Homogeneous Catalytic Hydrogenation of Unsaturated Fats: Cobalt Carbonyl[1]

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Abstract

Homogeneous hydrogenation of unsaturated fats by cobalt carbonyl has been compared with the previously reported catalysis by iron carbonyl. Soybean methyl esters, methyl linoleate and linolenate have been hydrogenated at 75–180C, 250–3,000 psi H_2 and 0.02 molar concn of catalyst. The cobalt carbonyl catalyst is more active at lower temp than iron carbonyl. The partially reduced products are similar to those observed with iron carbonyl, but the reaction differs in showing much less accumulation of conjugated dienes, no selectivity toward linolenate, almost complete absence of monoene hydrogenation to saturates, less double bond migration and more *trans* isomerization. No evidence was found for a stable complex between cobalt carbonyl and unsaturated fats as previously observed with iron carbonyl. The rates of hydrogenation/double bond were the same for linoleate and linolenate on one hand, and for alkali-conjugated linoleate and nonconjugated linoleate on the other.

Introduction

THE HOMOGENEOUS hydrogenation of soybean oil and methyl esters catalyzed by iron pentacarbonyl has been reported in the first paper of this series (4). This catalyst promoted the reduction of polyunsaturated fatty esters with considerable positional and geometric isomerization of double bonds. The formation of a stable fat-iron carbonyl complex during hydrogenation was also indicated. The reaction of methyl linoleate with iron pentacarbonyl yielded a mixture of conjugated methyl octadecadienoate-iron tricarbonyl pi-complexes (3). This paper reports an extension of work on homogeneous catalysis with dicobalt octacarbonyl.

Experimental

Materials. The $Co_2(CO)_8$ was a gift of Irving Wender, U.S. Bureau of Mines, Pittsburgh, Pa. Soybean methyl esters were prepared as described previously (4). Methyl linoleate was obtained from The Hormel Institute, Austin, Minn. Methyl linolenate was prepared from linseed methyl esters by countercurrent distribution (CCD) between hexane and acetonitrile (10). Gas-liquid chromatography (GLC) showed that the linoleate and linolenate were 100% pure. Infrared (IR) showed no *trans.*

Hydrogenation. All hydrogenations were carried out in cyclohexane solution (20–30%) in a 500-ml Magna-Dash high pressure autoclave. A sampling tube was used for sequential analyses. The products remained homogeneous when the hydrogenation temp was below 100C. Metallic precipitates caused by the decomposition of cobalt carbonyl were noted in those runs made above 100C. The catalyst was decomposed after hydrogenation by repeated washing with dilute HCl (2:1) until no more cobalt blue appeared in the aqueous phase. Decomposition of the catalyst was facilitated by removing most of the solvent on a rotating evaporator at 60C under suction (water aspirator) before washing with acid. For the hydrogenation runs at temp below 100C, it was necessary to evaporate over a steam bath to permit complete decomposition of the catalyst with HCl. The acid washings were followed with dilute KOH (10%) and then with distilled water washings to reach neutrality. The dried methyl esters were clear. No IR absorption around 5.0 μ in the carbonyl-stretching region indicated effective decomposition of the catalyst or any complex of it with fatty esters.

Analyses. The methodology relating to GLC, IR, ultraviolet (UV), alkali conjugation and thin-layer chromatography (TLC) on $AgNO_3$ coated plates was the same as described previously (4). The hydrogenated products were separated by CCD between hexane and acetonitrile into monoene, diene and triene fractions. Refinements in the analytical scheme included silver-resin column chromatography (2) to separate the CCD monoene fraction into *cis* and *trans* isomers, which were further characterized, qualitatively, by capillary GLC and, quantitatively, by $KMnO_4$–KIO_4 cleavage for double bond location. For capillary GLC, a 200-ft column (0.01 in I.D.) coated with Apiezon L was used with a Barber-Colman chromatograph equipped with a Radium D ionization detector. Pure methyl elaidate, petroselenate and the *cis* monoenes (9-,12-,15-) derived from hydrazine-reduced methyl linolenate (9) were used as reference compounds to identify peaks. The $KMnO_4$–KIO_4 cleavage technique of Jones and Stolp (6) was improved by analyzing butyl esters of monobasic acids, as well as methyl esters of dibasic acids, by programmed temperature GLC to locate position of double bonds (5).

Results

The hydrogenation of soybean methyl esters was effectively catalyzed by $Co_2(CO)_8$ at 75–180C and hydrogen pressures of 250–3,000 psi. Table I shows that hydrogenation takes place at relatively low temp. The degree of hydrogenation is not appreciable below 1,000 psi but increases with the hydrogen pressure. The decrease in triene and diene and the increase in *trans* unsaturation are related to the degree of hydrogenation as measured by iodine value (I.V.) drop. In contrast to $Fe(CO)_5$ (4), the $Co_2(CO)_8$ catalysis shows, under these experimental conditions, rather poor selectivity toward linolenate. There is almost complete absence of monoene hydrogenation to saturates except when the I.V. dropped below 80. The accumulation of conjuglated dienes is relatively small, whereas that of *trans* unsaturation is large. This is well demonstrated in Run 10, which was carried out under conditions approximating those used previously with $Fe(CO)_5$ (4).

The rates of hydrogenation of methyl linoleate, methyl linolenate and partially alkali-conjugated methyl linoleate are compared in Figure 1. Reaction conditions (75C, 3,000 psi H_2, 0.02 M catalyst) were chosen to obtain measurable rates within reasonable

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TABLE I

Hydrogenation of Soybean Methyl Esters with 0.02 Mole $Co_2(CO)_8$

Run No.	Temp C	Pres. psi	Time hr	Palmitate %	Stearate %	Monoene %	Diene %	Triene %	I.V. (calc.)[a]	Conj. diene [a]232 mμ	*trans* (as % elaidate)
Control	....	....	..	9.9	4.7	28.7	50.5	6.2	127.7	0	0
1	75	2890	3	11.8	6.3	45.5	33.8	2.5	103.6	2.48	28.5
2	100	1000	3	10.6	4.7	37.9	42.9	4.1	116.8	1.99	11.8
3	100	2000	2	10.8	4.8	40.0	39.8	4.6	114.8	2.27	13.6
4	100	3000	2	10.8	5.6	44.7	35.6	3.3	108.3	1.98	18.7
5	125	250	3	10.0	4.7	36.9	43.3	5.1	119.5	1.35	12.7
6	125	500	3	9.6	4.5	43.2	37.8	4.9	115.0	1.50	18.9
7	125	1000	3	10.6	13.2	72.2	1.9(2.1?)[b]	....	68.7	0	44.2
8	150	500	2	10.0	3.5	49.3	34.3	2.9	108.8	1.13	25.7
9	150	1000	1	10.3	3.5	71.1	15.0	0	86.7	0.67	48.0
10	180	300	2	10.0	15.9	58.5	15.3(0.3)[b]	..	76.9	0.38	45.3

[a] Calculated from GLC composition.
[b] Unidentified isomers.

experimental times. Under these conditions a short induction period (1 hr for linoleate and 0.5 hr for linolenate) was observed during which no hydrogenation took place. Similar runs carried out at 125C and 1,000 psi H_2 also showed an induction period of 0.5 hr but the rates of hydrogenation after this period were too high to measure accurately. Figure 1 shows that after the induction period the concn of linoleate and linolenate decreases exponentially with time. GLC analyses of triene are complicated by the conjugated dienes, which have the same retention time as linolenate. This interference, however, is small (not exceeding 5%) as indicated by UV analyses. The formation of conjugated dienes and conjugated diene-trienes (conjugated diene with a third isolated double bond) from linoleate and linolenate, respectively, indicates that they are intermediates in the reaction. With all of these fatty esters the rates approx first-order kinetics after the initial phase of the hydrogenation and omitting the induction period for linoleate and linolenate as shown in Figure 2 by the linear plots of the log percentage composition vs. time. The comparative first-order specific reaction constants summarized in Table II were calculated by the expression: $k_1 = \frac{2.303}{t_2 - t_1} \log \frac{C_1}{C_2}$, for percentage concn C_1 at time t_1 and C_2 at time t_2. The rates of hydrogenation divided by the number of double bonds are the same for linoleate and linolenate. With the alkali-isomerized linoleate, the rates of hydrogenation of nonconjugated and conjugated dienes are also of the same order of magnitude. Therefore, prior conjugation of the diene system in linoleate does not accelerate the reduction.

The hydrogenated fatty esters were analyzed in detail after CCD into monoene, diene and triene fractions. Table III summarizes analyses of CCD fractions from selected runs of hydrogenated soybean methyl esters, methyl linoleate and linolenate. The soybean esters hydrogenated at 75,125 and 150C (Runs 1,6 and 8, respectively) show little diene conjugation in the diene and triene fractions. The high amt of alkali-conjugatable dienes, i.e., 1,4-diunsaturation, in these fractions and in the diene of linoleate shows that little isomerization of multiple double bonds has taken place even at the higher temperatures. IR analyses indicate that the *trans* unsaturation in the monoene fractions is apparently related to the I.V. drop. Isolated *trans* unsaturation (absorption at 10.35 μ) in the diene and triene fractions is also related to the degree of hydrogenation and the amt of diene nonconjugatable with alkali, i.e., double bonds separated by more than one methylene groups. The small diene conjugation in these fractions is predominantly in the *trans, trans* configuration (absorption at 10.15 μ). Reduced methyl linolenate is characterized by high isolated *trans* and very low alkali-conjugatable unsaturation in the diene fraction. Therefore, one of the widely separated double bonds has the *trans* configuration. The triene fraction has a high proportion of conjugated dienes showing that two double bonds are conjugated and the third one is isolated.

The distribution of double bonds in the *cis* and *trans* monoenes separated by silver-resin column chromatography is given in Figure 3. These fractions were derived from samples hydrogenated under the same conditions [75C, 3,000 psi H_2, 0.02 M $Co_2(CO)_8$]. Over 80% of the double bonds in the *cis* monoene of the soybean esters is in the natural 9-position. The double bonds in the *trans* monoene are distributed mostly in positions intermediate between the original 9- and 12-position of linoleate. The double bonds in the *cis* monoene of reduced linoleate are scattered between the 8- and 13-positions with most in the 9-,10-,11- and 12-positions in about equal proportions. The *trans* monoene of linoleate shows more double bonds in the intermediate 10- and 11-positions than does the *cis* monoene. The monoene from hydrogenated linolenate shows distribution of double bonds between the 7- and 16-positions with a max in the 12-position. The amt of scattering of double bonds is equivalent in the *cis* and *trans* monoenes.

The above *cis* and *trans* monoenes were also analyzed by capillary GLC (Fig. 4). The *cis* monoenes are more complex than the *trans* monoenes. The capillary chromatograms show that no separation of *cis* isomers is obtained when the double bond is closer to the carboxyl groups than the 9-position (oleate) as evidenced by our failure to separate methyl oleate and methyl petroselenate (6-*cis* isomer). Therefore, the the isomers with double bonds before the 9-position apparently assume about the same retention as oleate. The other isomers (10- to 16-) have longer retention times than oleate and are partially resolved, as previously reported by Scholfield et al. (9). The *trans* fractions show much less resolution of positional monoene isomers. Unpublished work of this laboratory (1) showed that the *trans* 9-,12- and 15-monoenes from hydrazine-reduced linolenate are indeed more poorly resolved than the corresponding *cis* isomers.

Discussion

Dicobalt octacarbonyl catalyzes the same reactions

TABLE II

Kinetics of Hydrogenation [a]

Methyl esters	k_1, hr^{-1}	k_1/Double bond, hr^{-1}
Linoleate	0.052	0.026
Linolenate	0.078	0.026
Alkali-isomerized diene:		
Nonconjugated	0.044	0.022
Conjugated	0.036	0.018

[a] Conditions: 75C, 3,000 psi H_2, 0.02 M $Co_2(CO)_8$.

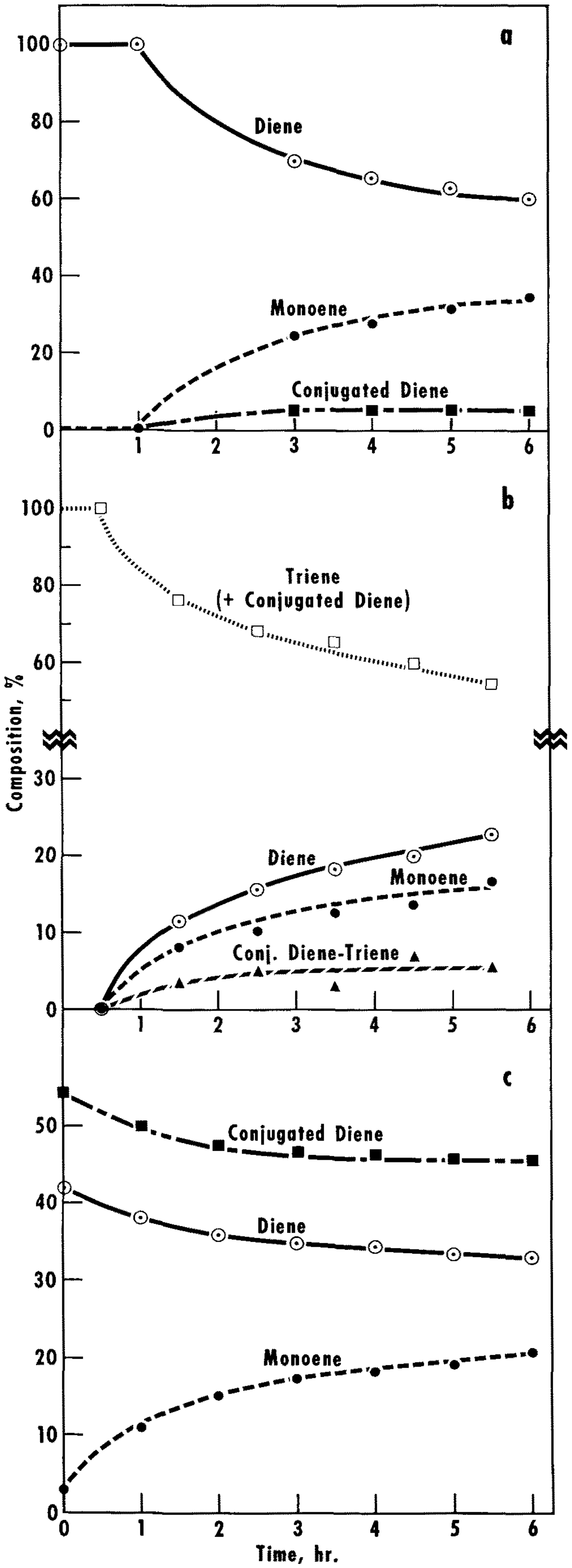


FIG. 1. Rate of hydrogenation of a) methyl linoleate, b) methyl linolenate and c) partially alkali-conjugated methyl linoleate. Conditions: 75C, 3,000 psi H_2, 0.02 M catalyst.

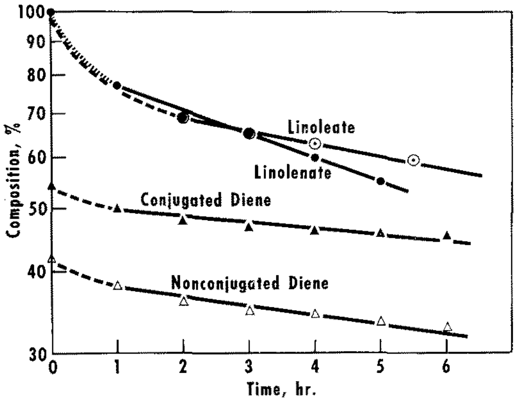


FIG. 2. Kinetics of hydrogenation. Same runs as in Figure 1.

as previously observed with iron carbonyl (4); namely, reduction, and both geometric and positional isomerization of double bonds in unsaturated fatty esters. A fourth reaction, the formation of stable complexes of fatty esters and metal carbonyl, was not observed with $Co_2(CO)_8$. However, such complexes may have been formed but either were not sufficently stable for isolation or were destroyed by the acid treatment used to decompose the catalyst. No attempt was made to detect such complexes before the acid treatment. The reduction with $Co_2(CO)_8$ takes place at lower temp than with $Fe(CO)_5$, but higher hydrogen pressures are required. Under these conditions *trans* isomerization is higher, but conjugation and migration of double bonds are much lower than with $Fe(CO)_5$ (180C, 100–400 psi H_2).

The formation of insoluble metallic cobalt at hydrogenation temp above 100C indicates some decomposition of the catalyst. $Co_2(CO)_8$ is known to decompose at these temp when the partial pressure of carbon monoxide is low (7). However, the catalytic hydrogenation is still considered homogeneous since heterogeneous catalysis from any finely divided cobalt would be poisoned by carbon monoxide evolved

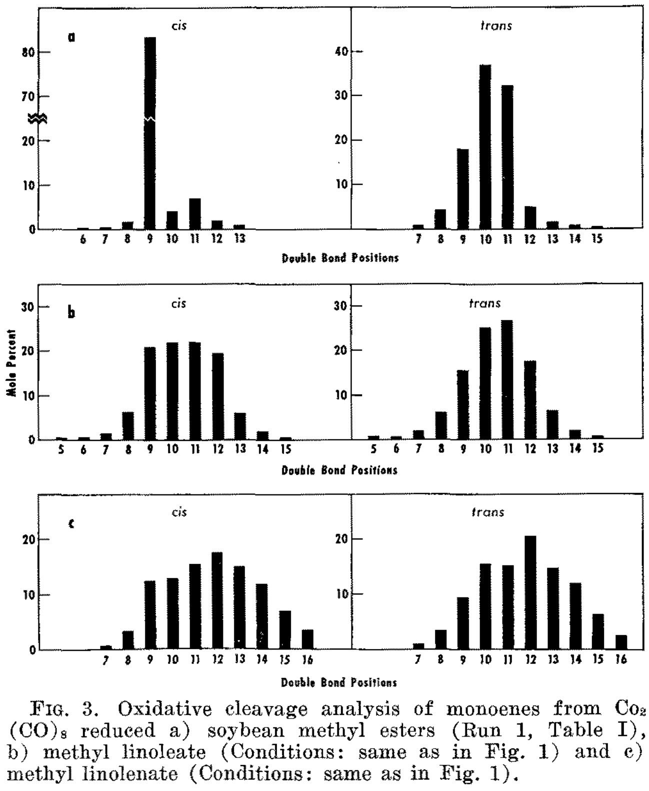


FIG. 3. Oxidative cleavage analysis of monoenes from $Co_2(CO)_8$ reduced a) soybean methyl esters (Run 1, Table I), b) methyl linoleate (Conditions: same as in Fig. 1) and c) methyl linolenate (Conditions: same as in Fig. 1).

TABLE III

Analysis of CCD Fractions[a]—Methyl Esters Hydrogenated with $Co_2(CO)_8$

Samples	Wt %		UV analysis			*trans* (% Elaidate)
			Before	After		
			Alkali isomerization[b]			
	CCD	GLC	a_{233} mμ	a_{233} mμ	a_{267} mμ	
Soybean methyl esters: [c]						
Run 1 (I.V. = 104)—						
Monoene (+sat's)	62.9	63.6	......	......	......	33.0 (43.5)[d]
Diene	33.8	32.4	4.44	68.0	......	25.2
Triene	3.3	2.5	9.92	24.8	15.9	16.8
Run 6 (I.V. = 115)—						
Monoene (+sat's)	60.7	57.3	......	......	......	26.3 (33.1)[d]
Diene	35.8	37.8	3.24	86.0	......	8.2
Triene	3.5	4.9	5.65	57.3	41.9	5.5
Run 8 (I.V. = 109)—						
Monoene (+sat's)	63.4	62.8	......	......	......	33.2 (41.3)[d]
Diene	31.7	34.3	2.92	82.3	......	10.6
Triene	4.9	2.9	5.90	42.0	26.7	5.0
Methyl linoleate (I.V. = 132):						
Monoene	39.0	35.5	......	......	......	64.0
Diene	61.0	64.5	10.05	80.5	......	15.3
Methyl linolenate (I.V. = 199):						
Monoene	24.0	21.1	......	......	......	69.3
Diene	26.2	27.6	3.25	7.8	1.2	92.9
Triene	49.8	50.3	19.7	54.0	46.4	8.5

[a] Separations monitored by GLC and TLC (4).

[b] Alkali isomerization of pure methyl linoleate gave a_{233} mμ = 90.0 and linolenate, a_{233} mμ = 59.7 and a_{267} mμ = 49.9.

[c] See Table I for conditions of hydrogenation.

[d] Adjusted values to take into account the content of saturates (Runs 1, 6 and 8 contained 25.1, 20.6 and 19.5% saturates in the monoene fractions).

from the decomposition. Similar reasoning has been used in support of the homogeneous character of the hydrogenation under conditions of the oxo or hydroformylation reaction (12). The active catalytic intermediate may be cobalt hydrocarbonyl, which is known to reduce and isomerize olefinic double bonds (11,13). The greater activity of $Co_2(CO)_8$ at lower temp than $Fe(CO)_5$ could be attributed to the lower stability of the active intermediate cobalt hydrocarbonyl and its complexes with unsaturated fatty esters.

Conjugated dienes formed during $Co_2(CO)_8$ catalysis may be considered intermediates in the reaction. However, the rate of hydrogenation for conjugated dienes was nearly the same as that for nonconjugated linoleate. Therefore, in the following simplified reaction scheme:

$$\begin{tikzcd}
\text{Linoleate} \arrow[rr, "k_1"] \arrow[dr, "k_2"'] & & \text{Monoenes} \\
& \text{Conjugated dienes} \arrow[ur, "k_3"'] &
\end{tikzcd}$$

two possibilities may be considered which account for the small accumulation of conjugated dienes during hydrogenation: 1) if k_1 and k_3 are approx the same, then k_2 is small; and 2) if k_1 is 0, i.e., only conjugated dienes are reducible to monoenes, then k_3 is much larger than k_2. Oxidative cleavage data obtained on monoenes showed that double bonds moved predominantly only one position on either side of the original 9-,12-positions of linoleate. This migration would be expected if conjugation was the principal reaction before reduction of one double bond. If conjugation gives 9,11- and 10,12-dienes as major components and gives 8,10- and 11,13-dienes as minor ones, then the observed distribution of double bonds in the monoenes would be obtained. There is no apparent difference in the degree of hydrogenation between either the original 9- or the 12-double bonds of linoleate.

Obviously the course of hydrogenation of methyl linolenate is more complicated than that of linoleate. The high level of conjugated dienes in the unreduced triene fraction indicates that they are important intermediates in the reaction. Oxidative cleavage analysis shows that less residual 9- and 15-double bonds remain in the monoene fraction than the 12-double bond. This result is in contrast to the course of heterogeneous catalytic hydrogenation with nickel (8) where less 12- than 9- and 15-double bonds of linolenate remain after reduction.

With $Co_2(CO)_8$ the following conjugated isomers

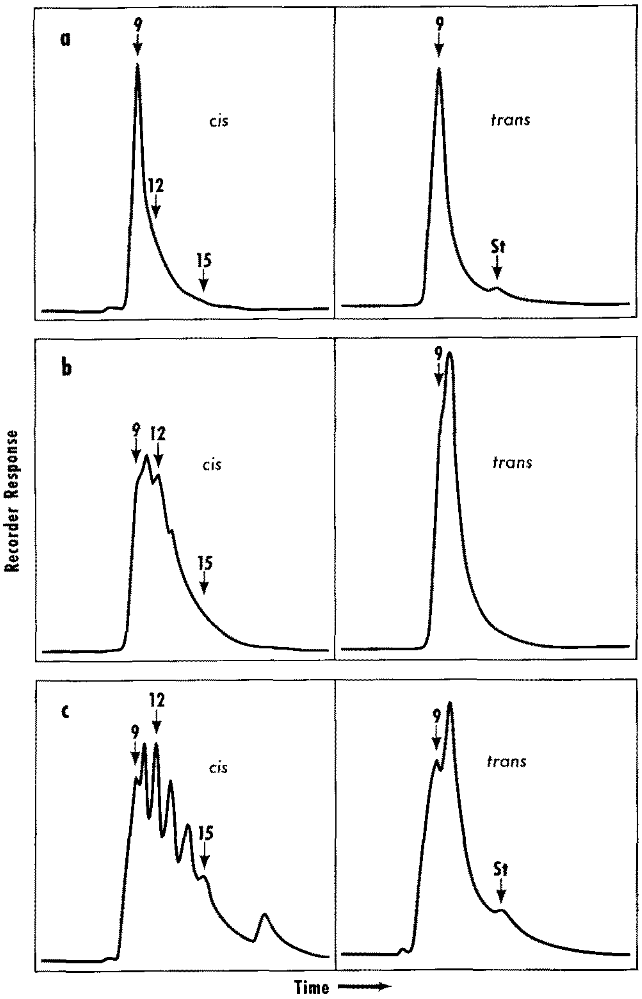
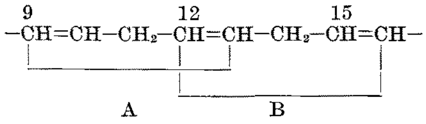


FIG. 4. Capillary gas chromatograms of monoenes from $Co_2(CO)_8$ reduced a) soybean methyl esters, b) methyl linoleate and c) methyl linolenate. Conditions: same as in Figure 3. (Figures over arrows indicate retention of pure standard monoenes added in independent runs for identification; st = stearate.)

may be considered as the major intermediates:



$$-\overset{9}{C}H{=}CH{-}CH_2{-}\overset{12}{C}H{=}CH{-}CH_2{-}\overset{15}{C}H{=}CH{-}$$

Linolenate

A gives:

$$-CH_2{-}\overset{9}{C}H{=}CH{-}\overset{11}{C}H{=}CH{-}CH_2{-}CH_2{-}\overset{15}{C}H{=}CH{-} \quad [1]$$

$$-CH_2{-}CH_2{-}\overset{10}{C}H{=}CH{-}\overset{12}{C}H{=}CH{-}CH_2{-}\overset{15}{C}H{=}CH{-} \quad [2]$$

B gives:

$$-\overset{9}{C}H{=}CH{-}CH_2{-}\overset{12}{C}H{=}CH{-}\overset{14}{C}H{=}CH{-}CH_2{-}CH_2{-} \quad [3]$$

$$-\overset{9}{C}H{=}CH{-}CH_2{-}CH_2{-}\overset{13}{C}H{=}CH{-}\overset{15}{C}H{=}CH{-}CH_2{-} \quad [4]$$

Reduction of either double bond of the conjugated diene system in [1] and [4] would give dienes in which the double bonds are separated by more than one methylene group and would be nonconjugatable with alkali. These unconjugatable dienes would not be reduced further. Their resistance to hydrogenation accounts for their high proportion in the diene fraction of linolenate. Since the conjugated dienes are mostly *trans,trans*, the unreduced double bond from the conjugated system would remain in the *trans* configuration, thus explaining the high isolated *trans* content of the diene fraction. Isomer [2] gives on reduction two dienes, one unconjugatable (10,15-) and the other conjugatable (12,15-) which is reducible to a mixture of 11-,12-,13-,14-,15- and 16-monoenes. Similarly, isomer [3] gives two dienes, 9,14- and 9,12-, the latter giving, like linoleate, a mixture of 8-,9-,10-, 11-,12- and 13-monoenes. By analogy with linoleate, the major isomers would include the 9-,10-,11- and 12-monoenes on one hand and the 12-,13-,14- and 15- on the other.

According to this scheme, a Gaussian distribution of isomeric monoenes is obtained with a max in the middle 12-position; such a distribution conforms to that observed by oxidative cleavage of the *cis* and *trans* monoenes of linolenate. This mechanism assumes that only conjugated systems are reduced and that no selectivity is exhibited for any of the double bonds of these systems. To elucidate further the mechanism of hydrogenation of both linoleate and linolenate, more definitive evidence could be obtained by experiments with radioactive intermediates.

ACKNOWLEDGMENTS

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REFERENCES

1. Butterfield, R. O., and C. R. Scholfield, private communication.
2. Emken, E., C. R. Scholfield and H. J. Dutton, JAOCS *41*, 388 (1964).
3. Frankel, E. N., E. P. Jones and C. A. Glass, *Ibid. 41*, 392 (1964).
4. Frankel, E. N., H. M. Peters, E. P. Jones and H. J. Dutton, *Ibid. 41*, 186 (1964).
5. Jones, E. P., and V. L. Davison, Abstract of Paper 77, AOCS Meeting, New Orleans, 1964.
6. Jones, E. P., and J. A. Stolp, JAOCS *35*, 71 (1958).
7. Mond, L., H. Hirtz, and M. D. Cowap, J. Chem. Soc. 798 (1910).
8. Scholfield, C. R., E. P. Jones and H. J. Dutton, Anal. Chem. *33*, 1745 (1961).
9. Scholfield, C. R., E. P. Jones, J. Nowakowska, E. Selke and H. J. Dutton, JAOCS *38*, 208 (1961).
10. Scholfield, C. R., J. Nowakowska and H. J. Dutton, *Ibid. 37*, 27 (1960).
11. Sternberg, H. W., and I. Wender, Intern. Conf. Coordination Chem., Chem. Soc. (London), 35 (1959).
12. Wender, I., M. Orchin and H. H. Storch, J. Am. Chem. Soc. *72*, 4842 (1950).
13. Wender, I., H. W. Sternberg, R. A. Friedel, S. J. Metlin and R. E. Markley, U.S. Bur. Mines, Bull 600 (1962).

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Phosphorus Derivatives of Fatty Acids. The Addition of Dialkyl Phosphonates to Unsaturated Acids and the Synthesis of Some 11-Dialkylphosphonoundecanoamides

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Abstract

A series of dialkylphosphonoundecanoic acids and 9(10)-dialkylphosphonostearic acids was prepared by the addition of dialkylphosphonates to 10-undecenoic acid and oleic acid under free radical conditions in 58–66% yield. The phosphonates used were: dimethyl, diethyl, di-*n*-butyl, di-*n*-hexyl and di-2-ethylhexyl. All of the products are colorless, odorless, thermally stable liquids, insoluble in water and soluble in organic solvents. The dialkylphosphonoundecanoic acids were converted into the corresponding acid chlorides by reaction with oxalyl chloride. The acid chlorides were then converted into the corresponding amides by addition of ammonia. All of the amides are white waxy solids except the 2-ethylhexyl derivative which is a high-boiling liquid. Two of the dialkylphosphonoundecanoic acids were converted into the N-decyl substituted amides by heating with *n*-decylamine. The N-*n*-decyl-11-dialkylphosphonoundecanoamides are white waxy solids.

Introduction

THE ADDITION of dialkylphosphonates to unsaturated compounds under free radical conditions has been shown to be a general reaction of wide applicability. Many unsaturated compounds have been used including terminal and non-terminal olefins (1), alkyl undecenoates, alkyl oleates and vinyl esters (2). The P,P-dialkyl 9(10)-phosphonostearates are of particular interest as they are efficient, primary plasticizers imparting good low temperature flexibility to poly(vinyl chloride) compositions containing them (3). In addition, these compounds have low migration losses.

While the literature lists many examples of the addition of dialkylphosphonates to olefins and unsaturated esters, no mention could be found of the reaction with unsaturated acids. The purpose of this investigation was to study the addition of dialkylphosphonates to 10-undecenoic acid and oleic acid and also to prepare certain derivatives of the resulting compounds, namely the amides.

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[1] Presented at the AOCS Meeting, New Orleans, 1964.