Linear Carboxylic Acid Esters from α-Olefins: 3. Catalysis by Dispersions of Palladium Complexes[1]
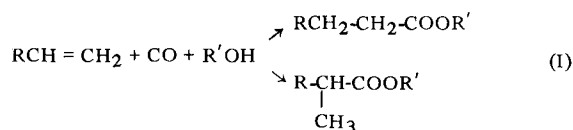
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ABSTRACT

Linear, fatty-type, carboxylic acid esters are prepared by regioselective 1-alkene carbonylation catalyzed by dispersions of ligand-stabilized palladium(II) chlorides in quaternary Group VB salts of trichlorostannate(II). The sensitivity of these syntheses to catalyst composition and alkene structure is described, together with techniques for multiple cycling and regeneration of the preferred palladium formulation, $PdCl_2[P(C_6H_5)_3]_2$-$10[(C_2H_5)_4N][SnCl_3]$.

INTRODUCTION

Short chain fatty acids (SFAs) of the C_5-C_{10} carbon range have in recent years gained new commercial importance in the formulation of synthetic turbine (3) and automotive engine oils (4) in plastics and chemical specialties (5). Presently, most SFAs are derived from natural sources, i.e., through the splitting and fractionation of coconut oils. An alternative petrochemical route would utilize available olefin stocks. In an extension of earlier studies (e.g., 6-9), particularly those employing homogeneous platinum (1) and palladium (2,10) bimetallic catalysts, we report here the use of dispersions of ligand-stabilized palladium chloride complexes in quaternary Group VB salts of trichlorostannate(II) as catalysts for the synthesis of linear fatty acid derivatives via regioselective olefin carbonylation (Eq. I) (11).

$$RCH=CH_2 + CO + R'OH \begin{array}{c} \nearrow RCH_2\text{-}CH_2\text{-}COOR' \\ \\ \searrow R\text{-}CH\text{-}COOR' \\ \qquad | \\ \qquad CH_3 \end{array} \qquad (I)$$

Intrinsic advantages of this class of catalyst over their solvent-solubilized counterparts (1,2) would be in (a) the ease of product ester separation from the catalyst residuum, (b) improved stability during recycle operations, and (c) potentially higher concentrations of active palladium within the reaction mix. Furthermore, the use of related platinum halide solutions in tetraalkylammonium salts of $SnCl_3^-$ has already been successfully demonstrated for a variety of selective hydrogenation (12,13) and hydroformylation (11,12) reactions.

EXPERIMENTAL SECTION

Materials

Carbon monoxide was CP grade. Reagents and solvents were commercial grade; olefins were generally of high purity, and were freed of peroxide prior to use by passage through a column of neutral alumina. Bis(triphenylphosphine)palladium(II) chloride, $PdCl_2[P(p\text{-}CH_3 \cdot C_6H_4)_3]_2$, and $PtCl_2[As(C_6H_5)_3]_2$ were prepared by published methods (14,15). Tetraethylammonium trichlorostannate(II) was prepared by the method of Jones (16). Related quaternary Group VB salts of trichlorostannate(II), includ-

ing $[(CH_3)_4N][SnCl_3]$, $[(n\text{-}C_4H_9)_4N][SnCl_3]$, $[(C_7H_{15})_4N][SnCl_3]$, $[(CH_3)_3C_6H_5N][SnCl_3]$, $[ClCH_2(C_6H_5)_3P][SnCl_3]$, and $[(C_6H_5)_4As][SnCl_3]$-nH_2O were prepared by modifications of this technique.

General Procedures

Olefin carbonylations were conducted in a 300 ml Autoclave Engineers' glass-lined reactor equipped with Magnadrive stirrer, temperature and pressure controls, and a sampling valve.

The extent of carbonylation and distribution of products were estimated by gas liquid chromatography (GLC) with the aid of 4-10 ft columns of 10-20% polyphenyl ether (five rings, Analabs Inc. GP77) on 60/80 mesh Chromosorb G. The esters were isolated by distillation in vacuo, and identified by GLC, IR, nuclear magnetic resonance, and elemental analyses techniques.

Synthesis of Ethyl Nonanoate

To a degassed sample of 1-octene (44.9 g, 400 mmole) and ethanol (18.4 g, 400 mmole) contained in a glass liner is added under a nitrogen purge, tetraethylammonium trichlorostannate(II) (14.2 g, 40 mmole) and bis(triphenylphosphine)palladium(II) chloride (2.81 g, 4.0 mmole). The solid-liquid mixture is transferred, in the glass liner, to the 300 ml autoclave pressure reactor, the reactor sealed, deoxygenated with a purge of nitrogen, and pressure tested with carbon monoxide. The mixture is heated to 80 C under 100 atm of CO with rapid sitrring to give a clear, yellowish-red solution with no suspended solids. After 3 to 6 hr CO uptake is complete, the reaction is terminated by rapid cooling, and the reactor vented. The crude liquid product (83 ml) is separated from the solid, repreciipated catalyst by filtration, distilled under reduced pressure (2-10 cm Hg) to remove unreacted alkene and excess ethanol, and fractionally distilled at 1-3 mm Hg. The fraction (61 g) distilling at 58-62 C is identified as ethyl nonanoate esters (purity >99%, linearity 89%). Calcd. for $C_8H_{17}COOC_2H_5$: C, 70.9%; H, 11.9%. Found: C, 70.9%; H, 12.1%; Pd, <5 ppm; P, <1 ppm. Ethyl nonanoate esters yield 82 mole %.

Recycle and Regeneration of Palladium Catalyst

The residual solid palladium catalyst, recovered during the filtration and distillation steps of a typical fatty acid esters synthesis (see above), is recharged to the glass-lined pressure reactor along with fresh, degassed samples of 1-alkene and alkanol (400 mmole each). The mixture is carbonylated as already described, and on cooling the liquid product is recovered by filtration or decantation and ethyl nonanoates are isolated by fractional distillation in vacuo.

After multiple cycling, the recovered palladium catalyst (10-40 g) is treated with a degassed sample of carbon tetrachloride (100 ml), and the mixture is heated to reflux for 1-12 hr in a stream of chlorine (flow rate 10-200 cc/min). Excess liquid is removed from the catalyst-carbon tetrachloride mixture by distillation under reduced pressure (5 cm Hg), and the solid is dried in vacuo. Triphenylphosphine (4-16 mmole) is added to the reddish-brown solid catalyst in the proportion of 2 mole phosphine per g atom Pd, prior to further cycling with fresh alkene/alkanol.

RESULTS AND DISCUSSION

During initial screening experiments, a variety of transi-

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[1] For parts 1 and 2 in this series, see References 1 and 2.

TABLE I

Ethyl Nonanoate Synthesis—Catalyst Composition Studies[a]

Expt.	Composition	Octene conv. (%)	Ethyl C_9-acid esters[b] Linearity (%)[c]	Yield (mole %)[d]	Liquid yield (%)[e]
1	$PdCl_2[P(C_6H_5)_3]_2$-5$[(CH_3)_4N][SnCl_3]$	<5	89.0	3.6	91
2	$PdCl_2[P(C_6H_5)_3]_2$-10$[(C_2H_5)_4N][SnCl_3]$	>90	83.3	86	90
3	$PdCl_2[P(C_6H_5)_3]_2$-10$[(n\text{-}C_4H_9)_4N][SnCl_3]$	66	78.8	63	88
4	$PdCl_2[P(C_6H_5)_3]_2$-5$[(n\text{-}C_7H_{15})_4N][SnCl_3]$	22	58	19	67
5	$PdCl_2[P(C_6H_5)_3]_2$-10$[(CH_3)_3C_6H_5N][SnCl_3]$	73	89.5	65	89
6	$PdCl_2[P(C_6H_5)_3]_2$-5$[ClCH_2(C_6H_5)_3P][SnCl_3]$	70	87.3	67	70
7	$PdCl_2[P(C_6H_5)_3]_2$-5$[(C_6H_5)_4As][SnCl_3]$	55	69.8	35	79
8	$PdCl_2[P(p\text{-}CH_3 \cdot C_6H_4)_3]_2-10[(C_2H_5)_4N][SnCl_3]$	>90	85.6	87	85
9	$PdCl_2[As(C_6H_5)_3]_2$-10$[(C_2H_5)_4N][SnCl_3]$	<2	92.5	1.6	70
10	$PdCl_2[P(C_6H_5)_3]_2$-25$[(C_2H_5)_4N][SnCl_3]$	25	91.5	23	82
11	$PdCl_2[P(C_6H_5)_3]_2$-10$[(C_2H_5)_4N][SnCl_3]$-2$P(C_6H_5)_3$	<10	88.0	7.8	94
12	$PdCl_2[P(C_6H_5)_3]_2$-10$[(C_2H_5)_4N][SnCl_3]$-33$LiCl^g$	32	90.5	31	88
13	$PdCl_2$-10$[(C_2H_5)_4N][SnCl_3]$	<2	ND[f]	<1	95
14	$PtCl_2[P(C_6H_5)_3]_2$-10$[(C_2H_5)_4N][SnCl_3]$	2.7	92	<1	85
15	$PtCl_2[As(C_6H_5)_3]_2$-10$[(C_2H_5)_4N][SnCl_3]$	<2	88	1.1	82
16	K_2PtCl_4-10$[(C_2H_5)_4N][SnCl_3]$	<2	ND[f]	<1	94

[a]Run conditions as per experimental section; $[1\text{-}C_8H_{16}]/[C_2H_5OH]/[Pd]$ = 100:100:1; 100 atm; 80 C; 8 hr.

[b]A mixture of ethyl nonanoate with some ethyl 2-methyloctanoate and ethyl 2-ethylheptanoate.

[c]Ester linearity calculated basis: ethyl nonanoate/total linear plus branched C_9-acid ester.

[d]Total linear plus branched C_9-acid ester yield, calculated basis 1-octene charged and Equation I.

[e]Total liquid yield recovered after carbonylation, calculated basis total liquid charged.

[f]ND = not determined.

[g]Initial $[1\text{-}C_8H_{16}]/[Pd]$ = 60:1.

tion-metal-containing salts and complexes dispersed in quaternary Group VB salts of trichlorostannate(II) were examined for olefin carbonylation activity. Ethyl nonanoate from 1-octene was the model synthesis. Active palladium and platinum combinations are illustrated in Table I. Basis these, and related results (11), the most promising formulations for typical SFA syntheses were found to be bis(triphenylphosphine)palladium(II) chloride, or its *para*-tolyl analogue $PdCl_2[P(p\text{-}CH_3 \cdot C_6H_4)_3]_2$, dispersed in tetraethylammonium trichlorostannate(II). Nonanoate ester yields consistently exceed 80 mole % for both systems under the specified conditions (expt. 2 and 8), product linearity is 83% or better, and isomerized olefins (primarily *cis* and *trans* 2-octene) are the only major by-products. Both Pd-catalyst combinations exist under carbonylation conditions as clear, homogenous liquid phases with the 1-octene, ethanol coreactants. However, the common quaternary salt, $[(C_2H_5)_4][SnCl_3]$, melts at 78 C (16), so following carbonylation, the reaction mixtures are cooled to reprecipitate the catalyst components, thereby ensuring ease of separation of the crude liquid product ester from the now solid Pd-catalyst (for details see Experimental Section).

Combinations of $PdCl_2[P(C_6H_5)_3]_2$ with other quaternary salts, including tetra-*n*-butylammonium trichlorostannate(II), trimethylphenylammonium trichlorostannate(II), and (chloromethyl)triphenylphosphonium trichlorostannate(II) (expt. 3,5, and 6), also provide >60 mole % yields of acid ester per pass. Some activity is in fact detected with each of the ligand-stabilized palladium salts tested when dispersed in one or more ammonium, phophonium, and arsonium salts of trichlorostannate(II) or trichlorogermanate(II) (11). Among the palladium-containing catalysts, only the palladium-tin system alone, in the absence of tertiary donor ligands, proved unstable to carbonylation (17,18) and close to inactive (expt. 13). Platinum analogues (20) generally are at least an oder of magnitude less active than the preferred palladium formulations (cf. expt. 2 and 14) under our moderate screening conditions. Salts and complexes of other Group VI, VII, and VIII metals, including those of iron, ruthenium, cobalt, nickel, and molybdenum, exhibited no activity (11).

While typical SFA syntheses have been demonstrated over a wide range of experimental conditions for the preferred catalyst formulation of expt. 2 (11), performance is particularly sensitive to even modest changes in catalyst structure. Two more notable examples, drawn from the data in Table I, include (a) the 3.6 to 86% variation in ester yield as n varies from 1 to 7 in the alkyl quaternary salt series $[(C_nH_{2n+1})_4N][SnCl_3]$-$PdCl_2[P(C_6H_5)_3]_2$ (see expt. 1-4) and (b) the >50% loss in activity upon the addition of either excess phosphine or chloride ion (expt. 11, 12). Even in the case of $PdCl_2[P(C_6H_5)_3]_2$-$[(C_2H_5)_4N][SnCl_3]$, optimum yields of fatty acid ester are realized only at tin-to-palladium ratios of ca. 5-10. Consistent with our earlier studies (2), higher ratios lead to slower reaction rates in this application (expt. 10), ratios of three or less, while closer to the stoichiometry of known Pd-$SnCl_3$ complexes (17-19), proved unsatisfactory due to the lower thermal stability of the formulation and difficulties encountered during catalyst regeneration (vide infra).

Although some, at least, of these differences in catalyst performance (Table I) can be traced to changes in the character and ease of formation of the active Pd-catalyst (2,10) others may be due to unique physical factors associated with the use of these quaternary salts both as cocatalysts and dispersent media. These factors include the higher mp of certain of the salts (e.g., $[(CH_3)_4N][SnCl_3]$ and $[ClCH_2(C_6H_5)_3P][SnCl_3]$, mp >120 C) above the temperature of carbonylation, the limited solubility of certain palladium salts (e.g., $PdCl_2$) in particular reactant combinations, and the tendency of salts like $[(C_{17}H_{35})_2(CH_3)_2N][SnCl_3]$ to form a separate liquid phase from the 1-octene, alkanol mixtures.

Other Acid Ester Syntheses

The synthesis of a variety of other acid derivatives is illustrated in Table II. Typical monosubstituted 1-alkenes, alkynes, and polysubstituted (internal and cyclic) alkenes in combination with variously substituted alkanols and phenolic coreactants provide evidence for the scope of this technique using the preferred palladium catalyst $10[(C_2H_5)_4N][SnCl_3]$-$PdCl_2[P(C_6H_5)_3]_2$. While reaction

TABLE II

Alkene/Alkyne Carbonylation Catalyzed by $PdCl_2[P(C_6H_5)_3]_2$-$10[(C_2H_5)_4N][SnCl_3]$[a]

Expt.	Alkene/alkyne	Alkanol	Conv. (mole %)	Major product ester Identity	Selectivity (%)[b]	Yield (mole %)
17	1-Hexene	Ethanol	51	Ethyl heptanoate	79.2	51
18	1-Octene	Ethanol	84	Ethyl nonanoate	86.3	62
19	1-Tetradecene	Ethanol	86	Ethyl pentadecanoate	90.9	64
20	3,3-Dimethyl-1-butene	Ethanol	40	Ethyl 4,4-dimethylpentanoate	99.5	36
21	2,4,4-Trimethyl-1-pentene	Ethanol	28	Ethyl 3,5,5-trimethylhexanoate	96.1	23
22	4-Methylcyclohexene	Ethanol	80	Ethyl 4-methylcyclohexane carboxylate[d]	80.0	42
23	cis-2-Heptene[c]	Ethanol	72	Ethyl 2-methylheptanoate / Ethyl octanoate	57.2 / 24.2	41
24	1-Heptyne[c]	Ethanol	96	Ethyl 1-heptene-2-carboxylate / Ethyl 2-octenoate	62.3 / 37.7	39
25	1-Octene	2-Chloroethanol	51	2-Chloroethyl nonanoate	80.7	21
26	1-Octene	2-Propanol	58	Isopropyl nonanoate	91.1	46
27	1-Octene	n-Hexanol	85	n-Hexyl nonanoate	85.8	57
28	1-Octene	Phenol	72	Phenyl nonanoate	83.2	14

[a]For run conditions see experimental section; [alkene]:[ethanol]:[Pd] = 100:200:1; 100 atm; 85 C; 8 hr.

[b]Selectivity calculated basis total acid ester product.

[c]Initial [alkene or alkyne]:[Pd] = 50:1; 1-heptyne reaction time 4 hr.

[d]Minor product: ethyl 3-methylcyclohexane carboxylate.

TABLE III

Ethyl Nonanoate Synthesis, $PdCl_2[P(C_6H_5)_3]_2$-$10[(C_2H_5)_4N][SnCl_3]$ Recycle Study[a,b]

Catalyst cycle	Octene conversion (%)	Liquid yield (%)	Ethyl C9-acid ester Linearity (%)	Ethyl C9-acid ester Yield (mole %)	Isolated ester purity (%)
I	80	78	71.0	84	99
II	90	100	75.9	88	99
III	70	100	89.7	69	99
IV	53	96	90.0	52	99
V	32	100	91.2	31	99
IV	14	100	92.0	14	99

[a]Run conditions as per experimental section; $[1-C_8H_{16}]:[C_2H_5OH]:[Pd] = 63:63:1$. For definition of terms see Table I.

[b]See Reference 11.

rates are generally highest for the linear α-olefin substrates (expt. 17-19), selectivity to linear acid ester improves with increasing carbon number, reaching 90.9% for ethyl penta-decanoate synthesis. Maximum selectivity for terminal CO addition is once again (1,2) achieved with certain sterically crowded α-olefins such as 3,3-dimethyl-1-butene (expt. 20). Overall performance is, in fact, reminiscent of that reported previously for the solvent-solubilized Pd-SnCl3 complexes (2,10). The catalytically active species may well be the same or similar in the two systems.

In this work, the careful pairing of reagents has, in many cases, been found to significantly enhance catalyst performance. During nonanoate ester syntheses, for example, the switch from coreactant methanol to a higher alkanol (e.g., ethanol) has the intrinsic advantages of bringing all reactants together in a single phase throughout the carbonylation and of reducing the degree of Pd precipitation. The latter effect is believed linked to the ease of nucleophilic attack by alkoxide ion (21).

Finally, since closely related homogeneous catalysts, e.g., $[(C_6H_5)_3P]_2PdCl_2$-$SnCl_2$, selectively hydrogenate soybean methyl esters (15) and other model polyunsaturates (22), there is the possibility of extending this catalysis, in salt or solvent media, to the development of dual-function palladium species which catalyze both the selective monocarbonylation and subsequent hydrogenation of polyene substances. Work along these lines has been described (23).

Catalyst Recycle and Regeneration

Following each SFA ester synthesis, the products may be isolated by one of at least two general methods, viz., a solvent extraction technique using, for example, ether as the extracting medium (24), or through fractional distillation of the crude liquid product. Distillation generally ensures a higher purity product (24) and involves the following minimum steps:

1. filtration of the crude liquid product from the residual catalyst,
2. flash distillation of the crude liquid to remove unreacted alkene and alkanol,
3. fractional distillation of the liquid residuum in vacuo to recover the fatty acid ester product as a distillate fraction.

Typical data for a multicycle experiment using a single sample of $[(C_2H_5)_4N][SnCl_3]$-$PdCl_2[P(C_6H_5)_3]_2$ to carbonylate six fractions of 1-octene are summarized in Table III. Here 213 moles of ethyl nonanoate esters were prepared and isolated per mole of $PdCl_2[PPh_3]_2$ complex initially charged. Overall catalyst recovery was 84 wt %. Performance reproducibility, basis ethyl C9-acid ester yield and linearity data, is generally within 15% for different catalyst samples (24).

Selectivity to linear nonanoate ester (column four, Table III) normally improves steadily upon successive cycling. Correspondingly there is a slower rate of 1-octene isomerization with used catalyst samples. Total olefin conversion

levels and nonanoate ester yields remain essentially equivalent over the first three cycles (see column five), particularly when allowance is made for the small quantity of catalyst lost in handling the 0.42 g of Pd initially charged. However, some catalyst deactivation is clearly evident during the fourth and subsequent cycles. Purity of the isolated ethyl nonanoates remains essentially constant at 99% or better.

Catalyst deactivation could be the result of any of a number of factors, including palladium reduction by CO or alkoxide ion (22), irreversible complexation with an acid ester or by-product fraction, and/or selective loss of one or more of the catalyst components during handling, carbonylation, distillation, etc. The active catalyst probably contains palladium coordinated to both triphenylphosphine and trichlorostannate(II) (22). Confirmation of some selective loss of palladium and phosphorus in this work comes from elemental analyses data for typical recovered catalyst samples after four to six carbonylation cycles. Losses range >10% on phosphorus and up to 12% on palladium. Furthermore, spectra of recovered samples show bands characteristic of triphenylphosphine oxide (1180, 1118, 750, 725, and 688 cm^{-1}).

Evidence for at least partial reduction of the palladium complex comes from changes in the color of the dispersions (reddish yellow → black) upon successive cycling. In some cases, discrete metal carbonyl species (2010-2030 cm^{-1}, see ref. 17,19) are in evidence. This is particularly true upon further cycling and for the less effective platinum catalysts, e.g., $PtCl_2[As(C_6H_5)_3]_2$-$10[(C_2H_5)_4N][SnCl_3]$, after only a single carbonylation cycle (v_{CO} 2020 cm^{-1}).

Various techniques for regenerating spent palladium catalyst samples have been considered. Particular emphasis has been given to reoxidizing inactive palladium(O) species; techniques which proved either completely or at least partially successful include the following:

1. treatment with mineral acid, e.g., HCl-HNO$_3$ mixtures (24);
2. in situ addition of hydrogen peroxide or certain organic peroxides (25);
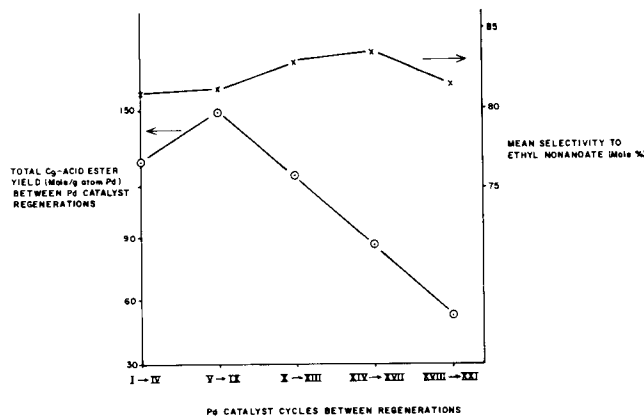3. oxychlorination techniques involving the use of HCl with oxygen or air (26);

FIG. 1. Ethyl nonanoate synthesis from 1-octene, palladium catalyst recycle, and regeneration studies.

4. gaseous chlorine in the presence/absence of a suitable chlorinated solvent (27).

Chlorination, while providing some long term changes in catalyst composition, does allow multiple, 30-40, cycling of the palladium catalyst with little overall loss in *specific activity* (activity basis Pd remaining, following mechanical losses, etc.)[2] The majority of catalyst life studies have in fact used this method. To ensure complete regeneration of the deactivated palladium catalyst and good contact between the solid suspension and the gaseous chlorine, regeneration is most successfully accomplished in the presence of highly chlorinated solvents. Suitable solvents include carbon tetrachloride, tetra- and penta-chloroethanes. Generally, the spent Pd-containing material is slurried with the chlorinated solvent, chlorine is passed through the mixture under solvent reflux, and excess liquid removed by stripping, Triphenylphosphine (2 mole per g atom Pd) is added prior to recycle, otherwise the treated catalyst remains inactive (25), and palladium metal is rapidly reprecipiated during subsequent carbonylations.

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[2] No correction for physical losses of palladium suffered during catalyst handling, carbonylation, regeneration, etc.

TABLE IV

Ethyl Nonanoate Synthesis, Palladium Catalyst Recycle and Regeneration Studies[a]

| Cycle | Octene conv. (%) | Ethyl C$_9$-acid esters | | | Liquid yield (%) |
		Linearity (%)	Yield (mole %)	Purity (%)	
I	88	69.6	84	99	88
II	90	88.9	87	99	95
III	22	91.0	21	99	99
IV[b]	<10	90.0	7.6	99	102
V	78	77.0	67	99	78
VI	76	80.0	81	99	80
VII	68	84.1	65	99	91
VIII	<20	89.4	18	99	92
IX[b]	<5	92.7	2.0	99	92
X	24	82.5	25	73	96
XI	85	83.4	82	98	91
XII	79	81.8	77	99	93
XIII[b]	<5	92.5	<5	99	97
XIV	7.4	79.6	14	68	88
XV	71	84.0	72	99	91
XVI	35	85.7	42	99	91
XVII[b]	5.2	86.4	3.2	99	94
XVIII	53	81.3	60	88	82
XIX	<5	81.9	7.6	88	90
XX	<5	80.9	3.8	84	82

[a]Run conditions as per experimental section; initial $[1-C_8H_{16}]:[C_2H_5OH]:[Pd] = 63:63:1; [Sn]:[Pd] = 10:1; 100$ atm; 85 C; 8 hr. For definition of terms see Table I.

[b]After this cycle the recovered Pd catalyst is regenerated by treatment with Cl$_2$ in the presence of CCl$_4$ or C$_2$HCl$_5$. For details see the experimental section.

Results of a typical 20-cycle experiment are summarized in Table IV. Following the procedures outlined in the Experimental Section, palladium is added as $PdCl_2[P(C_6H_5)_3]_2$ only at the start of the first cycle. Comparing then the performances of the fresh catalysts (cycles I → IV) with that after regeneration using Cl_2/CCl_4 reagent (cycles V → VIII), it may be noted that while initial rates of carbonylation may be slower for the regenerated catalyst, the total yield of ethyl nonanoates over four cycles is actually higher for the regenerated material (146 mole ester per g atom Pd^2 for cycles V → VIII versus 126 mole for fresh catalyst, cycles I → IV, see also Fig. 1). Furthermore, mean selectivity to desired linear ethyl nonanoate over each four cycle experimental series (Fig. 1) remains comparable for the fresh and regenerated catalysts (81.2 vs. 81.0%, respectively.). Total ester yields are lower following the second and subsequent regenerations (Fig. 1), but linearity of the C_9-acid ester generally remains above 80 mol %. In fact, the only distinct trend evident in the ester linearity data is the steady improvement upon successive cycling *between* regenerations (Table IV, Column 3). Likewise, olefin conversion levels and ester yields per cycle (columns two and four of Table IV) also appear to peak two-to-three cycles after each regeneration. Purity of the isolated nonanoate ester is 99% or better for the majority of the runs.

Further significant improvements in $PdCl_2[P(C_6H_5)_3]_2$-$[C_2H_5)_4N][SnCl_3]$ performance, and those of related dispersions, should be possible by operating on a larger scale and by intermittent washing of the regenerated catalyst samples with polar organic solvents, e.g., methanol (27).

ACKNOWLEDGMENTS

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