Scheme III (Lo, 1,4-, and CD, 1,3-diene).

To determine the most favorable stereochemistry of the diene–catalyst intermediate, a mixture of isomeric methyl 9,11-octadecadienoates was reduced with benzene–$Cr(CO)_3$ (Figure 4). The kinetic data were simulated according to a scheme involving direct reduction of each diene to monoene without interconversion of diene isomers. Accordingly, the calculated relative rates were 1.0 for *cis,cis*-, 8.0 for *cis,trans*-, and 25 for *trans,trans*-diene. The high stereoselectivity for the *trans,trans*-conjugated diene is consistent with formation of a cisoid-complexed diene intermediate of type **3** (Scheme I). The alkyl substituents in the cisoid *trans,-trans*-diene intermediate are in *syn* positions and favorably situated for 1,4 addition. In the *cis,trans*- and *cis,-cis*-dienes, however, one and two *anti* alkyl substituents interfere sterically with conjugate addition.

Reaction Course.—Much work has been reported on the catalytic reactions of organometallic complexes with olefins and hydrogen.[3] In the hydrogenation homogeneously catalyzed by metal carbonyls and by triphenylphosphine complexes of Ir, Ru, Pt, and Rh, it is usually necessary to activate the complex by dissociation or expulsion of a ligand (CO or Ph_3P) to form vacant ligand coordination site(s).[18] The reversible addition of H_2 to $IrCl(Ph_3P)_2$[19] and to $RhCl(Ph_3P)_2$[20] is another key step in the hydrogenation catalyzed by these complexes. The transition state in the hydrogen transfer involves an olefin–metal hydride complex derived from either (a) the reaction of the metal hydride and the free olefin, or (b) the reaction of an olefin–metal complex with H_2. Hydrogenation catalyzed by $RuCl_2$[21] and by $IrCl(CO)\ (Ph_3P)_2$[22] was considered to proceed by reaction b, whereas in those catalyzed by $Co(CN)_5^{3-}$ [23] and by $RhCl(Ph_3P)_2$,[20b] reaction a seems to be favored. The importance of these two reaction paths depends on the relative kinetic and thermodynamic stability of the hydride–metal and olefin–metal complex intermediates.

In the mechanism postulated in Scheme I, the catalyst complex is activated by dissociation (reaction 1). This step is supported by our detection of the free aromatic ligands during the course of hydrogenation and in the final products. That the formation of these free ligands is not due to thermal decomposition is indicated by our study of the fate of benzene–$Cr(CO)_3$ and methyl benzoate–$Cr(CO)_3$, which remained fairly constant throughout the hydrogenation of methyl sorbate. This observation and the relatively high temperatures required for these catalytic hydrogenations imply that reaction 1 is probably the slow step in the sequence. The dissociation step would also account for the induction period (0.5 to 1 hr) observed occasionally. Furthermore, this interpretation accords with our observation[10,11] that the following substituents on the arene part of the complex decrease catalytic activity in the order $Cl > COOCH_3 > H > CH_3 > (CH_3)_3 > (CH_3)_6$. The inductive effect of electron-repelling substituents is known to strengthen the π bond between arene and $Cr(CO)_3$, as shown by an increase in dipole moment.[24] Therefore, electron-repelling substituents would be expected to decrease the ease of dissociation of $[Cr(CO)_3]$, whereas electron-withdrawing substituents would facilitate dissociation.[25] Finally, we have observed that addition of free benzene or other aromatic ligands to the reaction system strongly interferes with hydrogenation. This result is demanded by reaction 1 (Scheme I) and substantiates the mechanism.

In Scheme I, activation of H_2 occurs by formation of dihydride and dideuteride complexes **2a** and **2**. The probable lability and high reactivity of **2** and **2a** would account for our failure to detect them by infrared and mass spectrometry. The analogy can be made, however, between **2** and **2a** and the better known dihydride complexes involved in the hydrogenation catalyzed by $IrCl(CO)(Ph_3P)_3$[19b] and by $RhCl(Ph_3P)_3$.[20] Furthermore, a chromium carbonyl hydride was reported from the reaction of $Cr(CO)_6$ with alcoholic KOH, and the formula $Cr(CO)_5H_2$ was suggested.[26] Thermal disproportionation of the cadmium ammonia derivative of this hydride gave $Cr(CO)_6$. In our hydrogenation mixtures we have also detected small amounts of $Cr(CO)_6$, and some disproportionation of **2** may be indicated. Further work is needed, of course, to identify complex intermediates in this catalytic hydrogenation system.

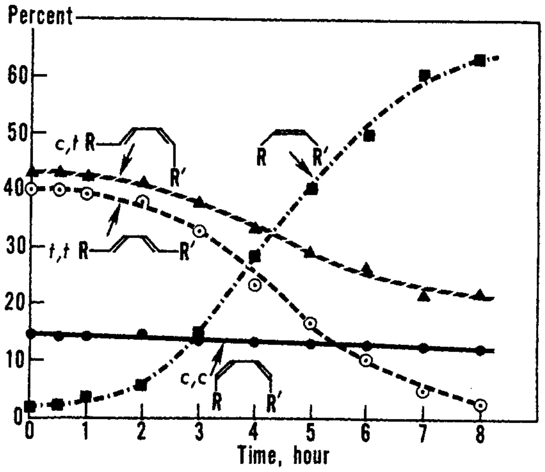


Figure 4.—Catalytic hydrogenation of isomeric methyl 9,11-octadecadienoates (9.5 mmol) with benzene–$Cr(CO)_3$ (0.5 mmol) in cyclohexane solution (50 ml) under 30 atm of H_2 pressure at 165°.

Experimental Section

Materials.—Methyl benzoate–$Cr(CO)_3$ and cycloheptatriene–$Cr(CO)_3$ were prepared according to procedures described by King.[27] Benzene–$Cr(CO)_3$ was purchased (Strem Chemicals).[28] All olefinic hydrocarbons were of high-purity grade (Aldrich Chemical Co., Chemical Samples Co., and K & K Laboratories Inc.). Unidentified impurities present in some hydrocarbons (1–5%) were inert under the hydrogenation and isomerization conditions. Methyl sorbate was prepared by methylation of sorbic acid (Eastman, recrystallized from water and then diethyl ether) with methanol and HCl. The distilled product showed one peak by glpc [diethylene glycol succinate (DEGS) column]. Methyl linoleate was prepared from safflower oil fatty esters by counter double current distribution.[29] Alkali-conjugated methyl linoleate was made as described previously.[4a] Methyl 9,11-octadecadienoates (*cis,trans*, *trans,trans*, and *cis,cis*) were derived from dehydrated methyl ricinoleate and purified by known procedures.[30,31] Methyl *cis*-9,*cis*-15-octadecadienoate was prepared by Butterfield.[32] Methyl oleate and elaidate were purchased (Hormel Foundation). All fatty esters were redistilled before use to ensure the absence of peroxidic impurities which inactivate $Cr(CO)_3$ catalysts. All other materials and solvents were reagent grade chemicals.

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(18) For a review, see J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); see also ref 3b.

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(20) (a) J. A. Osborne, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, 1711 (1966); (b) F. H. Jardine, J. A. Osborne, and G. Wilkinson, *ibid.*, 1574 (1967).

(21) J. Halpern, J. F. Harrod, and B. R. James, *J. Amer. Chem. Soc.*, **83**, 753 (1961); **88**, 5150 (1966).

(22) B. R. James and N. A. Mernon, *Can. J. Chem.*, **46**, 217 (1968).

(23) J. Kwiatek, *Catal. Rev.*, **1**, 37 (1967).

(24) H. Zeiss in "Organometallic Chemistry," American Chemical Society Monograph, No. 147, H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 408.

(25) With a series of substituted diene–$Fe(CO)_3$ complexes as catalysts, we observed that electron-repelling substituents also decreased activity and some electron-withdrawing substituents increased activity.[9] In the hydrogenation of methyl linoleate by diene–$Fe(CO)_3$, we observed that exchange of $Fe(CO)_3$ occurred between the catalysts and the substrate.[8] When methyl sorbate was hydrogenated with olefin–$Fe(CO)_3$ complexes, methyl sorbate–$Fe(CO)_3$ was formed by ligand exchange proceeding generally by an S_N1-type dissociation.[9]

(26) M. G. Rhomberg and B. B. Owen, *J. Amer. Chem. Soc.*, **73**, 5904 (1951).

(27) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, pp 123, 136.

(28) 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.

(29) R. O. Butterfield, H. J. Dutton, and C. R. Scholfield, *Anal. Chem.*, **38**, 86 (1966).

(30) W. J. Schneider, L. E. Gast, and H. M. Teeter, *J. Amer. Oil Chem. Soc.*, **41**, 605 (1964).

(31) E. A. Emken, C. R. Scholfield, V. L. Davison, and E. N. Frankel, *ibid.*, **44**, 373 (1967).

(32) R. O. Butterfield, C. R. Scholfield, and H. J. Dutton, *ibid.*, **41**, 397 (1964).

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]

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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.

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(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.

(3) E. N. Frankel and R. O. Butterfield, *J. Org. Chem.*, **34**, 3930 (1969).