Conjugation of Polyunsaturated Fats: Activity of Some Group VIII Metal Compounds

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ABSTRACT

Conjugation of methyl linoleate was studied by treatment with $RhCl_3$ or *cis*-$Cl_2[(C_6H_5)_3P]_2Pt$-$SnCl_2$. $PdCl_2$ appeared as effective as $RhCl_3$ in hot alcohols in conjugating linolenate but $PdCl_2$ decomposed to metal. Both $RhCl_3$ and the Pt-complex catalyzed transesterification in alcohols, especially the latter. When the conjugation is carried out in methanol at 180 C, the Pt-complex yielded as much as 64% conjugated dienes from linoleate in 24 hr. However, typical results in *n*-butyl carbitol at 150 and 180 C were only 25-35% conjugated dienes as methyl esters with either $RhCl_3$ or the Pt-complex.

INTRODUCTION

Cowan (1) reviewed the methods of conjugating polyunsaturated fats and their derivatives in 1949. Nickel in one form or another is possibly the metal catalyst most frequently mentioned (2). Among the substances reported as catalysts since this review are sulfur or selenium-nickel (3), *n*-bromosuccinimide (4), quinones (5), furfural (6), oxygen (7), sulfur dioxide (8), palladium on carbon (9), iodine (10), zinc, iron, lead and various clays (11). Potassium *t*-butoxide in dimethyl sulfoxide is rapid compared to potassium methoxide in methanol (12).

Transition metal carbonyl compounds have been studied as conjugation catalysts (13). Compounds of rhodium, ruthenium, iridium, palladium and platinum were described as olefin isomerization catalysts (14). Bailar and Itatani (15) investigated complexes of platinum and palladium chlorides with triphenylphosphine, arsine and stibine as homogeneous hydrogenation catalysts and observed conjugating activity. Frankel et al. (16) at this Laboratory observed conjugation during homogeneous hydrogenation of methyl linolenate.

In view of the activity of some of the transition metal compounds as olefin isomerization catalysts, we thought that some of them might be potent conjugation agents for polyunsaturated fats. This report covers an investigation of some of the olefin active catalysts on methyl linoleate and some other polyunsaturated fat derivatives.

RESULTS AND DISCUSSION

$PdCl_2$ in aromatic solvents proved rather inactive in conjugating methyl linolenate, possibly because of the chloride's low solubility. When a solution of 1 g of methyl linolenate in 10 ml of xylene was shaken with 50 mg $PdCl_2$ for 24 hr at 70 C, UV analyses showed ca. 6% and 2% of conjugated dienes and trienes, respectively. In 10 ml cyclohexanol at 160 C, 50 mg $PdCl_2$ and 1 g methyl linolenate gave a homogeneous system and after 24 hr. UV analyses of the product showed ca. 23% and 5% conjugated dienes and trienes, respectively. However the $PdCl_2$ decomposed slowly to Pd in hot alcohols and thus limits the usefulness of this catalyst in alcohols.

$RhCl_3$ (trihydrate) (4 mg) in 10 ml of xylene at 141 C gave a heterogeneous solution and attempts to conjugate methyl linolenate (1 g) with this system were not successful. $RhCl_3$ in cyclohexanol under the same conditions given above for $PdCl_2$ in cyclohexanol was stable and yielded 24% and 4% conjugated dienes and trienes, respectively, from methyl linolenate. Similar results were obtained on methyl linolenate with $RhCl_3$ in hexanol at 160 C for 24 hr. In ethanol (10 ml) at 80 C for 24 hr, 4 mg of $RhCl_3$ to 1 g of linolenate afforded 5% and 1% conjugated dienes and trienes, respectively. With a similar ratio of catalyst to linolenate and amount of dimethylformamide at 160 C and 24 hr, 13% and 4% conjugated dienes and trienes, respectively, were formed.

Thus $PdCl_2$ and $RhCl_3$ produce higher levels of conjugation with methyl linolenate in alcohols than in aromatic solvents. Others have suggested that isomerization of olefins by transition metal compounds proceeds through metal hydride intermediates (14). A metal hydride could be formed by removal of hydrogen from an alcohol. Therefore, $RhCl_3$ was further investigated as a conjugation catalyst for methyl linoleate in a high boiling alcohol as

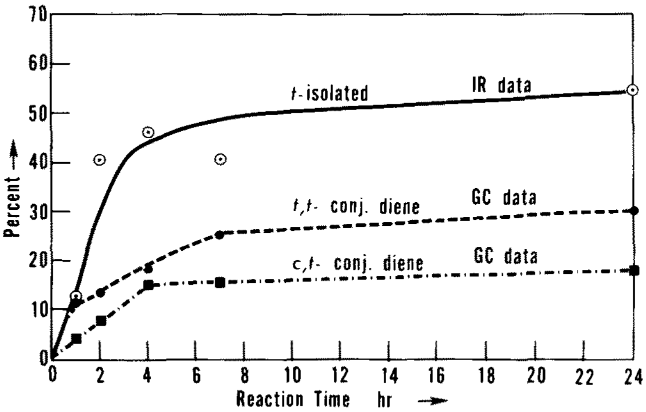

FIG. 1. Reaction of methyl linoleate with *cis*-$Cl_2[(C_6H_5)_3P]_2$ Pt-$SnCl_2$ (50 mg/g linoleate) at 180 C in methanol. Conjugated dienes from gas chromatographic data with *cis,cis*-conjugated diene about equally divided between estimated amounts of *cis,trans*- and *trans,trans*-conjugated dienes. *trans*-Isolated from IR as elaidate.

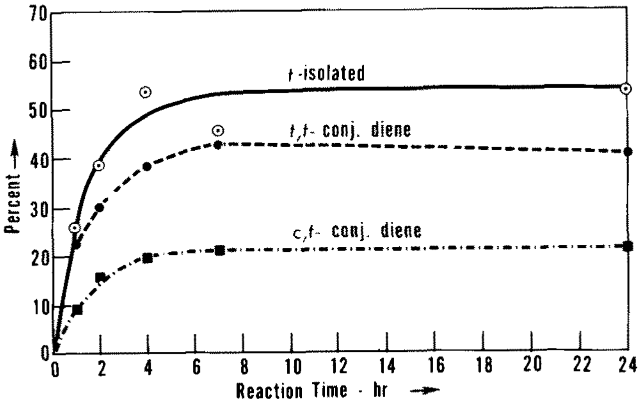

FIG. 2. Reaction of methyl linoleate with *cis*-$Cl_2[(C_6H_5)_3P]_2$ Pt-$SnCl_2$ (100 mg/g linoleate) at 180 C in methanol. Conjugated dienes from GC data with *cis,cis*-conjugated dienes about equally divided between estimated amount of *cis,trans*- and *trans,trans*-conjugated dienes. *trans*-Isolated from IR as elaidate.

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TABLE I

Isomerization of Methyl Linoleate[a]

Catalyst amount, mg/g	Reaction		Gas chromatographic analyses of products, %				
				Dienes			
	Temperature, C	Time, hr	Monoenes	Nonconjugated	Conjugated	Transesters	Polymer[b]
2	150	1	1	85	14	0	0
2	150	5	5	70	21	0	4
2	150	24	8	44	18	1	29
2	180	1	2	79	17	0	2
2	180	5	5	62	25	0	7
2	180	24	8	45	25	5	17
10	150	1	1	74	8	0	17
10	150	5	4	59	22	3	15
10	150	24	11	41	31	4	13
10	180	1	2	64	19	3	12
10	180	5	9	46	30	5	25
10	180	24	9	33	31	19	8

[a]Catalyst: $RhCl_3 \cdot 3H_2O$ Solvent: *n*-Butyl Carbitol.

[b]Polymer estimated by difference.

solvent. We selected *n*-butyl carbitol (BC) as a solvent since it can easily be washed from reaction samples by water.

The results of experiments to conjugate methyl linoleate with $RhCl_3$ in BC at two temperatures and two catalyst levels are shown in Table I.

Data from a low retention gas chromatographic (GC) column and thin layer chromatographic (TLC) plates showed that both BC esters of the fatty acid products (transesters) and polymers were formed in most of these reactions. Transesters were identified by comparison of the retention time (or R_f value) of an authentic sample of BC linoleate with the reaction products. Polymers were determined in the reaction mixtures using methyl palmitate as an internal standard on the short retention GC column. Accuracy of this method was determined with known mixtures of volatile and nonvolatile esters and showed an error of about ±5% in the polymer contents.

In a control experiment, methyl linoleate, 1 g in 10 ml BC was heated to 180 C for 24 hr without catalyst. Analyses on this product showed ca. 4% polymer and no transester. Transester probably requires catalyst in order to form.

Table I shows the result of experiments with $RhCl_3$ catalyst in BC on methyl linoleate. With 2 mg/g of catalyst at 150 and 180 C less conjugated diene and less transester formed compared to the corresponding reactions with 10 mg/g of catalyst. When 10 mg/g of catalyst was used at either 150 or 180 C for 24 hr, about 31% conjugated diene was produced. Formation of conjugated diene was more rapid at 180 C (30% in 5 hr) and more transester formed (19% vs. 4%) than at 150 C, while the amount of polymer produced at the two temperatures was similar. Some reduction of double bonds occurred as shown by an increase in monoenes.

The amount of conjugation produced in methyl linoleate by *cis*-dichlorobis(triphenylphosphine) platinum (Cl_2PtL_2) with stannous chloride as cocatalyst in BC was investigated. The results are shown in Table II. No conjugation occurs without stannous chloride (17). The reaction was studied at two catalyst concentrations at each of two temperatures. A molar ratio of 10:1 for ($SnCl_2 \cdot 2H_2O$):Cl_2PtL_2 was used as this was the optimum ratio found by Tayim and Bailar (17). The yield of conjugated dienes at 180 C and 24 hr with 50 mg/g of catalyst appears to be inferior to that obtained with $RhCl_3$ (based on methyl esters), but much transesterification (68%) occurred and the amount of conjugated diene in the transester fraction is unknown. However, one might expect the composition of transester (with respect to conjugated and nonconjugated dienes) to be similar to that of the methyl ester fractions, e.g., 50% of each isomer. When 100 mg/g of catalyst was used at 180 C for 24 hr, essentially all the nonconjugated methyl esters

TABLE II

Isomerization of Methyl Linoleate[a]

Catalyst[b] amount, mg/g	Reaction		Gas chromatographic analyses of products, %			
			Dienes			
	Temperature, C	Time, hr	Nonconjugated	Conjugated	Transester	Polymer[c]
50	150	1	100	Trace	0	0
50	150	5	87	Trace	9	4
50	150	24	66	7	22	5
50	180	1	77	Trace	10	13
50	180	5	32	22	33	13
50	180	24	5	5	68	22
100	150	1	100	Trace	0	0
100	150	5	98	2	0	0
100	150	24	62	15	23	0
100	180	1	84	2	2	12
100	180	5	40	24	19	17
100	180	24	Trace	Trace	70	30

[a]Catalyst: *cis*-$Cl_2[C_6H_5)_3P]_2Pt$-$SnCl_2 \cdot 2H_2O$ Solvent: *n*-Butyl Carbitol.

[b]Catalyst contained 10 moles of $SnCl_2 \cdot 2H_2O$/mole of $Cl_2[(C_6H_5)_3P]_2Pt$.

[c]Polymer estimated by difference.

disappeared and a 70% yield of transester was formed.

To avoid the formation of transester, reactions were carried out in methanol instead of BC. Results from the reaction of methyl linoleate with Cl_2PtL_2-$SnCl_2$ in methanol at 180 C under N_2 at two different proportions of catalyst are shown in Figures 1 and 2. The highest conjugation was ca. 64%. About a 10% increase in conjugation is obtained by increasing the catalyst from 50 mg/g to 100 mg/g. At the lower and higher catalyst proportions ca. 42 and 31% of nonconjugated dienes, respectively, remained after 24 hr. Ca. 7% and 5% of polymer was estimated at the respective lower and higher catalyst levels after 24 hr. The *trans*-isolated products were estimated by IR based on the extinction coefficient for elaidate. The *trans*-isolated contents suggest that one half, or with the higher catalyst and temperature levels, somewhat more than one half of the nonconjugated double bonds are in the *trans* configuration.

The reaction in methanol with Cl_2PtL_2-$SnCl_2$ slowed after 6 hr and suggested that the efficiency of the catalyst was reduced after prolonged heating at 180 C. Thus, a reaction which had been run for 24 hr at 180 C with 50 mg Cl_2PtL_2-$SnCl_2$/g methyl linoleate was treated again with 50 mg Cl_2PtL_2-$SnCl_2$. After another 24 hr at 180 C the yield of conjugated dienes was 54%. This yield was less than the result shown in Figure 2 for treatment with the same proportion of catalyst for 24 hr at 180 C.

Treatment of soybean oil with 50 mg Cl_2PtL_2-$SnCl_2$/g oil without solvent at 180 C for 24 hr produced 19% conjugated diene and 1% conjugated trienes, respectively. Similarly, linseed oil yielded 21% conjugated diene and 6% conjugated trienes as measured by UV.

EXPERIMENTAL PROCEDURES

All solvents were distilled before use. BC was stored in a brown glass bottle under N_2 in a refrigerator. Methyl linoleate, linolenate and palmitate were purchased from The Hormel Institute and were at least 99% pure. These esters were stored under N_2 at -10 C. Nitrogen with an oxygen content less than 0.002% was used for blanketing stored samples. Nitrogen used to blanket reaction mixtures was first passed through Fieser's solution and then a column of Drierite.

The gas chromatograph was a Varian Aerograph Model 1525C. For analysis of the volatile methyl ester portions of the samples, an 8 ft X 0.125 in. 10% EGSS-X on 100/120 mesh Gas Chrom P packed stainless steel column was used. Methyl palmitate was used as internal standard. High-boiling transesters were determined with temperature programming on a 1 ft X 0.125 in. 0.04% SE-30 on 100/120 mesh silane-treated glass beads packed in a stainless steel column. Polymer contents were estimated by difference.

All isomerizations, except runs in methanol, were conducted under a slight positive pressure of N_2 in a flask equipped with reflux condenser, sampling port and magnetic stirrer. The flask was heated by a magnetically stirred oil bath having a temperature controller. Typically, the flask was charged with the required amount of solvent, substrate and catalyst. Nitrogen was passed through to displace air and after 5 min the flask was lowered into the oil bath at the desired temperature. Products were taken up in hexane and partitioned with H_2O four times under N_2. The hexane solution was dried over $MgSO_4$, filtered and stripped in vacuo. The residue was analyzed by UV, IR and GC.

A small rocking autoclave equipped with glass liner was used for the runs in methanol. After closure, autoclave was flushed three times with 200 psig N_2 and then heated under 200 psig N_2 as rapidly as possible to 180 C. After the desired reaction time, the autoclave was cooled to room temperature before opening. The products were processed as before.

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REFERENCES

1. Cowan, J.C., Ind. Eng. Chem. 41:294 (1949).
2. Radlove, S.B. (Maytag Co.), U.S. Pat. 2,497,689 (1950); U.S. Pat. 2,501,851 (1950); Blekingh, J.J.A. (Lever Brothers), U.S. Pat. 2,692,886 (1954).
3. Gordon, E., Bull. Mens, Inform. ITER No. 11:38 (1948); Chem. Abstr. 43:279i (1949).
4. Rushman, D.F., and E.M.G. Simpson, Trans. Faraday Soc. 51:230-236 (1955).
5. Radlove, S.B. (Maytag Co.), U.S. Patent 2,575,529 (1951).
6. Rigamonti, R., and E. Sporcamela-Marahetti, Chim. Ind. (Milan) 39:261-264 (1957).
7. Wiebe, L.P. (Shell Development Co.), U.S. Patent 2,588,902 (1952).
8. Boer, J.H. de, J.P.W. Hautman and H.I. Waterman, Kon. Ned. Akad. Wetensch. Proc. Ser. 50:1181-1188 (1947); Chem. Abstr. 42:6547c (1948).
9. Takemura, K.H., and L.A. Goldblatt, JAOCS 34:15-17 (1957).
10. McMicoll, D. (Lever Brothers and Unilever Ltd.), British Patent 630,634 (1949); Chem. Abstr. 44:7572h (1950).
11. Ivanova, A.A., and A.S. Petrova, Kim. Prom. 8:20-21 (1947); Chem. Abstr. 43:4027g (1949); Gupta, M. LaS., J. Indiana Chem. Soc. Ind. News Ed. 19:185-192 (1956); Chem. Abstr. 52:1653g (1958); Drinberg, A.Y., and N.S. Cherminskaya, Zh. Prikl. Khim. 27:983-990 (1954); Chem. Abstr. 49:134lh (1955).
12. Ugelstad, J., B. Jensen and P.C. Mork, Acta Chem. Scand. 16:323-326 (1962); Ugelstad, J., O.A. Rokstad and J.S. Karstein, Acta Chem. Scand 17:208-214 (1963).
13. Frankel, E.N., and S. Metlin, JAOCS 44:37-39 (1967). Ogata, I., and A. Misono, Nippon Kagaku Zasshi 85:748-752 (1964); Chem. Abstr. 62:12031c&d (1965).
14. Cramer, R., and R.V. Lindsey, Jr., J. Amer. Chem. Soc. 88:3534-3544 (1966).
15. Bailar, J.C., Jr., and H. Itatani, Ibid. 89:1592-1599 (1967).
16. Frankel, E.N., E.A. Emken, H. Itatani and J.C. Bailar, Jr., J. Org. Chem. 32:1447-1452 (1967).
17. Tayim, H.A., and J.C. Bailar, Jr., J. Amer. Chem. Soc. 89:3420-3424 (1967).

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