Catalytic Carboxylation of Fats. Carboxy Acids and Esters from Monounsaturates[1]

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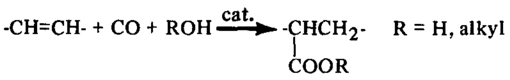
ABSTRACT

A highly selective catalytic, one-step synthesis converts oleic acid into 9(10)-carboxystearic acid in high yields (85-99%). Hydrocarboxylation with water and carbon monoxide under pressure (3000-4000 psi) is catalyzed with a mixture of palladium chloride and triphenylphosphine at 120-150 C with or without acetone or acetic acid solvents. Palladium supported on carbon is also an effective hydrocarboxylation catalyst in the presence of triphenylphosphine and HCl. Methyl 9(10)-carbomethoxystearate was prepared by catalytic carbomethoxylation of methyl oleate with methanol and carbon monoxide but in lower yields. The carboxystearic acids and esters consisted of the 9 and 10 isomers (87-94%) in approximately equal proportions. This catalytic carboxylation procedure is a more efficient route to carboxystearic acid and ester than the two-step hydroformylation-oxidation process reported previously. Carboxylated acids, methyl esters and triglycerides of potential industrial importance have been prepared.

INTRODUCTION

Carboxylic acid derivatives can be prepared by catalytic carboxylation of unsaturated compounds as follows:



$$\text{-CH=CH-} + \text{CO} + \text{ROH} \xrightarrow{\text{cat.}} \text{-}\underset{\displaystyle \text{COOR}}{\text{CH}}\text{CH}_2\text{-} \qquad \text{R = H, alkyl}$$

Hydrocarboxylation refers to the reaction of olefins with CO and H_2O to form carboxylic acids, and carboalkoxylation to the corresponding reaction with CO and an alcohol to form carboxylic esters. These reactions, known also under the originator's name—Reppe, have been reviewed by Bird (1) and by Falbe (2). In his original process, Reppe uses a nickel carbonyl catalyst under typical reaction conditions of 270 C and CO pressures of 200 atm. Since the work of Reppe, a large number of olefin carboxylation catalysts have been developed to permit milder reaction conditions and to minimize such side reactions as hydrogenation (from H_2 formed by the water-gas reaction, $CO + H_2O = CO_2 + H_2$), isomerization, polymerization and cleavage. Palladium catalysts are of particular interest because they are reportedly effective for the carboxylation of olefins at temperatures below 100 C.

The two main Pd catalyst systems include $PdCl_2$ and Pd complexes, e.g., $(Ph_3P)_2PdCl_2$, in alcoholic solution containing HCl. With $PdCl_2$, olefins react with CO in an alcoholic solution of HCl at 80 C and 100 atm to form saturated and unsaturated carboxy esters as well as acid chlorides (3,4). With Pd Ph_3P complexes, mono- and polyolefins react with CO in alcoholic-HCl solutions at 50-100 C and 300-700 atm to form mono-, di- and tricarboxyesters (5). The reaction catalyzed by Pd complexes has been developed commercially to prepare carboxylic acids and esters (6-8).

Various routes to carboxystearic acid and derivatives and many areas of applications have been reviewed recently (9). Among these routes, the Koch carboxylation of oleic acid by reaction with CO, H_2O and H_2SO_4 at atmospheric pressure is one of the more important. It yields a mixture of C_{19} diacids (10,11). This complex mixture of diacids consists of positional and methyl-branched isomers. Mass spectral analysis shows a wide distribution of isomers with carboxy branching centered around carbon-15 (12). Apparently methyl branching causes the Koch carboxystearic acid to be difficult to esterify (10,13).

Because of the greater reactivity of 9(10)-carboxystearic acid prepared by oxidation of selectively hydroformylated oleic acid (12,13), we have searched for a more direct catalytic route to this diacid. This paper describes a one-step synthesis of 9(10)-carboxystearic acid and methyl 9(10)-carboxystearate in high yields, by hydrocarboxyla-

TABLE I

Distillation of Crude Hydrocarboxylated Products

Substrates	Fractions	Temperature, C	P, mm Hg	Weight, g	Gas liquid chromatographic analysis,[a] %
Oleic acid[b] (run 1)					Carboxystearic acid
	1	155-170	0.02	5.5	44.9
	2	204-210	0.01	44.8	96.8
	3	201-210	0.01	43.4	96.8
	4	209-210	0.01	12.6	91.3
	Residue			5.3	
Methyl oleate[c] (run 4)					Methyl carboxystearate
	1	137-149	0.01	17.0	78.0
	2	178-184	0.01	59.7	96.0
	3	184-185	0.01	18.9	99.6
	4	192-217	0.01	10.1	85.6
	Residue			10.1	

[a]After methylation with diazomethane.
[b]Alembic distillation.
[c]Pot distillation.

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[1] Presented at the AOCS Meeting, Ottawa, September 1972.

TABLE II

Catalytic Hydrocarboxylation of Olive Fatty Acids with $PdCl_2$ and Ph_3P

Run no.[a]	$PdCl_2$, mol %	Ph_3P, mol %	H_2O, mol % excess	Solvent[b]	Additive (concentration)	Temperature, C	Final CO pressure, psig	Time, hr	Carboxystearic acid,[c] %	Conversion,[d] %
7	0.5	0.5	10	A	---	140	4000	12	55.5	68.3
8	0.5	1.0	10	A	---	140	4500	12	69.7	85.8
9	0.5	2.0	10	A	---	140	4500	10	77.1	94.9
10	1.0	2.0	10	A	---	140	4250	4[e]	80.8	99.4
11	1.0	4.0	10	A	---	140	4025	4[e]	79.0	97.2
12	1.0	4.0	10	A	---	120	4100	6	75.0	92.3
13	1.0	4.0	10	A	---	130	4110	6	76.2	93.7
14	0.5	2.0	10	A	---	150	4000	6	78.6	96.8
15	0.5	2.0	10	A	---	160	4000	6	72.9	89.8
16	1.0	4.0	10	A	---	140	2000	6	74.4	91.6
17	1.0	4.0	10	A	---	140	3000	6	76.3	93.9
18	0.5	2.0	20	A	---	150	4050	6	78.0	96.0
19	0.5	2.0	100	A	---	150	4000	6	75.1	92.4
20	0.5	2.0	200	A	---	150	4100	6	72.2	88.8
21	1.0	4.0	0	A	---	140	4100	6	73.3	90.2
22	1.0	4.0	20	A	---	140	4000	4[e]	74.1	91.2
23	1.0	4.0	40	A	---	140	4100	6	73.2	90.1
24	1.0	4.0	10	A	HCl[f] (1%)	100	4100	12	69.9	86.0
25	1.0	4.0	10	A	HCl[f] (2%)	100	4000	12	70.0	86.2
26	1.0	4.0	10	A	HCl[f] (1%)	110	4000	12	54.4	67.0
27	0.5	2.0	10	A	$CuCl_2$ (0.1 M)	140	4200	6	77.6	95.5
28	0.5	2.0	10	A	$CuCl_2$ (0.4 M)	140	4100	6	7.7	9.5
29	0.5	2.0	10	A	NaOAc (0.2 M)	140	4100	6	3.1	3.8
30	0.5	2.0	10	DMF	---	140	4050	6	5.5	6.8
31	0.5	2.0	10	HOAc	---	140	4000	4.5	75.7	93.1
32	0.25	1.0	10	HOAc	---	140	4000	6	75.9	93.4
33	0.25	1.0	10	HOAc	---	150	4100	6	77.3	89.0
34	0.25	1.0	10	HOAc	---	130	4125	6	79.0	97.2

[a] All runs were made with 35 g olive acids (0.1 M oleic acid) in a 300 ml autoclave at an initial CO pressure 2000-3000 psig.

[b] Sixty-five milliliters. A = acetone; DMF = N,N-dimethylformamide; HOAc = acetic acid.

[c] Determined by gas liquid chromatography after methylation (diazomethane); does not include small amounts of dicarboxystearic acid derived from linoleic acid in starting material.

[d] Based on 81.3% oleic acid in starting material.

[e] Reaction leveled off.

[f] Added as concentrated HCl (37.5%).

tion of oleic acid and methyl oleate with catalyst mixtures of $PdCl_2$ and Ph_3P or Pd/C, HCl and Ph_3P. Methyl 9(10)-carbomethoxystearate can also be made by catalytic carbomethoxylation of methyl oleate but in lower yields.

EXPERIMENTAL PROCEDURES

Materials and Methods

Commercial oleic acid ("Pamolyn-100," Hercules, Inc.) was distilled (95% oleate by gas liquid chromatography [GLC]). Oleic safflower oil (G. Fuller, Western Regional Research Laboratory) was refined (78.0% oleate and 14.0% linoleate by GLC). Olive fatty acids were distilled after saponification (81.3% oleate by GLC) and the methyl esters after transesterification (83.3% oleate by GLC). The catalysts, $PdCl_2$ (Fisher Scientific Co., dry, purified), 10% Pd on powdered charcoal (Matheson Coleman & Bell), $(Ph_3P)_2PdCl_2$, Pd acetate and Ph_3P (Strem Chemicals) were purchased.

Methods for GLC, thin layer chromatography (TLC), IR, NMR, acid value and mass spectrometry of carboxy acids and carbomethoxy derivatives were described previously (12,14). The carbomethoxy esters were distilled and purified by silicic acid column chromatography (14).

Carboxylations

9(10)-Carboxystearic Acid. Run 1: The catalyst consisting of 0.30 g $PdCl_2$ (0.5 mol % of substrate) and 1.77 g Ph_3P (2.0 mol % of substrate) was introduced into a 300 ml autoclave made of acid-resistant Hasteloy C stainless steel, previously flushed with N_2. To this mixture were added 7.74 g distilled H_2O (10 mol % excess of substrate), 100 g oleic acid (0.337 mol) and 50 ml acetone solvent. The autoclave was sealed, purged three times with ca. 200 psig of CO and then pressurized with the same gas to 2900 psig. The reaction mixture was heated to 150 C with magnetic stirring in 15 min. During this heating the pressure reached 3800 psig and was increased to 4000 psig. The temperature was then controlled at 150 ± 1 C for 2 hr and 20 min. During this time, the pressure declined to 3500-3000 psig and was restored repeatedly to 4000 psig until it remained essentially constant at 3995-4000 psig. The autoclave and contents were then cooled to room temperature, and the gas was vented. The reaction mixture was transferred with acetone and filtered through Whatman no. 1 paper. The solvent was removed on a rotating evaporator under vacuum. The pale yellow product (114 g) was analyzed by GLC after methylation with diazomethane (carboxystearate, 93.5%; dicarboxystearate, 3.8%; oleate, 0.5%; stearate, 2.1%). Calculated conversion is 96.4% (0.325 mol carboxystearic acid per 0.337 mol oleic acid in the starting material). All conversion yields reported in this paper are similarly calculated. Distillation of the reaction product in an Alembic flask yielded clear, colorless fractions (Table I). Fractions 2 and 3 were combined and analyzed directly by potentiometric titration (neutralization point, pH, 10.30; acid value, 329.3; calculated acid value for carboxystearic acid, 341.6). Elemental analysis: C, 69.85; H, 11.26%. Calculated for $C_{19}H_{36}O_4$: C, 69.47; H, 11.05%. Melting point: 51.6 C (by differential thermal analysis).

Run 2: Oleic acid (101 g) was hydrocarboxylated as in run 1 but without acetone solvent, with 0.35 g $PdCl_2$, 1.8 g Ph_3P and 8.0 g distilled H_2O. This reaction required a period of 4 hr at 150 C and 4000 psig CO to reach completion. The crude yellow product (112 g; 93.3% carboxystearic acid by GLC; calculated conversion, 94.4%) was subjected to Alembic distillation. Two fractions (73 g)

TABLE III

Catalytic Hydrocarboxylation of Olive Fatty Acids with Pd Catalysts

Run no.[a]	Catalyst	Catalyst concentration, mol %	Ph_3P, mol %	Concentrated HCl, %	Temperature, C	Final CO pressure, psig	Time, hr	Carboxystearic acid,[b] %	Conversion,[c] %
35	$(Ph_3P)_2PdCl_2$	0.5	0	0	120	4000	6	69.1	85.0
36	$(Ph_3P)_2PdCl_2$	0.5	0	0	130	4300	12	80.2	98.6
37	$(Ph_3P)_2PdCl_2$	0.5	0	0	140	4050	12	78.7	96.8
38	$(Ph_3P)_2PdCl_2$	0.5	0	0	150	4075	12	72.2	88.8
39	$(Ph_3P)_2PdCl_2$	1.0	0	0	140	4200	6	78.5	96.6
40	$(Ph_3P)_2PdCl_2$	1.0	2.0	0	140	4100	4	77.6	95.4
41	Pd Acetate	0.5	2.0	0	140	4050	6	0.0	0.0
42	Pd Acetate	0.5	2.0	0.2	140	4125	4	76.3	93.8
43	$Pd(acac)_2$[d]	0.5	2.0	0.2	140	4210	4	75.2	92.5
44	10% Pd/C	—[e]	2.0	0	140	4400	6	5.4	6.6
45	10% Pd/C	—[e]	2.0	0.05	140	4100	12	72.9	89.7
46	10% Pd/C	—[e]	2.0	0.1	140	4000	12	72.0	88.6
47	10% Pd/C	—[e]	2.0	0.2	140	4000	6	79.2	97.4

[a] All runs were made with 35 g olive acids (0.1 M oleic acid), 10 mol % excess H_2O, 65 ml acetone solvent in a 300 ml autoclave, at an initial CO pressure of 2000-3000 psig.

[b] See footnote c, Table II.

[c] See footnote d, Table II.

[d] Palladium bis-acetylacetonate.

[e] 3.4% Pd based on oleic acid in starting material.

analyzed 97% and 98% carboxystearic acid (by GLC and acid value), and two fractions (32 g) analyzed 80% and 94% carboxystearic acid.

Run 3: Olive fatty acids (35 g) were hydrocarboxylated with 1.10 g 10% Pd-on-carbon, 0.525 g Ph_3P, 2.10 g 10% HCl solution (w/v, concentrated HCl) and 64 g acetone. Reaction conditions were: 6 hr, 140 C, 4000 psig CO. The crude filtered product (33.5 g; 79.2% carboxystearic acid by GLC; calculated conversion, 97.4%) was distilled (150-225 C/0.01 mm; yield, 94%; acid value, 326).

Methyl 9(10)-Carboxystearate. Run 4: Methyl oleate (105 g) was hydrocarboxylated by the same procedure as run 1, with 0.297 g $PdCl_2$, 1.769 g Ph_3P, 7.74 g distilled H_2O and 65 ml acetone. The reaction period was 3 hr at 150 C and 4000 psig CO. The crude product (119.2 g; 90.1% methyl carboxystearate by GLC; calculated conversion, 99.7%) was distilled (Table I). Fraction 3 was identified as methyl 9(10)-carboxystearate by comparison (GLC, TLC, mass spectrometry) with an authentic sample (12). Analysis: C, 69.75; H, 11.22%. Calculated for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18%.

Glyceryl Tris(9[10]-Carboxystearate). Run 5: Oleic safflower oil (100 g) was hydrocarboxylated by the same procedure as run 1, with 0.35 g $PdCl_2$, 1.8 g Ph_3P, 8.0 g distilled H_2O and 50 ml acetone. Reaction conditions were: 4 hr, 150 C, 3500-4100 psig CO. The crude filtered product (118.5 g) was yellowish-green (acid value, 181.7; calculated acid value for glyceryl tris-carboxystearate, 164.4; for glyceryl tris-dicarboxystearate, 219.3). A sample was saponified (acid value, 299.5) and the resulting acids were methylated (75.1% carboxystearate and 13.0% dicarboxystearate by GLC; calculated conversion, 96.3%).

Methyl 9(10)-Carbomethoxystearate. Run 6: Olive methyl esters (33.6 g) were carbomethoxylated with 0.186 g $PdCl_2$, 1.1 g Ph_3P, 3.50 g methanol and 62 g acetone. Reaction conditions were: 12 hr, 140 C, 4000 psig CO. The crude filtered product (36.0 g; 61.7% methyl carbomethoxystearate by GLC; calculated conversion, 76.1%) was distilled without fractionation (134-154 C/0.01 mm; yield: 90%; 77.7% methyl carbomethoxystearate) and purified by silicic acid column chromatography (99.2% carbomethoxystearate by GLC). Elemental analysis: C, 70.36; H, 11.68. Calculated for $C_{21}H_{40}O_4$: 70.74; H, 11.31.

RESULTS

In a survey of various platinum group metal catalysts, a highly selective $PdCl_2$ system was discovered for the hydrocarboxylation of oleic acid and methyl oleate. A mixture of $PdCl_2$ and Ph_3P proved to be an efficient catalyst system and a more active one than preformed $(Ph_3P)_2PdCl_2$. Typical reaction conditions are in the temperature range of 140 to 150 C at 4000 psig pressure of CO, $PdCl_2$ 0.5-1.0 mol % of oleic acid, Ph_3P at 2.0-4.0 mol % of oleic acid, water in 10 mol % excess, with or without such solvents as acetone or acetic acid. Another good hydrocarboxylation catalyst for oleic acid consists of a mixture of Pd-on-carbon, Ph_3P and HCl. Because $PdCl_2$ is among the cheapest and most active catalysts examined, this system was chosen for studies designed to establish best reaction conditions.

Runs summarized in Table II were made to determine the effect of $PdCl_2/Ph_3P$ ratio, the temperature, CO pressure, water concentration, HCl, solvent and additives. At an optimum ratio of $PdCl_2$ and Ph_3P ranging from 1:2 to 1:4, conversion of oleic acid to carboxystearic acid varies from 95% to 99% (runs 9-11). Conversions are higher at

TABLE IV

Isomer Distribution of Methyl Carbomethoxystearate from Hydrocarboxylated Oleic Acid[a]

Run no.[b]	Relative percentage						
	C-8	C-9	C-10	C-11	C-12	C-13	C-9 + C-10
1	2.8	45.3	44.9	4.7	1.5	0.8	90.2
6	2.2	45.9	43.4	5.0	2.9	0.6	89.3
8	1.4	46.0	45.2	4.3	2.3	0.7	91.2
9	1.7	45.5	45.2	4.7	2.2	0.7	90.7
11	2.1	45.2	44.0	5.4	2.4	0.9	89.2
14	2.7	43.5	43.9	6.4	2.6	0.9	87.4
15	3.8	42.3	41.9	7.7	3.1	1.2	84.2
16	6.5	31.4	43.2	12.3	4.9	1.7	74.6
17	2.9	49.2	40.9	4.5	1.8	0.7	90.1
19	2.4	44.0	43.9	5.9	2.7	1.1	87.9
20	2.0	42.4	45.9	5.6	2.8	1.4	88.3
23	2.0	44.5	45.5	4.4	2.8	0.8	90.0
24	0.3	47.3	46.4	2.5	2.6	0.9	93.7
25	0.4	47.3	46.6	2.5	2.6	0.6	93.9
27	1.6	36.8	53.8	4.5	3.0	0.2	90.6
31	2.4	41.1	45.8	6.2	3.0	1.5	86.9
32	0.0	45.4	45.8	4.5	3.1	1.1	91.2
46	2.0	45.7	44.5	4.8	2.3	0.7	90.2
47	2.9	42.7	44.5	6.4	2.6	0.9	87.2

[a] Determined by mass spectrometry on carboxystearic acid after methylation with diazomethane.

[b] See Experimental Procedures, Tables II and III.

TABLE V

Hydrocarboxylation of Oleic Acid with Fresh and Used Palladium Catalysts[a]

Run no.	Catalyst systems	Catalyst wt, %	HCl, %	Temperature, C	Time, hr	Conversion, %
4	$PdCl_2$	0.3	0	150	4	99.7
48	Precipitate, run 4	2.2[b]	0	140	6	39.7
49	Oxidized pot residue,[c] run 4	8.1[d]	0	140	6	10.9
50	Oxidized pot residue,[c] run 4	8.1[d]	0.1	140	12	98.9
51	Not oxidized pot residue, run 4	8.1[d]	0.1	140	12	34.2
52	$PdCl_2$	0.3	0	150	4	100
53	Oxidized pot residue,[c] run 52	3.0[d]	0.1	150	12	93.8
54	$PdCl_2$	0.6	0	140	2.5	99.0
55	Precipitate + oxidized pot residue,[c] run 54	26[d]	0.1	140	12	98.0

[a] Conditions: 2 mol % Ph_3P, 10 mol % excess H_2O, acetone solvent, CO pressure 4000-4500 psig.

[b] Based on $(Ph_3P)_2PdCl_2$.

[c] With HNO_3 by the following procedure: The distillation residue (7 g) is stirred with 50 ml concentrated HNO_3 at room temperature for 10 min. The acid mixture is poured in ca. 50 ml ice H_2O and extracted with diethyl ether. The ether extract is washed with H_2O to neutrality and dried (Na_2SO_4). Yield: 6.6 g viscous light brown oil.

[d] Based on distillation yield.

140 and 150 C than at 160 C (runs 9, 14 and 15) and at 4025 psig than at 3000 and 2000 psig (runs 11, 16 and 17). When $PdCl_2$ and Ph_3P are used at respective concentrations of 0.5 and 2 mol %, yields of carboxystearic acid are higher with 10-20 mol % excess of H_2O (runs 14 and 18) than with 100-200 mol % excess of H_2O (runs 19 and 20). When $PdCl_2$ and Ph_3P are used at respective concentrations of 1.0 and 4 mol %, the highest yield of carboxystearic acid of 97.2% resulted with a 10 mol % excess of H_2O (compare run 11 with runs 21-23). Addition of 1% and 2% HCl permits reaction temperatures to be lower, but then conversions of oleic acid to carboxystearic acid are low and require longer reaction periods (runs 24-26).

The effect of an oxidizing agent was studied to determine if Pd(II) in the active form could be regenerated from any Pd(0) formed during the reaction. However addition of $CuCl_2$ had no effect at the 0.2 M level (run 27) and inhibited the reaction at the 0.4 M level (run 28). Hydrocarboxylation was almost entirely inhibited by NaOAc and DMF solvent. Both of these basic reagents would remove HCl liberated as the Pd catalyst is formed under hydrocarboxylation conditions. Therefore endogenous HCl is required for this reaction. The use of acetic acid as a solvent accelerated the rate of hydrocarboxylation (compare runs 9 and 31). With acetic acid as the solvent, yields of carboxystearic acid were good at lower catalyst concentration and temperature than with acetone (runs 32-34).

Other Pd catalysts investigated included $(Ph_3P)_2PdCl_2$, Pd acetate-Ph_3P, Pd bis-acetylacetonate-Ph_3P and Pd/C-Ph_3P. The complex $(Ph_3P)_2PdCl_2$ (5) is a good hydrocarboxylation catalyst but somewhat less efficient than $PdCl_2$ and Ph_3P. Almost complete conversion of oleic acid to carboxystearic acid resulted at 130-140 C with acetone as the solvent after 6 or 12 hr (Table III, runs 36, 37 and 39). The addition of Ph_3P accelerated the reaction (runs 39-40). Pd acetate is not active in the presence of Ph_3P, but in the presence of HCl it is an effective hydrocarboxylation catalyst (runs 41 and 42). Similarly, Pd bis-acetylacetonate and Pd supported on carbon are effective hydrocarboxylation catalysts only in the presence of HCl (runs 43 and 45-47).

The purified carboxy acid, ester and carbomethoxy ester (from runs 1, 4 and 6) were identified as the methyl 9(10)-carbomethoxy stearate by comparison with synthetic standards and the corresponding derivatives from methyl 9(10)-formylstearate (12). Functional characterization was based on chemical and elemental analyses (see Experimental Procedures), chromatographic behavior (TLC and GLC), IR (intense CO band at 1740 cm^{-1}), NMR (OCH_3 at 6.35τ, 6H) and mass spectral analysis (m/e 325: molecular ion-OCH_3; m/e 297: molecular ion-CH_3OCO_3). Isomeric composition was estimated by mass spectrometry based on m/e of fragment $(CH_3\text{-}[CH_2]_m\text{-}CH\text{-}COOCH_3 + H)^+$ where m = 17 - branch carbon number. This analysis was standardized by using known mixtures of synthetic methyl 9- and 10-carbomethoxystearates. Table IV contains the isomeric composition of various hydrocarboxylation products of oleic acid. The amount of 9- and 10-isomers varies from 87% to 94% in most of the samples of methyl carbomethoxystearate prepared. A greater distribution of isomers was evident in those samples prepared at low CO pressures (run 16) and at high temperatures (runs 14 and 15).

The activity of used Pd complex catalysts was investigated as a basis for a recovery and recycle hydrocarboxylation process. A crystalline precipitate isolated from a crude hydrocarboxylation product of methyl oleate was partially active (Table V, run 48). A crystalline precipitate was formed on the walls and dasher of the autoclave from another reaction mixture (Table II, run 26). On recrystallization, a yellow-orange compound was isolated which gave an acceptable elemental analysis for $(Ph_3P)_2PdCl_2$ (C, 61.33; H, 4.49; Cl, 9.96; P, 8.95%. Calculated for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.61; H, 4.31; Cl, 10.10; P, 8.83%). Distillation pot residues were catalticaly active when oxidized with HNO_3 and used with added HCl. Conversion of oleic acid to carboxystearic acid with these oxidized distillation pot residues was as high as with $PdCl_2$, but longer reaction times were required (Table V, runs 50, 53, 55). More reliable comparisons must await the development of suitable analyses for Pd. However these results suggest that a recycling catalytic process may be based on the use of suitably oxidized distillation pot residues. Studies along these lines are now in progress.

DISCUSSION

The catalytic carboxylation procedures described here provide more efficient routes to 9(10)-carboxystearic acid and esters than the two-step hydroformylation-oxidation process reported previously (12,15). Catalytic autoxidation of 9(10)-formyl esters is not only slow, but yields of carboxy esters are lowered by the formation of such side products as methyl stearate, hydroxy-, keto- and epoxystearate (15). The carboxy products obtained directly by carboxylation with Pd catalysts are free of these side products; they are of equal isomeric purity and reactivity toward esterification (13) as those from selective hydroformylation with Rh catalysts. Although the Pd hydrocarboxylation catalyst is much cheaper than the Rh hydroformylation catalyst (ca. \$36-\$38 vs. \$200 per ounce on a metal basis), the former is used at a higher concentration than the latter. Nevertheless our present study indicates that a recycling carboxylation process can be developed and that process economics will be largely dictated by the recoverability of the Pd catalyst. The C_{19} dicarboxylic acids prepared by these selective catalytic routes have many advantages over those made by conventional oxo and Koch processes (9). Many areas of applications have been reported for the C_{19} compounds derived from unsaturated fatty acids, esters and triglycerides. Various uses are reviewed in another paper (9). The next paper in this series will cover polycarboxy products from polyunsaturated fats.

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