Methyl 9(10)-Formylstearate by Selective Hydroformylation of Oleic Oils[1]

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ABSTRACT

A highly selective catalyst system has been discovered for the hydroformylation of methyl oleate into methyl 9(10)-formylstearate in high yields. A rhodium catalyst in the presence of triphenylphosphine is used with oleic esters, acids or triglycerides. Hydroformylation proceeds smoothly at 95-110 C with a 1:1 mixture of H_2 and CO at 500 to 2000 psi with or without a solvent, such as toluene. The formylstearate obtained in 90% to 99% conversion from oleate can be either hydrogenated (Raney Ni) or reduced ($NaBH_4$) to hydroxymethylstearate or oxidized ($KMnO_4$) to carboxystearate. According to TLC and mass spectrometry, the methylated carboxystearate consists of about equal proportions of the 9 and 10 isomers. Addition of triphenylphosphine inhibits isomerization of the double bond and leads to the formation of a rhodium carbonyl triphenylphosphine complex, which is apparently the active catalyst. Other known methods for hydroformylation (cobalt carbonyl) and carboxylation (Koch's method) of oleate give a wide distribution of isomers.

INTRODUCTION

In a previous study (1) we characterized products from the cobalt carbonyl-catalyzed hydroformylation of unsaturated fatty esters and vegetable oils as a mixture of branched and linear C_{19} fatty aldehydes and alcohols. The major branched products were a complex mixture with a formyl or hydroxymethyl substituent distributed between C-6 and C-13 of the C-18 chain. The proportion of linear isomers increased at higher hydroformylation temperatures and in the presence of a tributylphosphine-cobalt carbonyl complex catalyst. Lai et al. (2,3) reported the formation of aldehyde esters, acid esters and alcohol esters, as well as estolides during hydroformylation of methyl oleate catalyzed by cobalt salts and cobalt carbonyl. Our conclusion (1) that the formation of isomeric branched oxo products is due to the concurrent double bond isomerization catalyzed by cobalt carbonyl (4) was confirmed by Lai et al. (5) who demonstrated also the role of hydrido cobalt carbonyl, $HCo(CO)_4$.

Several novel hydroformylation catalysts reported include various substituted phosphine, phosphite, arsine and stibine ligands used together with organometallic complexes of cobalt (6-8), rhodium (9-14) and iridium (15). These new catalysts are generally more active than cobalt carbonyl and promote hydroformylation of olefins under milder conditions. The complexes, $(Ph_3P)_3Rh(CO)Cl$ and $(PhO_3P)_3Rh(CO)H$, with excess triphenylphosphine (Ph_3P) or triphenylphosphite are particularly selective in yielding high ratios of linear aldehydes from α-olefins (14,16).

In a survey of various metal triphenylphosphine and carbonyl catalysts, a highly selective rhodium system has been discovered for the hydroformylation of methyl oleate into methyl 9(10)-formystearate with high yields. This paper reports studies of the hydroformylation of oleic esters, acids and triglycerides with this Rh-Ph_3P catalyst system.

EXPERIMENTAL PROCEDURES

Materials and Methods

Most of the experiments were run on methyl esters obtained by transesterification of olive oil ($C_{16:0}$, 10.8%; $C_{18:0}$, 2.3%; $C_{18:1}$, 78.9%; $C_{18:2}$, 8.0%). Methyl oleate ($C_{16:0}$, 0.1%; $C_{18:1}$, 99.2%; $C_{18:2}$, 0.7%) was made from olive fatty acids purified by urea fractionation and acid soap crystallization (17). Oleic safflower oil introduced recently as a source of high oleic acid and triglycerides (18) was refined ($C_{16:0}$, 4.1%; $C_{18:0}$, 1.8%; $C_{18:1}$, 77.9%; $C_{18:2}$, 16.2%). The catalyst, 5% Rh supported on either C, $CaCO_3$ or Al_2O_3 (Engelhard Industries, Newark, N.J.), and Ph_3P (Strem Chemicals, Inc., Danvers, Mass.) were purchased. Methods for GLC, TLC, IR, NMR and mass spectrometry of aldehyde products and various derivatives were the same as described previously (1). Analysis for Rh was made by atomic absorption spectrometry (C.D. Evans, unpublished data).

Hydroformylation

Olive methyl esters (500 g) were charged into a 2-1 rocker-shaker autoclave (Autoclave Engineers, Erie, Pa.) with 2.5 g of 5% Rh on $CaCO_3$, 2.2 g Ph_3P and 300 ml toluene. The autoclave was sealed, purged three times with a 1:1 mixture of H_2 and CO and then pressurized with the same gas mixture to 2000 psi. The reaction mixture was heated to 110 C with mechanical shaking in 40 min. Hydroformylation began in the range between 103 and 110 C and during this period the pressure reached a maximum of 2600 psi and then decreased to 2525 psi. The temperature was then controlled at 110 ± 3 C. After 5 hr and 25 min the pressure declined to 1500 psi and then remained constant for 35 min. After the autoclave was water-cooled to room temperature, gases were vented. The reaction mixture was transferred with benzene and filtered by suction on a Buchner funnel through Whatman No. 1 paper. The solvent was removed on a rotating evaporator under vacuum. The crude light-yellow liquid product (579.5 g) was analyzed by GLC ($C_{16:0}$, 10.9%; $C_{18:0}$, 2.4%; $C_{18:1}$, 2.5%; $C_{18:2}$, 5.6%; formylstearate 78.9%). Calculated conversion is 90.8% based on unsaturates in the starting material. All yields reported in this paper are similarly calculated. Distillation of the crude product yielded clear, colorless fractions (Table I). Fraction 3 had an aldehyde value of 3.0 me/g (97.8% as methyl formylstearate) and the following elemental analysis: C, 73.68; H, 11.85%. Calculated for $C_{20}H_{38}O_3$: C, 73.60; H, 11.65%.

Methyl oleate was hydroformylated by the same procedure but on a 30 mM scale in a 250 ml autoclave with 5.1% Rh catalyst (5% on $CaCO_3$), 4.4% Ph_3P and 50 ml toluene. A crude yellow product resulted (GLC analysis: $C_{16:0}$, 0.4%; $C_{18:1}$, 8.1%; $C_{18:2}$, 0.3%; formylstearate, 89.1%; hydroxymethylstearate, 2.1%). Distillation through a short Vigreux column gave a fraction (140-148 C/0.005 mm Hg), in 72% yield, which contained 98.4% methyl formylstearate

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TABLE I

Distillation of the Crude Product From Olive Methyl Esters

Fraction	Temp, C	P, mm Hg	Weight, g	Formylstearate, % (GLC)
1	164-170	0.4	62.3	26.0
2	170-175	0.1-0.2	396.2	88.5
3	176-200	0.1-0.5	48.3	99.0
4	210	0.2	3.2	72.3

by GLC (aldehyde value: 3.01 me/g). Analysis: C, 73.61; H, 11.88%. Further identification was made by reduction, oxidation, IR, TLC, mass spectrometry and NMR of suitable derivatives (see Results).

Oleic safflower oil (998 g) was hydroformylated in a 2-1 autoclave with 10 g of 5% Rh/C and 9 g Ph_3P without solvent at 110 C, initial pressure of 2000 psi H_2:CO (1:1) for 3 hr. The filtered crude formyl triglyceride product (1212 g) was light brown. A portion was transesterified and analyzed by GLC ($C_{16:0}$, 5.3%; $C_{18:0}$, 2.8%; $C_{18:2}$, 1.4%; formylstearate, 90.5%). Calculated conversion is 96.2%. A short path distillation of the esters without fractionation yielded 92.0% of a colorless liquid (140-160 C/0.03 mm Hg).

Olive fatty acids (500 g) were similarly hydroformylated. The catalyst consisted of 5.0 g of 5% Rh/C and 2.0 g Ph_3P dissolved in 250 ml toluene. The reaction was carried out at 110 C, at an initial synthesis gas (H_2/CO, 1:1) of 600 psi for 5 hr during which period the pressure was restored from 500 to 600 psi nine times. The filtered crude formylstearic acid product (553 g) was a brown liquid and analyzed by GLC after methylation with diazomethane ($C_{16:0}$, 11.3%; $C_{18:0}$, 3.2%; $C_{18:1}$, 0.5%; $C_{18:2}$, 0.9%; formyl stearate, 84.1%). Calculated conversion is 97.8%.

$KMnO_4$ Oxidation

Distilled aldehyde esters from hydroformylated olive methyl esters (285 g, distillation fraction 2 containing 88.5% formylstearate) were dissolved in 1 liter of acetone and cooled in ice-water. The solution was agitated by air bubbling through a coarse fritted glass stick. A solution of 1 liter of acetone and 10 g $KMnO_4$ was added during 90 min at a rate adjusted to keep the temperature below 20 C. The reaction mixture was then allowed to warm to room temperature and air bubbling was continued for 4 hr. Most of the acetone was removed on a rotating evaporator under vacuum at room temperature. The ester solution was suspended in water, treated with $NaHSO_3$ to reduce unreacted $KMnO_4$ and extracted with petroleum ether. The brown organic layer was washed repeatedly with a saturated aqueous solution of $NaHSO_3$ until its color changed to yellow. It was then washed with water and dried (Na_2SO_4). The light-amber methyl carboxystearate product (267 g) was saponified. Distillation of a portion (224 g) of crude carboxystearic acid with an alembic still yielded two fractions (104 g) which showed one component by TLC (solvent: 1% HAc, 99% $CHCl_3$). These fractions were combined and analyzed directly by potentiometric titration (neutralization point, pH: 10.35; acid value: 329; calculated acid value for carboxystearic acid: 342) and after methylation by GLC ($C_{16:0}$, 0.3%; $C_{18:0}$, 1.0%; $C_{18:1}$, 0.1%; carboxystearate, 98.6%).

Distilled methyl formylstearate (98.4% by GLC) from hydroformylated methyl oleate was similarly oxidized with $KMnO_4$ to yield carboxystearic acid. The methyl carbomethoxystearate obtained after methylation was 97.2% pure by GLC. Analysis: C, 69.78; H, 11.21%; calculated for $C_{21}H_{40}O_4$: C, 70.80; H, 11.22%.

Hydrogenation and Reduction

Hydroformylated oleic safflower oil (90.5% formylstearate, by GLC) was hydrogenated with Raney nickel at 97-111 C and 500-1000 psi H_2. A portion of the light-brown filtered hydroxymethyl triglyceride product was saponified, methylated and acetylated (1) for GLC analysis ($C_{16:0}$, 4.5%; $C_{18:0}$, 2.2%; $C_{18:2}$, 1.7%; hydroxymethylstearate, 91.1%).

Distilled methyl formylstearate (98.4%) from hydroformylated methyl oleate was reduced with $NaBH_4$ (1). The methyl hydroxymethylstearate was acetylated. The distilled acetoxymethylstearate (135-158 C/0.005 mm Hg) was 98.7% pure by GLC. Analysis: C, 69.95; H, 11.19%; calculated for $C_{22}H_{42}O_4$: C, 71.4; H, 11.3%.

RESULTS

Reaction Conditions

Hydroformylation was studied over a wide range of reaction conditions to determine the effect of various parameters upon selectivity and conversion of oleic oils into formyl derivatives. The metal catalyst source was Rh supported on either C, $CaCO_3$ or Al_2O_3. Although the C-supported Rh was the most active catalyst, the crude aldehyde products obtained with it were brown, whereas those produced with Rh on $CaCO_3$ or on Al_2O_3 were yellow and lighter in color. Catalyst studies showed that a portion of Rh is solubilized in the fatty esters under hydroformylation conditions and that a homogeneous Rh carbonyl triphenylphosphine complex is probably the actual catalyst. This Rh-Ph_3P system was effective for the hydroformylation of oleic esters, acids and triglycerides, and methyl elaidate.

The experiments listed in Table II were intended to determine the effects of temperature, pressure, Rh and Ph_3P concentrations, as well as solvent, on the conversion of methyl oleate in olive esters into formylstearate. Conversion yields of formylstearate varied from 88% to 99% under a wide range of reaction conditions. Typical conditions were in the temperature range of 95 to 110 C at 1000 to 2000 psi initial pressure of H_2/CO (1:1), Rh catalyst concentration of 0.05% to 0.2%, Ph_3P concentration of 0.5% to 4%, with or without toluene as solvent. Although hydroformylation occurred at temperatures as low as 90-95 C (at 2000 psi synthesis gas), a range of 100 to 110 C was usually necessary to achieve more complete conversion of oleate to formylstearate. The Rh-Ph_3P catalyst system was highly selective for aldehyde formation at a wide temperature range. Most striking is the observation that formylstearate was the only product even at 180 C and 2400 psi of a 2:1 mixture of H_2 + CO (Table II, Run 4). Under these conditions hydroxymethylstearate is formed as the main product from methyl oleate hydroformylated with $Co_2(CO)_8$ (1) as well as with $(Ph_3P)_3RhCl$ (Frankel, unpublished results). Although essentially no hydroformylation of methyl oleate occurred at 300 psi initial pressure of H_2 + CO at 110 C (Table II, Run 5), good conversion resulted at 500 psi and 125 C (Table II, Run 3).

TABLE II

Hydroformylation of Olive Fatty Estesr

Run No.[a]	Reaction conditions							Analyses						
	Rh,[b] %	Ph_3P, %	Solvent, 50 ml	Pressure, psi		Temp., C	Time,[c] hr	Distillation,[d] %	GLC[e]					Conversion,[g] %
				H_2	CO				$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$[f]	Formyl	Hydroxy	
1	0.2	3.6	Toluene	1000	1000	95	6	97.9	11.2	2.9	7.0	1.1	77.1	0.7	89.5
2	0.2	3.6	None	1000	1000	110	5	88.4	11.4	2.7	0.0	0.1	84.8	1.0	98.7
3	0.2	3.6	Toluene	250	250	125	6	97.6	11.1	3.3	2.7	1.9	80.5	0.5	93.2
4	0.1	1.8	Toluene	1600	800	180	6	95.2	11.4	2.6	0.0	0.7	85.3	0.0	98.2
5	0.2	3.6	Toluene	150	150	110	6	---	10.7	2.4	80.2	6.3	0.4	0.0	0.5
6	0.2	3.6	Toluene	500	500	110	6	94.3	11.6	2.8	5.0	1.1	78.5	1.0	91.5
7	0.2	3.6	Toluene	1500	1500	110	6	92.6	10.8	4.2	6.4	2.5	74.7	1.4	87.6
8	0.05	0.9	Toluene	1100	1100	110	4	92.3	11.0	2.3	1.0	0.7	85.0	0.0	97.8
9	0.1	1.8	Toluene	1000	1000	110	4	96.1	11.6	3.7	0.4	0.8	83.5	0.0	96.1
10	0.4	7.1	Toluene	1000	1000	110	5	95.2	10.8	3.0	4.2	0.5	78.7	2.8	93.8
11	0.1	0.9	Toluene	1000	1000	110	4	94.2	11.6	2.6	0.0	0.6	85.2	0.0	98.0
12	0.1	0.45	Toluene	1000	1000	110	4	97.8	11.4	3.7	0.2	0.4	84.3	0.0	97.0
13	0.1	0.05	Toluene	1000	1000	110	4	97.7	10.8	3.0	0.3	0.7	85.2	0.0	98.0
14	0.1	0.0	Toluene	1000	1000	110	4	97.6	11.0	2.5	55.3	3.0	28.2	0.0	32.5
15	0.1	1.6	MeOH	1000	1000	110	5	97.0	11.8	3.3	0.7	0.0	84.2	0.0	96.9

[a]All runs were made with 55.5 g olive methyl esters in 250 ml autoclave.

[b]Added as 5% on $CaCO_3$ (Runs 1-6, 9-15) or as 5% on C (Runs 7,8).

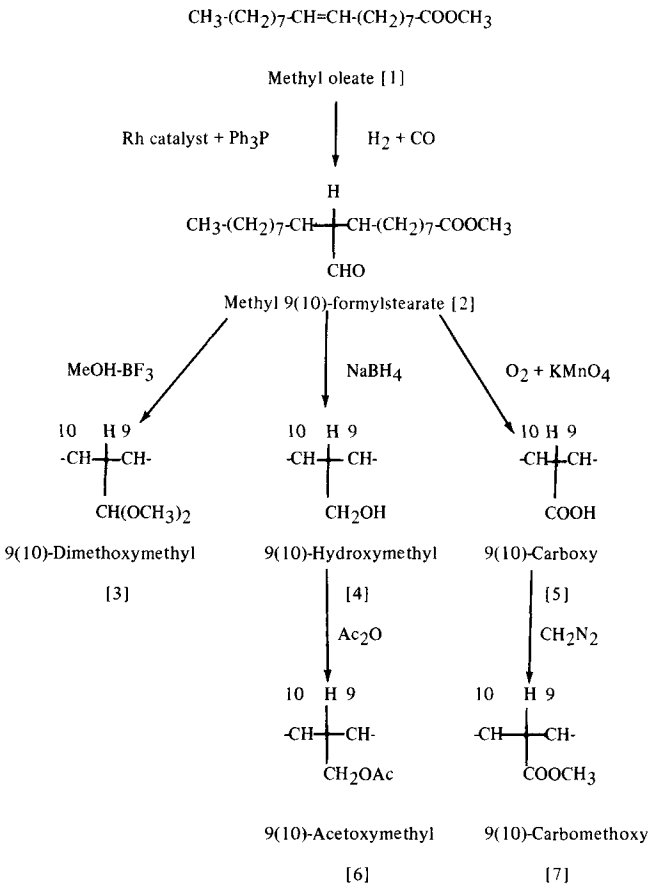
[c]Reaction was stopped usually about 1 hr after pressure leveled off.

[d]At 150-170 C/0.005 mm Hg with a short-path microstill. Yields were based on weights of total distilled products.

[e]Column: 10% DEGS on Chromosorb W 60/80, 5 ft X 1/8 in.; temperature programmed between 150 and 215 C at 4 C/min; instrument with a flame ionization detector.

[f]Includes conjugated dienes and minor unidentified components.

[g]From GLC analyses for total formyl- and hydroxymethylstearate, based on unsaturates in original olive esters: 86.9%.



SCHEME 1

The Rh catalyst was active at a concentration as low as 0.025%, but a range of 0.05% to 0.1% Rh was optimum for complete conversions. A concentration higher than 0.2% Rh led to the formation of a small amount of hydroxymethylstearate (Table II, Run 10). Yields of formylstearate were good at a wide range of Ph_3P concentrations. The ratio of Ph_3P to Rh was varied from 0.5 to 18 with little effect on the yield. Without Ph_3P the yield of formylstearate decreased drastically to only 33% (Table II, Run 14). Further characterization of the products (see below) showed that with no Ph_3P double bond isomerization was appreciable and resulted in a complex mixture of isomeric formyl products.

Hydroformylation occurred equally as well with toluene and methanol solvents as in the absence of solvent. There was no evidence of acetal formation in the presence of methanol.

One experiment was carried out to determine whether the formylstearate product could be further reduced to the hydroxymethylstearate in the presence of the Rh-Ph_3P catalyst system. After hydroformylation the synthesis gas was replaced with H_2 and the reaction mixture was heated between 110 and 180 C for 4 hr. No reduction of the formyl product occurred under these conditions. Therefore, the Rh-Ph_3P catalyst is completely ineffective for reducing aldehydes to alcohols. There was also evidence of little or no hydrogenation of oleate to stearate with this catalyst system under a wide range of hydroformylation conditions. Furthermore, the crude hydroformylation products containing Ph_3P were much more resistant to air oxidation than the corresponding distilled products free of Ph_3P. Protection of the aldehyde group is apparently afforded by Ph_3P during hydroformylation. This effect of Ph_3P would contribute to the high conversion of oleate to formylstearate.

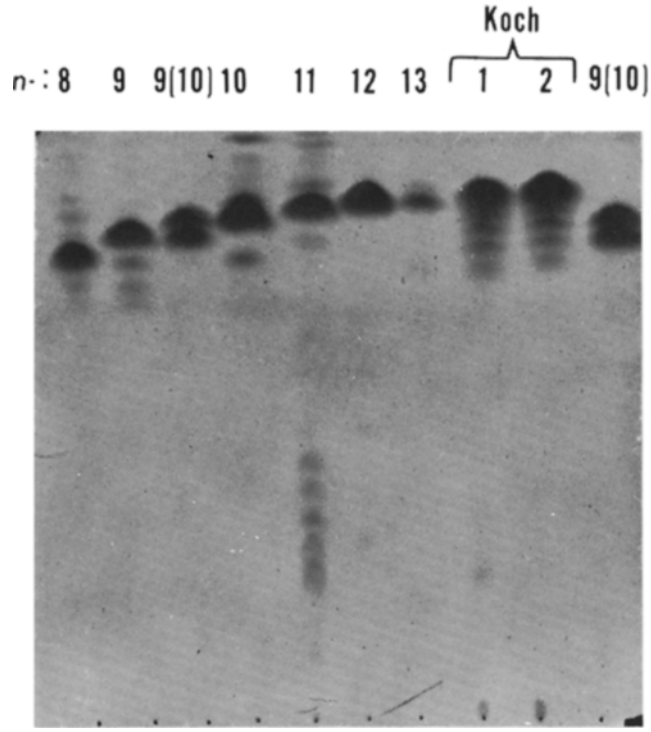


FIG. 1. TLC of methyl *n*-carbomethoxystearate, from left to right: 8- and 9-carbomethoxy (synthetic); 9(10)-carbomethoxy (Rh-Ph_3P hydroformylation); 10-, 11-, 12- and 13-carbomethoxy (synthetic); carboxylated oleate 1 and 2 (Koch reaction); 9(10)-carbomethoxystearate, repeated. Solvent: 8% ethyl ether-92% petroleum ether, plate developed seven times.

Characterization

The hydroformylation product of methyl oleate was characterized as methyl 9(10)-formylstearate by the reactions in Scheme 1.

GLC of methyl 9(10)-formylstearate [2] gave one sharp peak with retention time relative to methyl oleate [1] of 2.3 (for conditions, see Table II, footnote e). Sharp single peaks also occurred with the dimethoxymethyl [3], carbomethoxy [7] and acetoxymethyl [6] derivatives, with respective retention times of 1.6, 2.0 and 2.5 relative to methyl oleate.

TLC [Silica Gel G, 10% ethyl ether (EE)-90% petroleum ether (PE)] of [2] showed a partially resolved double spot of R_f relative to methyl oleate of 3.0. A carbonyl test was positive for [2] by a dinitrophenylhydrazine indicator spray. Evidence of two components was also indicated by TLC of the hydroxymethyl derivative [4] with a more polar solvent (30% EE-70% PE). No resolution of components resulted by TLC of either the dimethoxymethyl [3], which moved too fast (10% EE-90% PE), or the carboxy derivative [5], which moved too slowly and tailed (30% EE-70% PE). Resolution was best with the carbomethoxy derivative [7]. Multiple development with a weakly polar solvent (8% EE-92% PE) resulted in almost complete resolution of methyl carbomethoxystearate[7] into two components corresponding to the 9- and 10-carbomethoxystearates synthetic standards (Fig. 1). Carbomethoxystearate made by carboxylation of methyl oleate with CO and H_2SO_4 by the Kock reaction (19) was also included for comparison. These samples show a large number of isomers with carbomethoxy substituents located mostly on carbon positions higher than C-12 and C-13. The isomeric carbomethoxy derivatives were quantitatively estimated by mass spectrometry (see below).

The IR spectrum of methyl formylstearate [2] showed a medium aldehyde band at 1740 cm^{-1} accompanied by a

TABLE III

Distribution of Branched Methyl *n*-Carbomethoxystearate[a] From Hydroformylated and Carboxylated Methyl Oleate

Treatment	*n*: 6	Relative percentage 7	8	9	10	11	12	13	14	15	16	17
Hydroformylated with Rh-Ph_3P[b]												
Ph_3P, % 0	1.5	3.8	8.9	24.2	28.1	13.3	8.5	5.6	4.3	1.7	---	---
Ph_3P, % 0.05	---	2.8	7.6	33.4	36.4	9.6	4.8	2.7	2.7	---	---	---
Ph_3P, % 0.45	---	1.6	4.6	40.3	43.7	3.2	2.9	1.6	2.0	---	---	---
Ph_3P, % 0.9	---	1.5	4.4	39.9	43.1	3.0	3.6	2.1	2.4	---	---	---
Ph_3P, % 1.8	---	---	1.8	44.2	49.8	2.4	1.7	---	---	---	---	---
Ph_3P, % 4.4	---	---	---	45.9	54.1	---	---	---	---	---	---	---
Hydroformylated with $Co_2(CO)_8$[c]	3.9	6.4	11.7	14.3	18.0	23.5	9.8	12.4	---	---	---	---
Carboxylated by Koch method[d]	1.6	1.8	3.3	6.0	8.3	9.8	11.0	12.2	13.4	16.7	14.4	1.6

[a]By mass spectrometry (1), based on relative intensity of fragment $[CH_3\text{-}(CH_2)_m\text{-}CH\text{-}COOH_3 + H]^+$ and assuming that it is not affected by *n* (branch carbon number).

[b]Olive esters used for 0%, 0.05%, 0.45%, 0.9% and 1.8% Ph_3P (Table II, Runs 14, 13, 12, 11 and 9); methyl oleate for 4.4% Ph_3P.

[c]Data from Reference (1).

[d]Method of Roe and Swern (19); sample supplied by F. Scholnick, Eastern Regional Research Laboratory, Philadelphia, Pa.

strong carbonyl band at 1730 cm^{-1}, which was partially resolved from that of the ester carbonyl at 1750 cm^{-1}. The rest of the spectrum was the same as that of oleate, except that the C-H stretching band at 3020 cm^{-1} and the *cis* C=C band at 1655 cm^{-1} were absent. Dimethoxymethyl [3] was characterized by C-O-C stretching vibration bands at 1060-1080 and at 1120 cm^{-1}. Hydroxymethylstearate [4] had a stretching vibration OH band at 3450 cm^{-1} and a medium -C-OH stretching band for primary alcohol at 1040 cm^{-1}. The acetoxymethyl derivative [6] had a strong C-O stretching vibration band at 1240 cm^{-1}, characteristic of acetates (20), which disturbed the three-band pattern of methyl esters of fatty acids at 1170, 1200 and 1250 cm^{-1}. A medium stretching band was also evident at 1040 cm^{-1}. Carboxystearate [5] showed the very broad bonded OH stretching absorption at 2700-3300 cm^{-1} accompanied by a new strong carbonyl band at 1720 cm^{-1} separated from the ester band at 1750 cm^{-1}. In the carbomethoxy derivative [7] the CO bands are not separated and absorb together between 1730 and 1750 cm^{-1}.

The NMR spectrum of methyl formylstearate [2] showed the following bands (in τ values relative to tetramethylsilane): 9.15 (CH_3), 8.75 (CH_2), 7.70 ($CH_2\alpha$ to $COOCH_3$), 6.35 (OCH_3) and 9.55 (CHO). The spectrum for the acetoxymethyl derivative [6] showed an acetyl band at 7.98 τ. The spectrum of the carbomethoxy derivative [7] was the same as that of formylstearate except that the CHO band at 9.55 τ was absent and the OCH_3 band at 6.35 τ was double in intensity.

Previously (1) we found that mass spectrometry was most useful to determine the location of the branch on the C-18 chain of carbomethoxystearate but not of the formyl or hydroxymethyl derivatives. Mass spectral analysis of [7] confirmed its identity as approximately an equal mixture of the 9- and 10-branched isomers. The fragmentation pattern showed peaks at mass 200 and mass 186 with respective intensities of 35.06 and 41.35 relative to the base peak of mass 98. Peaks 200 and 186 correspond to fragments $[CH_3\text{-}(CH_2)_m\text{-}CH\text{-}COOCH_3 + H]$ for m = 7 and 8 (1). Comparison with synthetic standards (methyl 8- to 13-carbomethoxy stearate) led to an estimate of 46% 9- and 54% 10-isomers present in methyl carbomethoxystearate [7].

The carbomethoxystearates from methyl oleate hydroformylated with Rh-Ph_3P were compared with those from oleate hydroformylated with $Co_2(CO)_8$ (1) and also those carboxylated by the Koch reaction (19). Mass spectral analyses were made of the carbomethoxy derivatives of various formyl products prepared with Rh catalyst containing different concentrations of Ph_3P. Table III shows that the proportion of 9- and 10-isomers decreased as the concentration of Ph_3P decreased. At concentrations ranging from 0.45 to 1.8% Ph_3P, the 9- and 10-isomers were present in the range of 83% to 94%. In the absence of Ph_3P the 9- and 10-isomers represented only 52% of the total formyl product in the partially hydroformylated sample (Table I, Run 14). Furthermore, IR analysis showed the presence of 26.5% isolated *trans* unsaturation in this product. Therefore, an important effect of Ph_3P in the Rh catalyst system is its strong inhibition of double bond isomerization during hydroformylation of methyl oleate.

The branch in oleate hydroformylated with $Co_2(CO)_8$ is distributed between C-6 and C-13 and peaks at C-11. In the oleate carboxylated by the Koch reaction the branch is even more scattered and ranges between C-6 and C-17 with a maximum at C-15. Because appropriate carbomethoxystearate standards were not available, the results for isomers with branches outside the range C-8 to C-13 are only approximations and should be interpreted with caution. Nevertheless, TLC also showed the presence of a complex mixture of isomers in the products of $Co_2(CO)_8$ hydroformylation (1) and of Koch carboxylation (Fig. 1). Evidently these reactions lead to considerable double bond isomerizations resulting in complex mixtures in which the 9- and 10-carbomethoxy isomers constitute only a small proportion of the total.

Catalyst Studies

Evidence for the presence of a soluble Rh carbonyl Ph_3P catalyst in filtered crude hydroformylation products was obtained by IR and analyses for Rh by atomic absorption spectroscopy. These analyses also showed that the soluble Rh catalyst was concentrated in the distillation residues from hydroformylated oleate. IR studies showed the presence of free and complexed Ph_3P by characteristic bands at 700 and 745 cm^{-1}. Less intense bands at 1590 and

3050 cm^{-1} were only visible when high concentrations of Rh catalyst and Ph_3P were used. Atomic absorption spectroscopy gave values for Rh which increased with the amount of supported Rh catalyst used. Values of 78, 81 and 160 ppm Rh resulted in runs carried out with 1.0%, 2.0% and 4.0% added catalyst (as 5% Rh on $CaCO_3$). Distillation residues from these hydroformylated products gave values ranging from 330 to 370 ppm Rh.

The soluble Rh-Ph_3P complex is an active hydroformylation catalyst. Hydroformylation was almost complete when methyl oleate was mixed 1:1 or 2:1 with filtered crude hydroformylated reaction products containing 160 and 170 ppm of Rh and reacted with CO + H_2 (2000 psi) at 110 C for 6 hr. Results were similar when a distillation residue (330 ppm Rh) from hydroformylated oleate was used as catalyst in the presence of added Ph_3P.

A soluble Rh complex was also prepared by the treatment of 5% Rh on C catalyst with Ph_3P in the absence of unsaturated substrate with toluene under hydroformylation conditions. The crude complex isolated after removal of solvent contained 3.5% Rh and exhibited a characteristic metal carbonyl band at 1980-1990 cm^{-1} and Ph_3P bands at 700 and 745 cm^{-1}. This complex was fat-soluble and very active as a hydroformylation catalyst. Its addition at the rate of 1.4% to methyl oleate, together with 0.9% Ph_3P, resulted in almost complete hydroformylation within approximately 1 hr (110 C, 2000 psi H_2 + CO). Purification and further characterization of the active Rh complex are now in progress.

DISCUSSION

The complexity of branched C_{19} products from conventional hydroformylation of methyl oleate is due to the double bond isomerization catalyzed by cobalt carbonyl (1,5). Carboxylation with CO and H_2SO_4 by the Koch reaction (19) yields an even more complex mixture of isomeric carboxy acids from oleate.

The remarkable selectivity of the Rh-Ph_3P hydroformylation catalyst used in this study can be attributed to the effective elimination of such side reactions as isomerization and hydrogenation of the double bond, reduction, oxidation and condensation of formyl products. Ph_3P plays an important role in inhibiting these side reactions. At the same time it provides a solubilizing ligand and increases the activity of the Rh-supported catalyst. By preventing double bond isomerization the Rh-Ph_3P catalyst converts monounsaturated fatty acids and esters into essentially only two isomers with formyl groups attached to the original unsaturated carbons. Oleic oils have been effectively hydroformylated with this catalyst to give mainly 9- and 10-formyl esters, acids or triglycerides. Other monounsaturated fatty acids, such as erucic acid, as well as polyunsaturated fats, have also been hydroformylated with the Rh-Ph_3P catalyst (unpublished work). The aldehyde products can be readily oxidized to the carboxystearic or reduced to the hydroxymethylstearic derivatives.

Crude formyl products and the residue left after their vacuum distillation showed evidence of a soluble rhodium compound, which catalyzed hydroformylation of methyl oleate. An active Rh carbonyl Ph_3P complex was also prepared by the reaction of Rh on C with Ph_3P in the absence of substrate under hydroformylation conditions. The catalytic activity and selectivity of this soluble Rh complex differ from that derived from $(Ph_3P)_3RhCl$, which is a known homogeneous hydroformylation catalyst (9-14). We found that $(Ph_3P)_3RhCl$ not only is a weak catalyst for the hydroformylation of methyl oleate but also can reduce formylstearate to hydroxymethylstearate when the reaction is carried out at 180 C with a 2:1 H_2 + CO gas mixture. This RhCl complex is similar in this respect to $Co_2(CO)_8$, which also converts methyl oleate into hydroxymethyl esters at 175-190 C (1-3). In contrast to these soluble RhCl and $Co_2(CO)_8$ catalysts, the Rh-Ph_3P catalyst system is highly selective for the formation of formyl esters and is more active. Even at 180 C with a 2:1 H_2 + CO gas mixture formyl products were obtained in high yields (Table II, Run 4).

The formyl, carboxy and hydroxymethyl products prepared in this study should provide various outlets for industrial utilization. These oxygenated derivatives with essentially only two positional isomers may lead to polymers of more uniform, homogeneous and predictable properties than those made from the complex isomeric products of conventional hydroformylation and carboxylation of methyl oleate. Studies are now under way in this laboratory to determine whether or not the simple branched formyl product from the selective Rh-Ph_3P catalyst system is indeed superior for various industrial applications.

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