which was obtained was treated with 15 ml. of ethanolic ammonia (previously saturated at 0°) at room temperature for 2 days. After evaporation of the solvent and washing of the residue with chloroform to remove acetamide, the sirupy residue was dissolved in 10 ml. of methanol. A small amount of chloroform was added to the methanol solution to incipient cloudiness and kept overnight in a refrigerator. A brownish sirup that formed was separated by decantation of the solvent and crystallized from 10 ml. of a 1:1 mixture of methanol and ethanol. The compound, 250 mg. (32%), m.p. 231° (sintered), 241–242° dec., crystallized as white stars, $[\alpha]^{23}D$ +2.0 (*c* 0.37, water). For analytical data see ref. 2.

Acknowledgment.—The authors are indebted to Dr. George B. Brown for his warm and continued interest.

Homogeneous Hydrogenation of Methyl Linolenate Catalyzed by Iron Pentacarbonyl. Formation of Methyl Octadecatrienoate–Iron Tricarbonyl Complexes[1]

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Studies with $Fe(CO)_5$ as a soluble catalyst for the hydrogenation of unsaturated fatty esters have been extended to methyl linolenate. The products were separated into monoenes, dienes, trienes, and iron carbonyl complexes of dienes and trienes by countercurrent distribution. Further separation of isomers was carried out by argentation (countercurrent distribution and chromatography). Trienes included isomers in which two and three double bonds are conjugated. Dienes were 50% conjugated with double bonds distributed between the 5- and 16-positions. Nonconjugated dienes had double bonds separated by several methylene groups. Monoenes had a distribution of double bonds consistent with a reduction of the complexed conjugated dienes by 1,2-addition. The diene–$Fe(CO)_3$ complexes have the same structure as the corresponding complexes of linoleate but have a wider distribution of positional isomers. The triene complexes were characterized as a mixture of isomers containing a stable conjugated diene–$Fe(CO)_3$ unit and a noncomplexed olefinic bond either α,β to the π-complexed system (I) or separated by several methylene groups (II). These triene complexes are postulated as intermediates in the homogeneous hydrogenation.

The homogeneous hydrogenation of olefins catalyzed by complexes of transition metals constitutes an important development in coordinated ligand reactions.[3] Metal complexes used as homogeneous hydrogenation catalysts include those of ruthenium(II),[4] pentacyanocobaltate(II),[5–7] metal carbonyls,[8–10] Ziegler-type catalysts,[11] and platinum(II)-tin(II).[12,13] Metal carbonyl complexes of unsaturated compounds have been studied extensively[14] and their role in catalyzing hydrogen transfer reactions has been well documented.[8,9]

We have previously reported the homogeneous hydrogenation of methyl linoleate catalyzed by $Fe(CO)_5$.[15] This reaction yielded isomeric conjugated methyl octadecadienoate–iron tricarbonyl complexes which were shown to be efficient homogeneous hydrogenation catalysts. This paper reports an extension of these studies to the hydrogenation of methyl linolenate.

Results

Hydrogenation.—Reduction with $Fe(CO)_5$ was achieved under the same conditions as linoleate.[15] Rates were more difficult to follow analytically because of the greater complexity of the reaction products. Composition data in Table I show that monoenoic fatty esters are the main hydrogenation products. Other products determined by gas–liquid chromatography (g.l.c.) include dienes, conjugated diene–trienes (trienes with two double bonds conjugated and one isolated), and small amounts of stearate. Conjugated trienes were also determined in minor amounts by ultraviolet spectrophotometry. The level of conjugated products increased with catalyst concentration. Infrared analyses showed isolated *trans* unsaturation in large proportions and iron tricarbonyl complex. The concentration of this complex was directly related to the initial concentration of $Fe(CO)_5$.

Typical rate curves are shown in Figure 1. A 50% reduction of trienes occurred after 3 hr. with 0.1 *M* $Fe(CO)_5$ and after approximately 1 hr. with 0.5 *M* $Fe(CO)_5$. Diene is formed in lower concentration than is monoene, but a large proportion of the diene is conjugated and complexed with iron carbonyl. Methyl

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[2] One of the laboratories of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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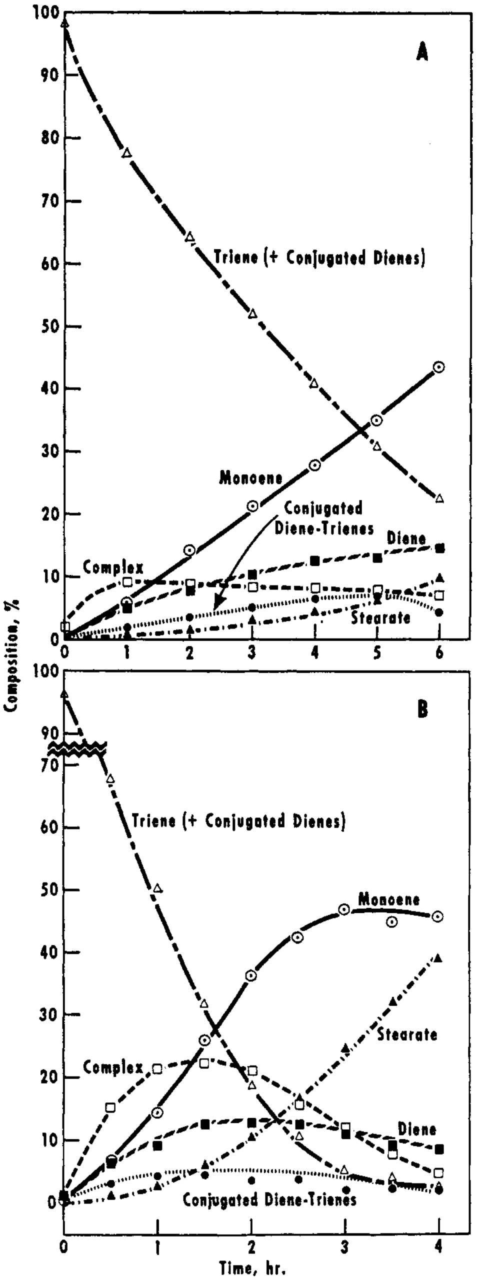

Figure 1.—Rate of hydrogenation of methyl linolenate catalyzed by $Fe(CO)_5$: A, run 4, 0.1 *M* $Fe(CO)_5$, 180°, 400 p.s.i. of H_2; B, run 5, 0.5 *M* $Fe(CO)_5$, 180°, 400 p.s.i. of H_2. Concentration of individual components was normalized to take into account concentration of complex not detectable by gas–liquid chromatography.

TABLE I

HYDROGENATION OF METHYL LINOLENATE[a]

	Run 1	Run 2	Run 3
$Fe(CO)_5$, *M*[b]	0.1	0.5	1.1
Time *t*, hr.	3	4	5
Composition at time *t*, %[c]			
Stearate	5.7	3.0	0.9
Monoene	41.3	32.8	17.0
Diene	28.9	20.5	19.8
Triene + conjugated diene	22.1	30.4	34.6
Conjugated diene–triene	2.0	13.3	27.8
Ultraviolet			
a_{230}	8.9	24.0	31.1
a_{268}	1.6	5.9	7.3
Infrared[d]			
trans, %	47.6	33.8	33.3
Complex, %	7.7	23.9	31.3

[a] Reaction conditions: 180°, 40 p.s.i., H_2, in cyclohexane solution; run 1, distilled; runs 2 and 3, not distilled. [b] Per mole of methyl linolenate. [c] Determined by g.l.c. Triene and conjugated diene were not separated by g.l.c. Data do not include conjugated triene and iron carbonyl complex. [d] The *trans* is expressed as methyl elaidate, $a_{10.4\mu}$; the complex, as methyl octadecadienoate–iron tricarbonyl, $a_{4.88\mu}$ 4.54 and $a_{5.05\mu}$ 7.95. Run 1 was analyzed for complex before distillation.

stearate is formed in small amounts initially but becomes an important product after 80% reduction when 0.5 *M* $Fe(CO)_5$ is used (Figure 1B). Independent experiments[16] have shown that pure methyl oleate is readily reduced with $Fe(CO)_5$ to methyl stearate. However, in a mixture such as the fatty esters of soybean oil, the reduction is highly selective for trienes and dienes.[10] These results and those with linolenate indicate that, in the presence of dienes and trienes, $Fe(CO)_5$ forms reactive complexes preferentially and is not available for the reduction of monoenes unless it is present in excess. Thus, with 0.1 *M* $Fe(CO)_5$, the iron carbonyl complex reaches a maximum concentration of 10% and then decreases only slowly, whereas with 0.5 *M* $Fe(CO)_5$, the complex reaches a maximum of 22% and decreases rapidly at later stages of hydrogenation. The rate curves suggest that the iron carbonyl complex at high levels is consumed in the reduction of monoene to stearate. Conjugated diene–trienes and conjugated trienes are minor products in these hydrogenation runs.

The hydrogenated products of methyl linolenate were separated by countercurrent distribution (c.c.d.) between hexane and acetonitrile (Figure 2). Analyses of the monoene and diene fractions 1 and 2 (Table II) show high proportions of isolated *trans* unsaturation. The diene is about 50% conjugated. The iron carbonyl complex was separated into diene–$Fe(CO)_3$ (fraction 3) and triene–$Fe(CO)_3$ (fraction 4). Fraction 3 includes noncomplexed trienes, conjugated diene–trienes, and conjugated trienes. Fractions 2 and 3 were further separated by argentation–c.c.d. (hexane–$AgNO_3$ in 90% methanol).[17] Diene fraction 2 was resolved into conjugated (36.5% *cis,trans* and 63.5% *trans,trans*)

TABLE II

ANALYSIS OF COUNTERCURRENT DISTRIBUTION FRACTIONS[a] (FIGURE 2)

	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Compn., %				
Monoene	95.4	...	...	...
Diene	4.6	52.1	...	...
Conjugated diene	...	47.9	...	...
Triene	...	...	28.2	...
Conjugated diene–triene	...	...	19.2	...
Conjugated triene	...	...	3.2	...
Complex[b]	...	...	49.4	100[c]
trans (% elaidate)	57.5	49.0	18.0	30.9
a_{233}	...	39.2	33.5	...
a_{267}	...	...	7.9	...

[a] Per cent: 1, 18.0; 2, 20.2; 3, 43.2; 4, 18.6. [b] See footnote *d* in Table I. [c] Expressed as triene–$Fe(CO)_3$.

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TABLE III

DOUBLE-BOND DISTRIBUTION IN FRACTIONS OF HYDROGENATED METHYL LINOLENATE

Run 3[a]										Run 1[a]	
Nonconjugated dienes		Conjugated dienes					Monoenes				
				Diene–Fe(CO)$_3$ complex							
Dibasic acids, carbon no.	Mole %	Bond positions	Free, mole %	Un-decompd., mole %	Decompd.,[c] mole %	Reduced triene–Fe(CO)$_3$ complex,[b] decompd.,[c] mole %	Bond positions	Found, mole %	Calcd.,[d] mole %	*cis*, mole %	*trans*, mole %
2	3.9	5,7	0.9	1.6	0.5	. . .	4	. . .	. . .	0.9	. . .
3	1.8	6,8	0.7	1.5	2.3	. . .	5	1.0	0.3	1.6	. . .
4	7.2	7,9	1.6	2.8	2.2	1.8	6	1.6	1.2	1.0	1.3
5	14.8	8,10	5.5	6.8	6.3	8.4	7	2.6	1.3	2.4	2.4
6	14.4	9,11	20.3	16.5	15.8	28.9	8	4.8	4.3	8.5	5.9
7	10.2	10,12	19.5	21.2	20.9	19.6	9	9.9	9.0	20.9	11.9
8	8.9	11,13	21.9	19.8	20.3	19.4	10	13.8	13.6	25.8	13.2
9	26.4	12,14	17.5	16.8	17.8	10.5	11	17.1	18.1	22.7	16.2
10	7.6	13,15	10.1	9.6	10.2	9.6	12	17.6	19.3	9.7	14.8
11	1.9	14,16	2.0	3.4	3.7	1.7	13	14.5	15.3	4.3	13.9
12	2.6						14	10.0	10.7	1.4	10.4
13	0.2						15	6.9	5.1	0.9	6.8
							16	0.3	1.8	. . .	3.4

[a] See Table I for analysis and reaction conditions. [b] Data based on analyses of dibasic acids only. [c] With $FeCl_3$. [d] Assuming that they are derived from decomposed diene–Fe(CO)$_3$ complex, by unselective 1,2 reduction.

and nonconjugated isomers. The unconjugated diene contained 70% isolated *trans* unsaturation and was only 13% conjugatable with KOH, indicating that the double bonds of the remainder are separated by more than one methylene group. Fraction 3 was separated into pure diene–Fe(CO)$_3$, mixtures of conjugated diene–trienes and conjugated trienes, pure conjugated diene–trienes (*cis,trans* and *trans,trans*), and unconjugated trienes.

The double-bond distribution in various fractions determined by $KMnO_4$–KIO_4 oxidative cleavage is summarized in Table III. In the nonconjugated dienes, which are 87% nonconjugatable with KOH, it may be assumed[17] that the dibasic acids with less than 7 carbons are internal fragments. Therefore, the primary double bond shows migration of 3 carbons on either side of the original 9-position and separation from the secondary double bond by 4 to 6 methylene groups. The distribution of double bonds in the free conjugated dienes corresponds to that of the diene–Fe(CO)$_3$ complex before or after its decomposition with $FeCl_3$. The distribution in the monoenes is in reasonably good agreement with that calculated by assuming that they are derived from the complexed conjugated dienes and that the reduction is unselective and by 1,2-addition. The monoenes were also separated into *cis* and *trans* isomers by argentation column chromatography.[18] The *trans* monoenes show a somewhat broader distribution of double bonds than the *cis* monoenes.

Iron Carbonyl Complexes.—The diene–Fe(CO)$_3$ and triene–Fe(CO)$_3$ complexes separated by c.c.d. from hydrogenated methyl linolenate were isolated in yields of 21 and 19%, respectively. The diene complex had the same elemental analysis, infrared and n.m.r. spectra, and retention on $AgNO_3$–silica gel thin layer chromatography (t.l.c.) as the diene–Fe(CO)$_3$ complex of linoleate.[15] On decomposition with $FeCl_3$, pure *trans,trans*-conjugated dienes were obtained which showed a broader distribution of double bonds (Table III) than the conjugated diene–Fe(CO)$_3$ complex of linoleate.

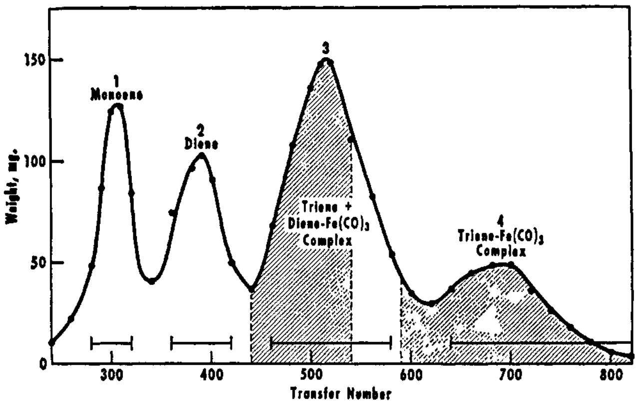

Figure 2.—Countercurrent distribution of hydrogenated methyl linolenate (run 3, Table I) between hexane and acetonitrile in a 200-tube instrument. The shaded areas show the presence of iron carbonyl complexes by $AgNO_3$–thin layer chromatography.

The triene–Fe(CO)$_3$ complex of linolenate was more complicated and difficult to characterize. This complex was separated by $AgNO_3$–silica gel t.l.c. into three main components whose retentions indicate the presence of a free *trans* and *cis* double bond in the two slower moving components. Analytical data are consistent with the empirical formula for methyl octadecatrienoate–iron tricarbonyl, $C_{22}H_{32}FeO_5$. The infrared spectrum shows strong carbonyl-stretching absorption bands at 4.89 and 5.07 μ of the same intensity as the diene–Fe(CO)$_3$ of linoleate.[15] The rest of the infrared spectrum is the same as that of diene–Fe(CO)$_3$ except for an absorption band at 10.4 μ due to free isolated *trans* unsaturation. Decomposition with $FeCl_3$ yielded a mixture of *trans,trans*-conjugated diene–trienes (λ_{max} 233 mμ, 10.1 μ) and conjugated trienes (λ_{max} 268 mμ, 10.1 μ) containing also isolated *trans* unsaturation (λ 10.4 μ). On g.l.c. these conjugated products had the same retention times as the conjugated diene–trienes and conjugated trienes of partially alkali-conjugated methyl linolenate.

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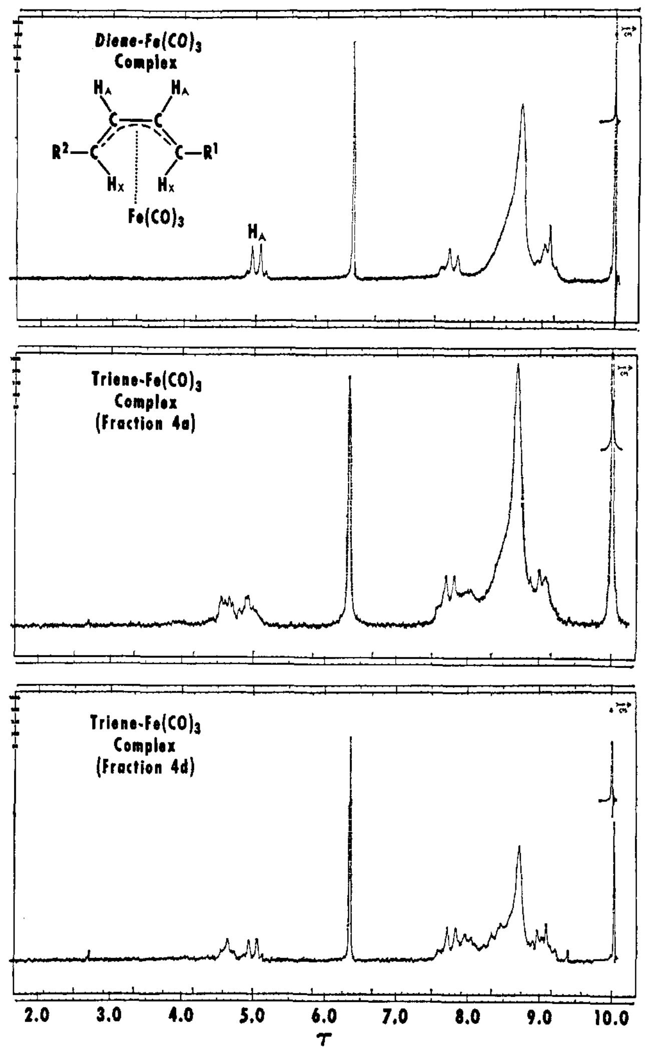


Figure 3.—N.m.r. spectra (60 Mc.) of triene-Fe(CO)$_3$ complexes (chromatographic fractions 4a and 4d, see text) compared with that of the diene-Fe(CO)$_3$ complex (top spectrum) of methyl linoleate,[15] using tetramethylsilane (τ 10) as internal standard.

The triene-Fe(CO)$_3$ complex was separated by argentation column chromatography into four fractions characterized by decomposition with FeCl$_3$ (Table IV). The first two fractions (4a and b) yielded predominantly all-*trans* conjugated trienes. Partially separated fraction 4c gave a mixture of all-*trans* conjugated diene-trienes and conjugated trienes. Both fractions 4b and 4c contained isolated *trans* unsaturation. Fraction 4d gave fairly pure conjugated diene-trienes with no isolated *trans* unsaturation indicating that the isolated double bond is in the *cis* configuration. The n.m.r. spectra of fractions 4a and 4d, before FeCl$_3$ decomposition, showed two groups of signals due to olefinic protons (τ 5.0 and 4.65) (Figure 3). The signal at τ 5.0 in fraction 4d had the same characteristic "quartet" structure as that of diene-Fe(CO)$_3$ of linoleate and was assigned to the central protons of the diene complex system.[15] The band at τ 4.65 therefore would be due to the noncomplexed olefinic bond. The rest of the spectra was similar to that of diene-Fe(CO)$_3$ of linoleate except for the presence of an allylic proton signal ($-CH_2-C{=}C-$) at τ 8.0, not well separated from the α-methylene ($-CH_2-COOMe$) (τ 7.8) and the CH$_2$ bands (τ 8.8). This allylic proton band provides another evidence of a free olefinic bond. Also, the methyl band (τ ~9) consisted of a complex multiplet, which was not well resolved from the large CH$_2$ band (τ 8.8).

TABLE IV

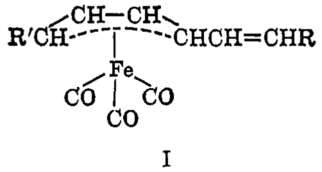
FRACTIONATION OF TRIENE-Fe(CO)$_3$ COMPLEX[a] BY AgNO$_3$-COLUMN CHROMATOGRAPHY[b]

	Fractions			
	4a	4b	4c	4d
Conjugated diene-triene, %	0	30.2	51.7	100
Conjugated triene, %	100	69.8	48.4	0
a_{233}	24.4	34.2	48.6	80.0
a_{268}	117.2	39.6	47.6	7.2
$a_{10.1\mu}$	0.462	1.252	0.731	0.938
$a_{10.4\mu}$	...	0.145	0.224	...

[a] Fraction 4, Figure 2. [b] After decomposition with FeCl$_3$.

Additional evidence on the structure of the triene-Fe(CO)$_3$ complex was obtained by reduction. The complex could not be hydrogenated catalytically with palladium owing to its strong poisoning effect on heterogeneous catalysts.[15] However, reduction with hydrazine was partially successful. After saponification, the complex of the free fatty acids was reduced with hydrazine at room temperature to minimize decomposition. Although about 20% decomposition occurred during saponification, little occurred in the reduction. The n.m.r. spectrum of the reduced complex was the same as that of diene-Fe(CO)$_3$ of linoleic acid and showed only one characteristic quartet olefinic signal at τ 5.0. This confirmed the assignment of the band at τ 4.65 in unreduced triene-Fe(CO)$_3$ (Figure 3) to the noncomplexed olefinic bond. The reduced complex was then decomposed with FeCl$_3$ and yielded 71% *trans,trans*-conjugated dienes and 12% hydrogenated products. Distribution of double bonds was similar to that in the free conjugated dienes (Table III).

The results characterize the triene complex as a mixture of isomeric conjugated diene-triene and conjugated triene attached to iron tricarbonyl. The proposed structures are based on evidence that a noncomplexed olefinic bond is present either α,β to the conjugated diene-Fe(CO)$_3$ system (I) or separated by several methylene groups (II). The free double bond in I and II can be either in the *cis* or *trans* configuration. The α,β double bond apparently modifies the quartet olefinic structure at τ 5.0 in the n.m.r. spectrum (Figure 3, fraction 4a). The free double

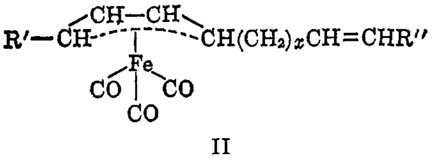


$$\mathrm{R'CH{\cdots}\overset{CH-CH}{}{\cdots}CHCH{=}CHR},\ \mathrm{Fe(CO)_3}$$

I

R = $-(CH_2)_vCOOCH_3$; R′ = $-(CH_2)_wCH_3$

$v + w = 10$



$$\mathrm{R'{-}CH{\cdots}\overset{CH-CH}{}{\cdots}CH(CH_2)_xCH{=}CHR''},\ \mathrm{Fe(CO)_3}$$

II

R″ = $-(CH_2)_yCOOCH_3$

$x + y + w = 10, x > 1$

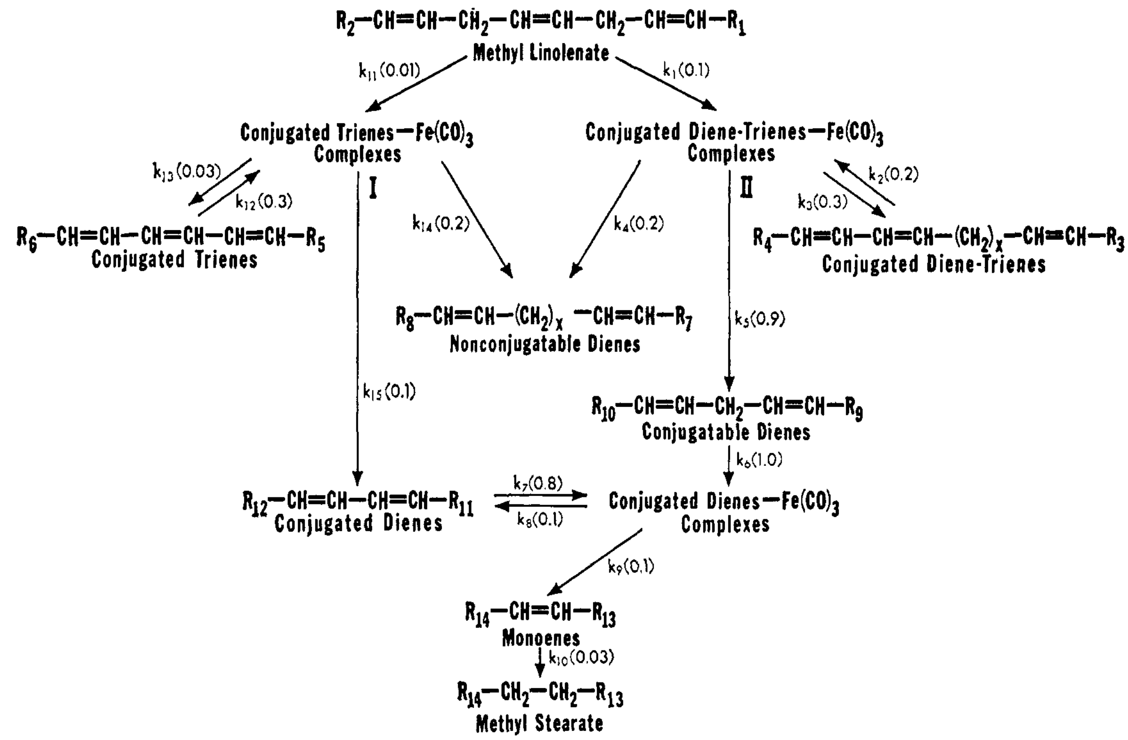


Figure 4.

bond in I and II can also occur on either side of the complexed diene–$Fe(CO)_3$ group, but resolution of these isomeric structures has not been achieved.

Discussion

The structures of complexes I and II of linolenate are supported by several studies of iron carbonyl complexes of cyclic conjugated trienes and tetraenes. These studies established that $Fe(CO)_3$ is attached to a diene unit and not to the fully conjugated ring.[19] Since these iron carbonyl complexes assume a cisoid conformation,[19] participation of a third olefinic bond in the complex would seem to be prevented by serious steric strains. Only two acyclic triene-iron tricarbonyl complexes have been reported. The complexes obtained from the reaction of *trans*-1,3,5-hexatriene[20] and $Fe_3(CO)_{12}$ have not been well characterized. The complex obtained from alloocimene[21] (2,6-dimethyl-2,4,6-octatriene) was shown to be of the type L–$Fe(CO)_3$ where L is alloocimene. The occurrence of triene–$Fe(CO)_2$ complexes is doubtful and has been questioned.[19] Recently, Murdoch and Weiss[22] isolated from the reaction of hexatriene and $Fe_2(CO)_9$, hexatriene–$Fe(CO)_3$ as the most stable complex. Evidence was obtained for other less stable complexes including hexatriene–$[Fe(CO)_4]_2$, hexatriene–$[Fe(CO)_3]$-$[Fe(CO)_4]$, and hexatriene–$Fe(CO)_4$. The remarkable stability of the diene–$Fe(CO)_3$ unit is now well established. However, the question has not been resolved whether this structure involves complete delocalization of the π-electrons of the diene system or 1,4-addition of the iron across the diene.[19,23,24] Most likely a structure somewhere intermediate between these two extremes (sp^2 or sp^3 hybridized carbon atoms 1 and 4 of the complexed diene system) may best fit the evidence at hand.

The mechanism we previously postulated for the homogeneous hydrogenation of linoleate by $Fe(CO)_5$ involved conjugated dienes and their iron carbonyl complexes as important intermediates.[15] Our most recent evidence from radioactive tracers, however, indicates that, although the diene–$Fe(CO)_3$ complex is an intermediate in the reduction of linoleate to monoenes, the importance of the free conjugated diene as an intermediate is doubtful.[25] For linolenate, it may be postulated therefore that the triene–$Fe(CO)_3$ complexes are the initial intermediates in the homogeneous hydrogenation. According to the reaction scheme in Figure 4 the triene–$Fe(CO)_3$ complexes dissociate to a small extent into free conjugated diene–trienes and conjugated trienes. Reduction of the triene–$Fe(CO)_3$ complexes at the conjugated system leads to conjugatable (1,4-), nonconjugatable, and conjugated dienes. The nonconjugatable dienes with double bonds separated by more than one methylene group are not further reduced, as shown by their accumulation in the diene fraction. That these dienes would not be reactive is expected since they presumably do not form conjugated diene–$Fe(CO)_3$ complexes. The diene–$Fe(CO)_3$ complexes formed from either 1,4-conjugatable dienes or conjugated dienes are the important intermediates leading to monoenes and stearate. These diene complexes have been previously shown to be active hydrogenation catalysts and to be reducible to monoenes and stearate.[15]

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[24] H. S. Gutowsky and J. Jonas, *ibid.*, **4**, 430 (1965).

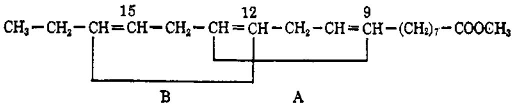
[25] E. N. Frankel, T. Mounts, R. O. Butterfield, and H. J. Dutton, unpublished data.

The relative first-order rates, shown in parentheses in Figure 4, were estimated by simulating the rate curves with an analog computer.[26] Although reasonably good fits were obtained, this evidence can only be taken as presumptive. Variations on this reaction scheme would probably have fit the kinetic data as well. Likely alternatives are the formation of complex I directly from complex II (*i.e.*, putting k_{11} between II and I) and the formation of diene–Fe(CO)$_3$ directly from I or II by hydrogen transfer. The second possibility has found precedence in the prolonged reaction of cycloheptatriene with Fe(CO)$_5$ that leads to the formation of cycloheptadiene–Fe(CO)$_3$ in addition to the principal product cycloheptatriene–Fe(CO)$_3$.[27] Direct paths from complexes I, II, and diene–Fe(CO)$_3$ to stearate, postulated previously,[15] could also become important at high concentrations of Fe(CO)$_5$. Better matching of the kinetic data was indeed obtained at low rather than at high concentrations of Fe(CO)$_5$. The direct reduction path might involve iron hydrocarbonyl and cause the formation of dienes and monoenes from trienes and dienes, respectively. Further studies with iron hydrocarbonyl in the absence of molecular hydrogen are needed to verify this possibility.

The distribution of double bonds in the isomeric monoenes and dienes from linolenate can be accounted for in Table V based on the principal conjugated complexed intermediates in Figure 4.

TABLE V

METHYL LINOLENATE



$CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_7-COOCH_3$

	Trienes		Dienes		Conjugated dienes		Monoenes
A →	8,10,15- (III)	→	8,15- + 10,15-				
	9,11,15- (IV)	→	9,15- + 11,15-				
	10,12,15- (V)	→	10,15- 12,15-	⟶	11,13- 12,14- 13,15- 14,16-	→ → → →	11-,13- 12-,14- 13-,15- 14-,16-
	11,13,15- (VI)	→	11,15- +		11,13- 13,15-	→ →	11-,13- 13-,15-
B →	9,14,16- (IIIa)	→	9,14- + 9,16-				
	9,13,15- (IVa)	→	9,13- + 9,15-				
	9,12,14- (Va)	→	9,12- 9,14-	⟶	8,10- 9,11- 10,12- 11,13-	→ → → →	8-,10- 9-,11- 10-,12- 11-,13-
	9,11,13- (VIa)	→	9,13- +		9,11- 11,13-	→ →	9-,11- 11-,13-

Two conjugatable systems A and B are considered. If only the conjugated systems [complexed with Fe(CO)$_3$] are reduced, trienes V and VI from A lead to the reactive 12,15-, 11,13-, and 13,15-dienes. Trienes Va and VIa from B lead to the reactive 9,12-, 9,11-, and 11,13-dienes. The other dienes are not conjugatable and do not reduce further. As with linoleate[15] the 9,12- and 12,15-dienes form conjugated Fe(CO)$_3$ complexes leading to monoenes with double bonds distributed between the 8- and 16-positions. The conjugated 9,11-, 11,13-, and 13,15-dienes give the corresponding 9-, 11-, 13-, and 15-monoenes. According to this scheme, the isomeric monoenes would show a Gaussian distribution with maximum in the 11- through 13-positions. Such a distribution conforms to that observed in the monoenes (Table III).

The diene and triene–Fe(CO)$_3$ complexes can be regarded as good model catalytic systems. Basic information on the mechanism of homogeneous catalytic hydrogenation can be derived from a knowledge of the structure of these intermediate complexes. The analogy between these catalytically active complexes and similar π-complexed species postulated during heterogeneous catalysis[28,29] remains to be established.

Experimental

Materials and Methods.—The Fe(CO)$_5$ and the analytical methods (g.l.c., ultraviolet, infrared, argentation, t.l.c. and column chromatography, and KMnO$_4$–KIO$_4$ oxidative cleavage analysis of double-bond position) were the same as described previously.[15] Methyl linolenate was prepared from the methyl esters of linseed oil fatty acids by c.c.d. between *n*-hexane and acetonitrile.[30] It analyzed 100% by g.l.c. Conjugated diene–trienes and conjugated trienes used as standards were prepared from alkali-conjugated linseed oil.[10]

Hydrogenations and Fractionations.—The hydrogenation procedures were the same as described.[15] In run 1 (Table I) 21.01 g. (71.9 mmoles) of methyl linolenate was hydrogenated in a 500-ml. Magne-Dash[31] autoclave with 1.4 g. (7.1 mmoles) of Fe(CO)$_5$ and 80 ml. of cyclohexane. The hydrogenated product (20.62 g.) was treated with dilute HCl to decompose the catalyst, washed, and dried.[15] After distillation (170° at 0.4 mm.) it yielded 16.39 g. of clear methyl esters and a deep reddish brown residue. The distilled product had no carbonyl stretching absorption due to iron carbonyl complex. This complex persisted in the distillation residue as shown by absorption bands at 4.89 and 5.07 μ (a 3.62 and 5.42). In run 3, 19.49 g. of methyl linolenate was hydrogenated with 14 g. of Fe(CO)$_5$ and 40 ml. of cyclohexane. The product (18.32 g.) treated as described was not distilled and absorbed at 4.89 and 5.07 μ (a 1.47 and 2.39). Other analyses are given in Table I. It was then fractionated by c.c.d. between *n*-hexane and acetonitrile[30] (Figure 2). Analyses of fractions are given in Table II. Kinetic runs 4 and 5 (Figure 1) were made on a scale of 10 mmoles of linolenate. Sequential analyses were made by g.l.c. and infrared.

Separation by argentation–c.c.d.[17] between *n*-hexane and 0.2 N AgNO$_3$ in 90% methanol was carried out on diene and triene fractions 2 and 3 (Figure 2) from hydrogenation run 3. The diene fraction was separated into conjugated and nonconjugated isomers (transfers 220–300, 360–450). The nonconjugated diene fraction (diene 92.8, conjugated diene 7.2%) showed 70.0% *trans* unsaturation (as methyl elaidate) and gave on alkali conjugation[32] a_{233} 10.91. Under the same conditions pure methyl linoleate gave a_{233} 86.8. The conjugated diene fraction was further purified by chromatography through a silver-saturated ion-exchange resin column.[18] The pure conjugated diene obtained (36.5 *cis,trans*- and 63.5% *trans,trans*-conjugated diene by g.l.c.) gave a_{230} 86.4, $a_{10.15\mu}$ 0.623, and $a_{10.6\mu}$ 0.152. The position of double bonds in the above fractions was determined by analysis of acid cleavage products obtained after KMnO$_4$–KIO$_4$ oxidation (Table III). The triene fraction 3 separated by argentation–c.c.d. gave successively pure diene–Fe(CO)$_3$ (3a), a mixture of conjugated diene–trienes and conjugated trienes (3b), pure conjugated diene–trienes (3c), and nonconjugated trienes (unreduced linolenate) (3d). Fraction 3c showed *cis,trans* and *trans,trans* conjugation (a_{233} 62.2, $a_{10.15\mu}$ 0.301, $a_{10.6\mu}$ 0.160) and isolated *trans* unsaturation ($a_{10.4\mu}$ 0.315).

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Diene–Iron Tricarbonyl Complex.—The iron carbonyl complex separated from triene fraction 3 by argentation–c.c.d. was isolated in 47.9% yield (20.7% of original hydrogenated linolenate). T.l.c. ($AgNO_3$–silica gel) showed one component of same retention as diene–$Fe(CO)_3$ from linoleate.[15] Infrared showed bands at 4.88 and 5.05 μ (ϵ 1420 and 2830).

Anal. Calcd. for $C_{22}H_{34}FeO_5$: C, 60.9; H, 7.8; Fe, 12.9; mol. wt., 434. Found: C, 61.0; H, 7.8; Fe, 12.3; mol. wt. 427 (osmometric, benzene).

The n.m.r. spectrum was the same as the n.m.r. spectrum of diene–$Fe(CO)_3$ from linoleate[15] (Figure 3). Decomposition of 0.415 g. of complex with $FeCl_3$[15] gave 0.230 g. of conjugated diene (recovery 82.2%; ϵ_{230} 25,800, $\epsilon_{10.15\mu}$ 315; 100% *trans,trans*-conjugated diene by g.l.c.). Oxidative cleavage analysis is given in Table III.

Triene–Iron Tricarbonyl Complexes (I and II).—The separation of hydrogenated methyl linolenate by c.c.d. between *n*-hexane and acetonitrile gave a fraction (4, transfer 640–820, Figure 2) in 18.6% yield, shown to be pure triene–$Fe(CO)_3$ complex. Argentation–t.l.c. ($AgNO_3$–silica gel) showed three main components with same R_f as that of diene–$Fe(CO)_3$ (from linoleate), methyl elaidate, and methyl oleate, successively. The infrared spectrum showed bands at 4.89 and 5.07 μ (ϵ 1920 and 3220; corresponding bands for diene–$Fe(CO)_3$ of linoleate, ϵ 1970 and 3450) and at 10.4 μ (isolated *trans*, ϵ 42.7).

Anal. Calcd. for $C_{22}H_{32}FeO_5$: C, 61.2; H, 7.4; Fe, 12.9; mol. wt., 432. Found: C, 61.8; H, 7.9; Fe, 11.6; mol. wt., 405.

Decomposition of 0.1075 g. of triene–$Fe(CO)_3$ with $FeCl_3$ gave 0.0582 g. (recovery 80%) of a mixture of *trans,trans*-conjugated diene–triene and conjugated triene (g.l.c., 68% conjugated diene–triene, 32% conjugated triene; infrared, $\epsilon_{10.1\mu}$ 209, $\epsilon_{10.4\mu}$ 45.4; ultraviolet, ϵ_{231} 18,750, ϵ_{267} 9950). On fractionation through a silver-saturated ion-exchange resin column[18] (225 × 2.1 cm.) 0.782 g. of triene–$Fe(CO)_3$ complex yielded four fractions (4a, 0.075; 4b, 0.143; 4c, 0.321; and 4d, 0.144 g.). Analysis by t.l.c. ($AgNO_3$–silica gel) showed one component in fraction 4a with a retention corresponding to diene–$Fe(CO)_3$, two components in both fractions 4b and 4c migrating like methyl elaidate, and one component in fraction 4d migrating like methyl oleate. These fractions were decomposed with $FeCl_3$ and the conjugated products were analyzed by g.l.c., ultraviolet, and infrared (Table IV). Complex fractions 4a and 4d were also analyzed by n.m.r. (CCl_4, Varian A-60) (Figure 3). The following signals given in τ values were obtained: 4.95 and 4.65 in fraction 4a, 5.01 and 4.65 in fraction 4d (olefinic protons), and in both fractions 6.3 (methoxy protons), 7.75 (methylene α to C=O), 8.0 (allylic protons), 8.7 (methylene), and 8.9–9.0 (methyl). The intensity of the olefinic bands corresponded to 4 protons [2 protons due to –CH=CH– and 2 central protons of diene–$Fe(CO)_3$ system] assuming a total of 32 protons. The other bands were too poorly resolved to estimate accurately.

The triene–$Fe(CO)_3$ complex (0.227 g.) was treated in a manometric system under 1 atm. of hydrogen with a reduced palladium catalyst (5% on alumina) in 4 ml. acetic acid, but no hydrogen absorption occurred within 3 hr. at 25°. The recovered product (0.224 g.) showed no change by t.l.c. ($AgNO_3$–silica gel). To reduce the complex with hydrazine it was first saponified by refluxing 0.506 g. with 10 ml. of 95% ethanol and 0.5 ml. of 50% KOH for 45 min. under nitrogen. The product was neutralized, extracted with petroleum ether (b.p. 39–52°), and dried over Na_2SO_4 (0.315 g., $a_{4.87\mu}$ 3.43, $a_{5.09\mu}$ 6.34). The triene–$Fe(CO)_3$ fatty acid was reduced by treating a solution of 0.295 g. in 15 ml. of absolute ethanol with 0.5 ml. of hydrazine (64% in water), bubbling air, and stirring magnetically at ambient temperature. After 22 hr. the solvent was evaporated; the product was neutralized, extracted with diethyl ether, and dried over Na_2SO_4. The reduced complex (0.244 g., $a_{4.87\mu}$ 3.29, $a_{5.05\mu}$ 6.41) gave the same n.m.r. spectrum as a preparation of linoleate–$Fe(CO)_3$ complex subjected to the same saponfication and hydrazine reduction. The relative intensity of the olefinic band at τ 5.0 was equivalent to 1.6 protons compared with 3.7 before reduction. Decomposition of the reduced triene–$Fe(CO)_3$ complex with $FeCl_3$ yielded a mixture containing 70.6% *trans,trans*-conjugated diene, 17.2% unreduced conjugated trienes, and hydrogenated products (stearate 7.2, monoene 3.7, and diene 1.0%) apparently derived from decomposition of the complex ($a_{10.15\mu}$ 0.816, a_{233} 66.0, a_{267} 15.5). The dibasic acids obtained on oxidation with $KMnO_4$–KIO_4 showed a similar distribution to that of the double bonds in the free conjugated dienes (Table III), but the larger levels of C_9 acids are due to impurities.

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The Pyrolysis of Alkyl Diphenylphosphinates[1]

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Examination of the thermal decomposition of a series of alkyl esters of diphenylphosphinic acid indicates the pyrolysis occurs smoothly to give olefins in essentially quantitative conversions. A mechanism for the thermal transformation is postulated to involve a cyclic transition state.

Although the pyrolysis of phosphonium hydroxides, corresponding to the Hofmann degradation of amines, has been known for many years,[3] it has very little synthetic utility and is more useful as a degradative process. Pyrolysis of organophosphorus compounds involving elimination reactions to give olefins[4] in preparative yields has become available only recently,[5–11] and, in most cases, the starting materials are somewhat difficult to obtain.

Results included herein describe a simple process by which alkenes of high purity are obtained in excellent yields from readily accessible phosphinates. A series

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