Hydroformylation with Recycled Rhodium Catalyst and One-Step Esterification-Acetalation: A Process for Methyl 9(10)-Methoxymethylenestearate from Oleic Acid[1]

R.A. AWL, E.N. FRANKEL, and E.H. PRYDE, Northern Regional Research Center,
ARS, USDA, Peoria, Illinois 61604

ABSTRACT

Previous studies on hydroformylation of methyl oleate with rhodium and triphenylphosphine or triphenylphosphite have led to a laboratory process for recycling the precious metal catalyst. Another catalyst recycling process has now been studied as the basis for converting commercially available oleic acid into the enol ether of methyl formylstearate. The process involves one-step esterification-acetalation of formylstearic acid made by hydroformylating oleic acid with rhodium and triphenylphosphine. Esterification-acetalation is done in a recycling system with methanol, an acid-exchange resin for catalysis, and molecular sieves to remove water from the reaction mixture. The dimethyl acetal methyl ester formed from formylstearic acid is thermally cracked and distilled in one pot to produce the enol ether, methyl methoxymethylenestearate. The soluble rhodium catalyst in the distillation residue is combined with the insoluble catalyst from filtration and recycled for hydroformylation. The product methoxymethylenestearate is a versatile and stable derivative for various potential industrial applications.

INTRODUCTION

Hydroformylation of methyl oleate with Rh-Ph_3P catalyst (1) produces a potentially important industrial chemical (2), methyl 9(10)-formylstearate (Fig. 1, IIa). Reactions of this intermediate, investigated at the Northern Laboratory, include acetalation to different acetal esters (3), oxidation to carboxystearate (4), hydrogenation to hydroxymethylstearate (5,6), and reductive alkylation to C-19 amino acids (7). Applications for the various derivatives of IIa or their polymers include plasticizers for polyvinyl chloride (3,6,8), modifying agents for polyamides (7,9), bonded stationary phases for chromatography (10), and other uses currently being investigated.

Frankel reported (1,11) that the supported Rh catalyst recovered by filtration of the solid support and that the soluble Rh in the distillation residue were active and could be recycled. Subsequently, Friedrich et al. (12) developed a laboratory batch process and estimated processing costs at 13 cents/lb to produce distilled formyl ester IIa from methyl oleate with recycled Rh catalyst. In their procedure, methyl oleate is required for hydroformylation because the product is separated from the catalyst by distillation $(PhO)_3P$ is substituted for Ph_3P as a ligand because it is cheaper. However, their substitution results in a less selective catalyst (presence of C-7 to C-12 positional isomers; Frankel and Thomas, unpublished work).

This paper deals with a study aimed at developing a hydroformylation process for oleic acid, a cheaper, more readily available starting material than methyl oleate. However, the product must be distillable to recover the catalyst and should be in a form more easily distilled than formyl acid II (Fig. 1). Formyl ester IIa is lower boiling, but esterification also causes partial acetalation. The acetal ester III and its enol ether IV are also easily distillable, are not decarbonylated, are more stable than IIa, and are suitable intermediates for synthesis. Therefore, a one-step esterification-acetalation was developed to convert the formyl acid II to acetal ester III or enol ether IV.

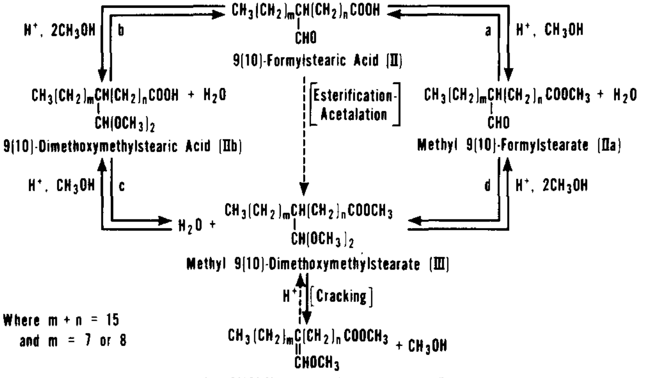

FIG. 1. Reactions and compounds

EXPERIMENTAL PROCEDURES

Materials and Methods

Commercial oleic acid (Hercules Pamolyn 100; 96% by gas-liquid chromatography [GLC]) was used as purchased. Commercial catalyst and reagents were 5% Rh:Al_2O_3 (Engelhard Industries, Newark, NJ); Ph_3P, $(PhO)_3P$, $(Ph_3P)_3RhCl$, and $RhCl_3$ (Strem Chemicals, Inc., Danvers, MA; $CH(OCH_3)_3$ (98%; Aldrich Chemical Co., Inc., Milwaukee, WI); and Linde 3A molecular sieves, 1/16 in. pellets, (Ventron Corp., Danvers, MA). The cation exchange resins, AG50W-X4 (200-400 mesh, H^+ form; Bio-Rad Laboratories, Richmond, CA) and Amberlyst 15 (bead-type 10-50 mesh, H^+ form; Rohm and Haas Co., Philadelphia, PA), were treated before use as described below.

General Procedures

Hydroformylations with Rh catalysts were performed, as described earlier (12), with 900 g of oleic acid under conditions given in Table I. Catalyst from distillation residues and supports was recovered essentially as before (12). Analytical methods were described elsewhere (3,8). The ion-exchange resins AG50W-X4 and Amberlyst 15 were washed repeatedly with hot CH_3OH until the filtrates were no longer colored and then dried in vacuo at 105 C. Amberlyst 15 was also treated with hot, concentrated H_2SO_4 (13).

Small-Scale Esterification-Acetalation

A CH_3OH solution of crude formyl acid II (100-g aliquot) was refluxed in a three-necked flask fitted with a N_2

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[1] Presented at the AOCS meeting, Cincinnati, September 1975.

TABLE I

Process Hydroformylation of Oleic Acid

Process cycle[a]	Catalyst system[b]	Catalyst wt (g)	Hydroformylation conditions: Temp (C)	Press (psi)	Time (hr)	Uptake (psi)	Percent formyl acid II[c]: By GLC[d]	By AV[e]
			Process run 1					
First	Commercial: 5% $Rh:Al_2O_3 + Ph_3P$	9.0	120-123	800-950	4.4	2535	98.6	---
Second	ARC + Ph_3P	8.6	125-130	850-950	3.5	2730	---	99.6
Third	ARC + Ph_3P	8.4	125-130	700-950	4.0	2685	93.7	100
			Process run 2					
First	ARC[f] + $(PhO)_3P$	9.0	120-124	700-950	1.8	2555	96.5	97.7
Second	ARC + $(PhO)_3P$	10.4	120-124	700-950	5.5	2560	96.6	96.9
Third	ARC + $(PhO)_3P$	14.9	125-126	790-950	1.8[g]	ca. 95[g]	3.2	---

[a] Cf. Figure 2.

[b] Ph_3P = triphenylphosphine (4.5 g); $(PhO)_3P$ = triphenylphosphite (9.0 g); ARC ≐ activated Rh catalyst (cf. Fig. 2, step 5).

[c] Cf. Figure 1. Crude formyl acid II was obtained in 100% yield in every cycle but cycle 3 of run 2.

[d] All samples were methylated (CH_2N_2) and analyzed as formyl ester IIa (Fig. 1). GLC = gas-liquid chromatography.

[e] AV = acid value.

[f] Commercial 5% $Rh:Al_2O_3$ was roasted before use; as in Figure 2, step 5.

[g] Ca. 60 psig uptake occurred in first 47 min.

TABLE II

Esterification-Acetalation of Crude 9(10)-Formylstearic Acid with Mineral Acids or Acid Exchange Resins

Catalyst		Reaction conditions			GLC Analysis (%)[b]				Acid value	Crude yield
Run	(%, w/w oil)	Medium[a] (ml/g)	Temperature	Hours	MEE	MFS	DMA	Total	as % FSA[c]	(%)[d]
Mineral acids										
1	HCl(2)	CH_3OH:TMOF(2:0.8)	Ambient	2	2.0	0.6	95.3	97.9	---	f
			Ambient	4	0.8	0.9	90.0	91.7	0.2[e]	93.8
2	H_2SO_4(2)	CH_3OH:TMOF(2:0.8)	Ambient	4	2.5	2.4	91.6	96.5	0.2[e]	100
3	H_2SO_4(7)	CH_3OH:TMOF(2:0.8)	Ambient	2	1.7	1.7	87.8	91.2	---	f
			Ambient	4	0.7	1.5	91.3	93.5	0.3[e]	93.7
4	H_2SO_4(7)	CH_3OH(2.5)	Reflux	2	1.5	8.4	84.3	94.2	0.1[e]	84.9
5	H_2SO_4(0.5)	$CH_3OH:CHCl_3$(2:1.7)	Azeotropic[g] distillation	9	2.8	14.5	81.3	98.6	1.6[e]	87.4
Catalytic resins										
6	AG50W-X4(35)	CH_3OH(2.5)	Reflux	2	11.8	29.4	52.3	93.5	---	f
			Reflux	4	6.4	28.7	61.8	96.9	---	f
					4.9	13.8	75.4	93.8	5.6	95.4
7	Recycled AG50W-X4(35)	CH_3OH(2.5)	Reflux	4	3.3	27.9	65.9	97.1	---	f
					35.9	20.8	40.4	97.1	1.0	102
8	Amberlyst 15 (35)	CH_3OH(3.5)	Reflux	4	1.6	20.7	74.6	96.9	17	f
			Reflux	6	1.7	22.0	73.2	96.9	10	f
					46.9	15.0	35.1	96.2	1.7	98.2
Resins and molecular sieves 3A										
9	Recycled AG50W-X4(20)	CH_3OH(3.5)	Ambient	5	2.7	14.2	77.4	94.3	---	f
					14.9	11.1	67.3	93.3	37	94.4
10	Recycled AG50W-X4(20)	CH_3OH(3.5)	Reflux	1	15.2	20.2	62.5	97.9	---	f
			Reflux	2	5.9	16.7	69.5	91.8	---	f
					19.8	16.6	59.3	95.7	12	98.5
11	Recycled AG50W-X4(20)	CH_3OH(3.5)	Reflux	3	8.2	17.8	68.7	94.7	---	f
					69.4	19.0	8.1	96.5	1.6	99.8

[a] TMOF = trimethyl orthoformate.

[b] Cf. Figure 1. MEE = methyl enol ether IV; MFS = methyl formylstearate IIa; DMA = dimethyl acetal III; GLC = gas-liquid chromatography. (Because of differences between hydroformylation runs, the theoretical percent DMA was: with mineral acids, 90.7; with catalytic resins, 91.9; and with resins and sieves, 95.3.)

[c] Cf. Figure 1. FSA = formylstearic acid II.

[d] Based on GLC and corrected for percentage of enol ether IV and aldehyde IIa not converted to acetal III.

[e] Runs with mineral acid catalysts were neutralized with aqueous carbonate solutions and washed with water before the product was isolated.

[f] Product was not isolated. Analyses were made on samples of the reaction solution.

[g] Ternary azeotrope (BP 52.6 C): 4% H_2O, 81% $CHCl_3$, 15% CH_3OH (14).

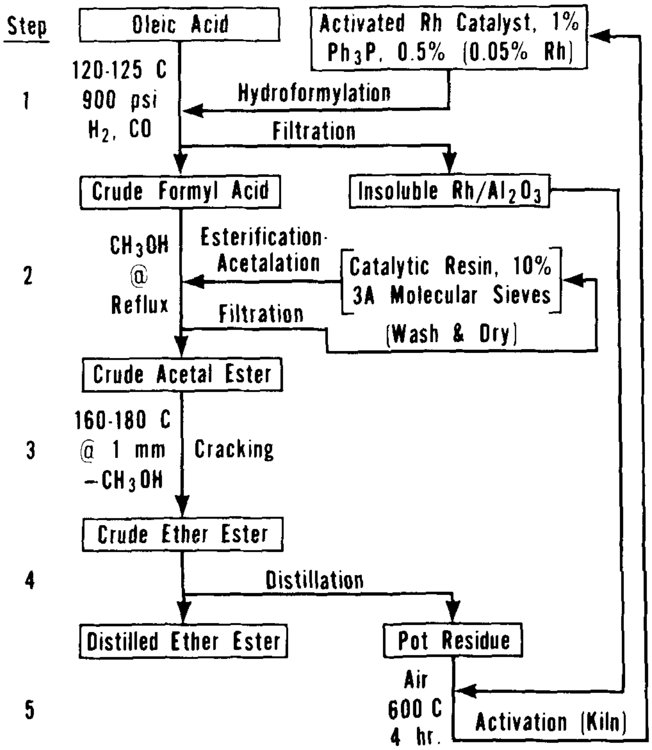

FIG. 2. Process flow diagram (cf. Fig. 1).

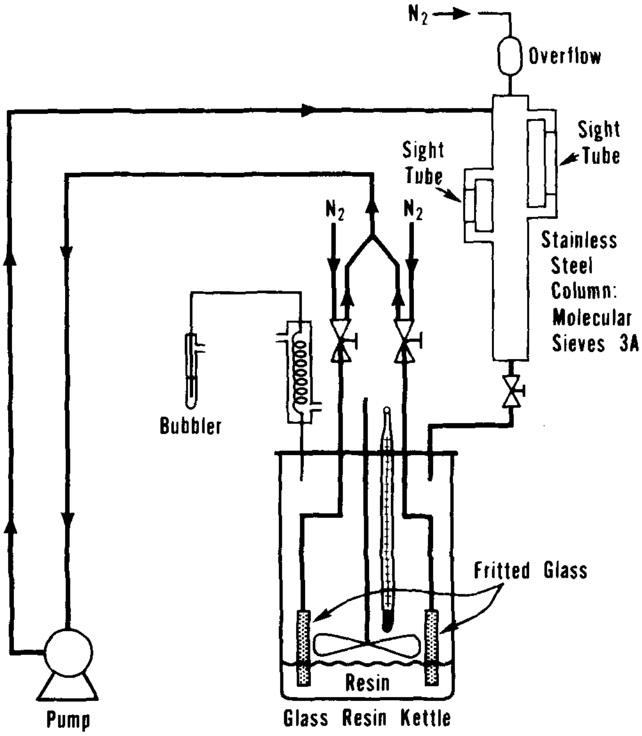

FIG. 3. Process esterification-acetalation apparatus.

capillary, mechanical stirrer, and Friedrich condenser and connected to a bubbler (Table II). For reactions using molecular sieves (125 g), a glass column (2.1 cm outside diameter x 51 cm) with a Teflon stopcock was employed. After reaction, the air-dried molecular sieves were transferred to an evaporating dish and regenerated in a vacuum oven.

When mineral acid was used, it was neutralized with dilute $NaHCO_3$ before isolation and analysis by GLC of the crude product. After removal of CH_3OH with a rotary evaporator, the liquid residue was washed, dried with $MgSO_4$, and filtered. When ion-exchange resin was used, the reaction mixture was only filtered and CH_3OH was removed with rotary evaporator. The washed resin was dried at 105 C in vacuo before reuse.

Process Investigations

Esterification-acetalation, Step II (Fig. 2): A 3-liter glass resin kettle was connected to a microbellows pump (1 in. diameter s.s. bellows; max. recommended rate, 6 liters/hr; Research Appliance Co., Gibsonia, PA) and a column for molecular sieves (Fig. 3). This column was constructed from two stainless-steel pipe sections to permit disassembling after the reaction. It was reassembled with a U-tube to fit inside an oven to regenerate the molecular sieves. The loosely packed molecular sieves were supported on a plug of glass wool over wire cloth at the bottom of each column section. Glass tubing was attached between sidearms on the column to monitor the liquid level during the reaction. This tubing could be removed and the sidearms plugged with screw caps before regeneration of the molecular sieves in situ at 320 C. For automation purposes, liquid level sensors could be attached to the sight tubes and used to operate both the pump and a solenoid valve (in place of the stopcock). Two gas dispersion tubes were alternately switched between the pump and N_2 line to aid filtration and circulation of solution to the column.

The reaction system was purged with N_2, and 2 liters of CH_3OH were added to the kettle containing 100 g of dry resin. The column containing 1270 g of dry molecular sieves was filled with ca. 500 ml CH_3OH pumped from the kettle, drained, and refilled several times. Crude formyl acid II (992 g) was transferred to the kettle with CH_3OH (150 ml total) and this mixture was stirred mechanically. A slight increase in the solution temperature was observed. The column was allowed to drain while the reaction was heated to reflux (ca. 45 min). Then, with a slow, constant stream of liquid flowing from the column, solution was pumped to the column intermittently so that the liquid meniscus was kept between the sight levels above the molecular sieves. The column was drained after 4.5 hr. Removal of solvent from a sample left a liquid residue with an acid value of 14.3 (8.0% as acid II). Additional CH_3OH (500 ml) was added to the kettle after filling the column from the kettle. The reaction mixture was again stirred and refluxed, and the column was slowly drained and refilled. After refluxing had resumed, the liquid level in the column was maintained as before by intermittent pumping and controlled drainage. After the reaction mixture was refluxed an additional 2 hr, the column was allowed to drain completely and the reaction mixture was cooled. A sample of the residue gave an acid value of 5.2 (2.9% as acid II). The product solution was then pumped from the kettle to a storage bottle, and the column was washed 4 times with 500-ml portions CH_3OH. Each column wash was drained into the kettle and stirred for 5 min before pumping it to another storage bottle. CH_3OH was removed on a rotary evaporator at 65-70 C under reduced pressure to obtain 1117 g of crude ester acetal III from both the product solution and column wash.

Resin in the kettle was dried for recycling by evacuating and heating the contents at 105-110 C. Molecular sieves were regenerated in situ by heating the column at 320 C with dry N_2 flowing slowly through the column to a dry-ice trap until no further liquid was collected (ca. 6 hr).

Cracking and distillation: Crude acetal III from esterification-acetalation of acid II was heated to 150-180 C at 1-2 mm for 1.5 hr, and the generated CH_3OH was collected in two dry-ice traps. Completion of the cracking was determined by GLC (<0.5% acetal III) and the wt of CH_3OH collected.

TABLE III

Process Study Yields and Analyses[a]

	First:Catalyst, Rh-Ph$_3$P[b]			Second:Catalyst, Rh-(PhO)$_3$P[c]	
Process run cycle	No. 1	No. 2	No. 3	No. 1	No. 2
Crude DMA (III)[d]					
Yield (%)[e]	101	99.8	97.4	99.1	98.9
Acid value	1.7	1.0	6.3	3.0	6.1
GLC analysis:[d]					
MEE (%)	10.2	28.3	5.2	33.8	17.5
MFS (%)	21.7	7.5	9.4	13.1	14.7
DMA (%)	60.4	59.2	83.1	50.9	65.5
Total	92.3	95.0	97.7	97.8	97.7
Crude MEE (IV)[d]					
Yield (%)[e]	99.7	101	99.8	100	99.8
GLC analysis:[d]					
MEE (%)	82.8	86.4	---	87.4	83.2
MFS (%)	11.4	7.6	---	10.3	13.6
DMA (%)	1.6	1.1	---	0.2	0.2
Total	95.8	95.1	---	97.9	97.0
Distillation:					
Residue (g)	52.5	48.5	46.4	39.7	83.4
Distillate (g)	993.6	1008.4	967.6	1005.4	953.9
Volatiles (g)	2.0	---	14.2	4.9	3.4
Recovery (%)	97.4	97.8	99.4	98.8	99.6
Main fraction:					
Distilled @ C/mm	160-2/ 0.1	153-8/ 0.004	126-63/ 0.3-0.1	148-66/ 0.15	151-66/ 0.1
Wt (g)	751.8	973.6	905.5	874.9	869.8
Acid value	6.8	---	< 7	9.0	7.2
GLC analysis:[d]					
MEE (%)	85.5	88.2	90.9	88.9	83.9
MFS (%)	12.4	6.7	6.9	9.6	12.3
DMA (%)	0.0	0.2	0.0	0.0	0.3
Total	97.9	95.1	97.8	98.5	96.5

[a] Cf. Figures 1, 2, and Table I.

[b] Triphenyl phosphine (4.5 g added at start of each cycle). Commercial 5% Rh:Al_2O_3 (9.0 g) was used for the first cycle; subsequent cycles, recycled catalyst (cf. Table I).

[c] Triphenyl phosphite (9.0 g at start of each cycle). First cycle used activated (roasted) 5% Rh:Al_2O_3 (9.0 g); subsequent cycle, recycled catalyst..

[d] MEE = enol ether IV; MFS = formylstearate IIa; DMA = dimethyl acetal III; GLC = gas-liquid chromatography.

[e] Calculated from GLC analyses.

Crude enol ether IV from cracking of crude acetal III was distilled until the pot temperature reached 265 C at 0.2 mm. Analyses and distillation data are given in Table III. For catalyst reactivation, the pot residue was combined with the insoluble catalyst fraction collected by filtration in step 1 (Fig. 2).

RESULTS AND DISCUSSION

One-Step Esterification-Acetalation (Fig. 1)

Conversion of 9(10)-formylstearic acid (II) to its methyl acetal ester (III) can occur either by pathway a-d or by pathway b-c. Since both esterification by pathway a or c and acetalation by pathway b or d are catalyzed by acid, are reversible, and generate water, they should be driven to completion by removal of water. Acetalation is faster than esterification and is favored by lower temperature (15,16). On the one hand, acetal acid IIb will form quickly at room temperature and its concentration will increase until equilibrium is established. On the other hand, formyl ester IIa will form relatively slowly unless the reaction temperature is raised. Therefore, efficient conversion of formyl acid II to its acetal ester III requires external heating, a strong acid catalyst, and an efficient dehydrating agent.

Esterification-acetalation of crude formyl acid II in one step was investiagated first on a small scale to optimize conditions and reagents for a large-scale process. Conversion was most complete with mineral acid catalysts and with $CH(OCH_3)_3$ as a water scavenger (Table II, runs 1-3). However, $CH(OCH_3)_3$ would be too expensive for an economic process because it cannot be recycled. Azeotropic distillation was considered as an alternative means of removing the water. One of the several azeotropic mixtures reported (14) for CH_3OH was tried (run 5), but the reaction was too slow and acetal conversion relatively low. A comparison of runs 2-4 suggests that an acceptable conversion of formyl acid II to its acetal ester III is possible without $CH(OCH_3)_3$ if the reaction is refluxed >2 hr with a high concentration of H_2SO_4. However, mineral acids would also be impractical for a process because of their corrosive nature and would require neutralization and washing steps which may inactivate and remove some soluble Rh catalyst. For these reasons, investigations were made with two strong acid exchange resins, which can be removed by filtration after the esterification-acetalation. The dry resins may also serve as drying agents, albeit ineffectively at higher temperatures. Both resins could be recycled and catalyzed conversions of 94-97% if the reaction mixture was refluxed for 6 hr (cf. Table II, runs 6-8). Although esterification was 90-99% complete after 4-6 hr of refluxing, conversions to the acetal with these resins was only ca. 80-85% complete (Table II, runs 6-8). For a process, complete acetalation was desirable but not essential, whereas esterification was essential to permit distillation of the product.

Both ester (17,18) and acetal (19,20) conversions are reportedly improved by the use of either molecular sieves with strong acids or catalytic dehydrators, a synergetic combination of ion exchange resin and drying agent. Patwardhan and Dev (21) claimed that Amberlyst 15 with

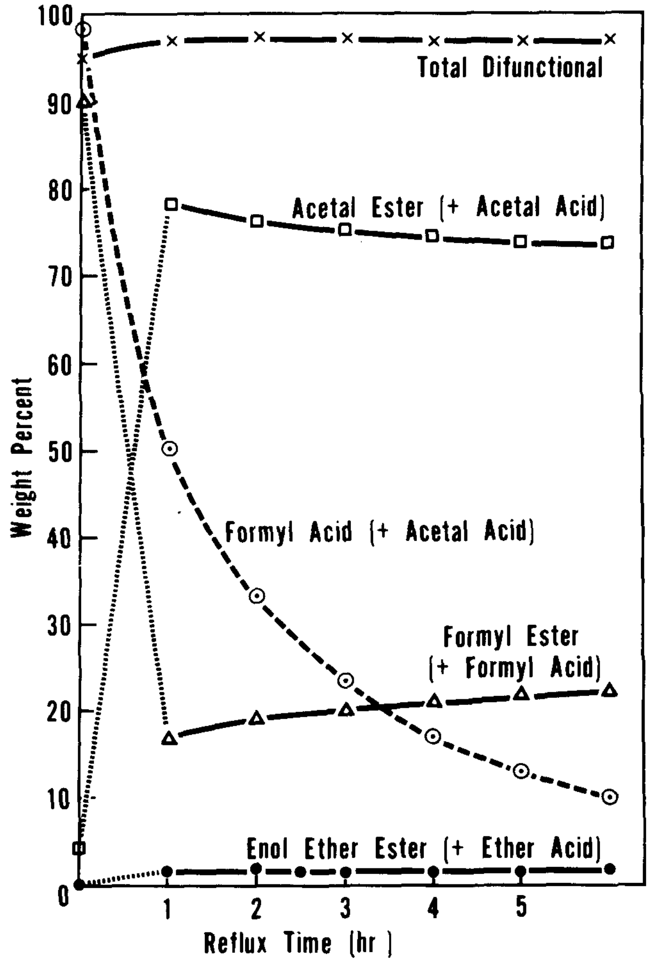

FIG. 4. Esterification-acetalation of crude 9(10)-formylstearic acid with Amberlyst 15 resin in methanol. Solid lines indicate determinations by gas-liquid chromatography on methylated (CH_2N_2) samples; dashed line, determinations by acid values (calculated as percent formyl acid II). Dotted lines indicate that because of methylation, initial concentrations for the ester derivatives actually represent concentrations of their acids (cf. Fig. 1).

orthoformate is a superior catalytic resin for the preparation of enol ethers and acetals. In view of these reports, a system combining catalytic resin and molecular sieves was examined. A portion of the reaction mixture was continuously filtered and circulated between a column of molecular sieves and the reaction kettle containing the resin. With this resin-sieves combination (Table II, runs 9-11), satisfactory esterification was achieved after 3 hr refluxing, but acetal conversion improved only slightly. This reaction system was considered the most suitable and was adopted for our process studies.

Changes in composition of the reaction mixtures during esterification-acetalation were followed by acid values and by GLC analyses (Fig. 4). Acid values showed the progress of esterification, which is relatively slower and less sensitive to the generated water than acetalation. GLC data (after sample methylation with CH_2N_2) indicated initially rapid acetalation followed by a small decrease in acetal concentration due to hydrolysis by the increasing concentration of water (Fig. 2, pathways b and d). Because samples for GLC were methylated, the concentration of formyl ester IIa corresponds initially to that of formyl acid II minus the acetal acid IIb as represented by the concentration of acetal ester III (Fig. 4). The contribution of acetal acid IIb appears to be relatively important in earlier stages of the reaction but becomes less important as the reaction progresses. Because no means were available for readily distinguishing between formyl acid and acetal acid, the percent acidity was calculated as formyl acid. The difference in mol wts (312 vs. 358) of these two compounds then results in a maximum error of ca. 15%.

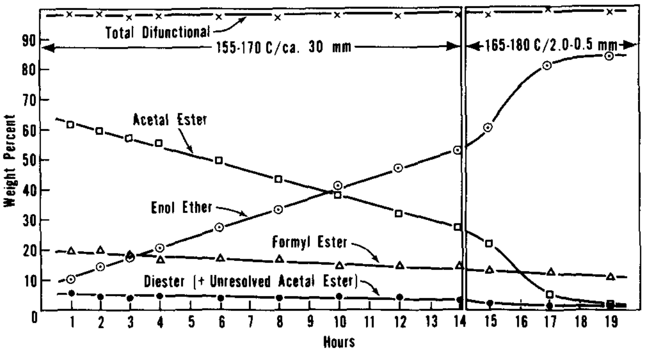

FIG. 5. Effects of temperature and pressure on the conversion of dimethyl acetal III to enol ether IV with soluble Rh catalyst (cf. Fig. 1).

Although CH_2N_2 is known to react with many formyl groups (22), perhaps because of steric hindrance, no such reaction was noted here. No differences were apparent in the chromatograms of formyl ester, acetal ester, and enol ether treated with CH_2N_2 compared to those not treated with CH_2N_2.

The sharp change in composition observed in the isolated product is due to additional esterification-acetalation and acetal cracking during solvent removal. For example, the percent composition of isolated product versus that of the final (6 hr) solution in Figure 4 was: ether ester IV, 47.0 vs. 1.7; formyl ester IIa, 15.0 vs. 22.0; and acetal ester III, 34.5 vs. 73.2. In the absence of acid catalyst under anhydrous conditions at temperatures lower than ca. 70 C, no cracking is observed. Apparently the soluble Rh complex is sufficiently acidic to catalyze cracking and to esterify further during solvent removal and distillation.

Compositional changes were studied during distillation of crude acetal ester III. The combined effects of Rh catalyst, high temperature, and reduced pressure cause rapid cracking of crude dimethyl acetal III to enol ether IV (Fig. 5). Because IV is stable and just as useful as III (3), cracking crude acetal was carried out subsequently before distillation to eliminate problems caused by CH_3OH generation.

Hydroformylation-Esterification-Acetalation

Previous work demonstrated that hydroformylated methyl oleate is not acetalated in alcohol with nonchloride containing $Rh\text{-}Ph_3P$ catalysts (1). However, acetalation of steroid ketones was observed with $(Ph_3P)_3RhCl$ in CH_3OH saturated with H_2 (23). Therefore, we determined whether oleic acid would undergo hydroformylation-esterification-acetalation in one step with Rh chloride catalysts.

With synthesis gas (H_2 + CO), the complex $(Ph_3P)_3RhCl$ catalyzed partial acetalation of the formyl ester IIa (Table IV, run 12). The yield of acetal ester III from oleic acid was increased, however, if the hydroformylation was followed by a treatment with H_2 for 1-4 hr. Without the H_2 treatment, a mixture of $RhCl_3$ and Ph_3P in a 1:3 molar ratio was just as effective as the corresponding complex (run 12 vs. run 14). This mixture was less effective in a 1:6 molar ratio but gave higher concentrations of acetal if H_2 treatment followed the hydroformylation (run 15). The most complete acetalations occurred in the presence of $CH(OCH_3)_3$, but in this case no improvement resulted from H_2 treatment. IR analyses indicated only partial esterification and that the product of run 15 with a high concentration of Ph_3P was esterified the most. Small amounts of free hydroxyl group, evident in all samples,

TABLE IV

Hydroformylation-Esterification-Acetalation of Oleic Acid[a]

		H_2 + CO[c]		H_2[d]	GLC analyses[e] (%)				
Run	Catalyst[b]	Temp (C)	Time (hr)	Time (hr)	MEE	MFS	DMA	Di	Total
12	$(Ph_3P)_3RhCl$	120	1	0	2.9	38.4	30.1	8.0	79.4[f]
				4	12.5	8.4	69.0	5.0	95.4
13	$(Ph_3P)_3RhCl$	110	5	0	2.4	56.7	35.9	3.1	98.1
				1	3.2	61.2	29.8	2.6	96.8
14	$RhCl_3 + Ph_3P(3)$[g]	110	6	0	1.9	54.8	38.0	1.6	96.3
15	$RhCl_3 + Ph_3P(6)$[h]	120	4.5	0	3.2	65.6	25.8	0.6	95.2
				1	3.6	43.5	41.5	7.8	96.4
16	$RhCl_3 + Ph_3P(3) + CH(OCH_3)_3$	110	1	0	3.0	17.7	74.9	2.4	98.0
				2	4.5	19.2	72.4	2.3	98.4

[a] Hasteloy autoclave (300 ml): 50 g oleic acid + 66 g CH_3OH.

[b] 0.5 mol % Rh catalyst.

[c] Initial pressure: 2000 psig (1:1 H_2 + CO).

[d] After flushing out synthesis gas: 50-100 psig/75-80 C.

[e] Gas-liquid chromatographic analyses performed on methylated (CH_2N_2) samples. MFS = methylformylstearate; DMA = dimethyl acetal of MFS; MEE = enol ether from DMA; Di = diformylstearate or polar material. Also present: 1-3% stearate.

[f] Hydroformylation was incomplete; oleic acid is also present.

[g] 1.5 mol % (3 mol Ph_3P/mol $RhCl_3$).

[h] 3.0 mol % (6 mol Ph_3P/mol $RhCl_3$).

indicated partial hydrogenation of the formyl group. These Rh chloride catalysts were not considered practical for our process because of (a) incomplete conversions obtained with oleic acid, (b) partial hydrogenation of aldehydic products, and (c) corrosive effect on stainless-steel autoclaves from any HCl generated.

Process Investigations

The feasibility of a process (Fig. 2) for preparing enol ether IV (Fig. 1) from oleic acid with recycled Rh catalyst was tested through three cycles. No loss in the activity of recycled Rh catalyst was apparent when Ph_3P was the ligand (Table I, run 1). However, when $(PhO)_3P$ was substituted for Ph_3P and Amberlyst 15 for AG50W-X4, the Rh catalyst became inactive after the second cycle (Table I, run 2). Apparently, Ph_3P is a better ligand than $(PhO)_3P$ in stabilizing the soluble Rh complex during the different processing steps. A colored fore-run consisting of 63% PhOH by GLC was collected during distillations when $(PhO)_3P$ was used. The recovered, reactivated catalyst increased wt and changed its physical character (hard, metallic black chunks were present instead of the usual fine, gray powder). These changes may be due to decomposition products from $(PhO)_3P$ reacting with the soluble Rh catalyst.

The successful completion of run 1 under conditions given in Figure 2 and Table I is also confirmed by product yields and analyses in Table III. Overall material balance was good. Crude product yields by GLC were >97%. Ester conversions for step 2 (Fig. 2) ranged from 96.5 to 99.5% according to acid values. Acetal conversions by GLC were all >80% and increased to >90% in the second and third cycles. In a typical run, 900 g of oleic acid produced ca. 1000 g of distilled enol ether IV as a clear, colorless liquid. A heart-cut (ca. 850 g) analyzed >85% enol ether IV and 5-10% formyl ester IIa.

The feasibility of a recycle, catalytic process to convert oleic acid to enol ether IV has been demonstrated. Improvements in the process should be possible (a) by the use of more effective ligand-cocatalyst than Ph_3P and $(PhO)_3P$, (b) by engineering designs to minimize catalyst handling losses, and (c) by further refinements in procedure and techniques. The product, enol ether IV, is a valuable intermediate for the preparation of various acetal esters (3).

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