The sample was further purified by preparative glpc (SAIB, 170°), α_{578}^{27} +0.02° (neat, *l* 0.1 dm). The amide of hydraptropic acid was prepared by saponification of methyl hydratropate and treatment of the intermediate acid chloride ($SOCl_2$) with concentrated ammonia, mp 91–92° (lit.[15] mp 91–92°).

Similar results were obtained when the reaction was repeated for a 3-hr reflux period with 0.05 mol of phenylcadmium reagent and 0.025 mol of bromo ester. Control experiments to determine the degree of racemization of bromo ester were carried out by measuring the optical rotation and glpc peak area before and after the addition of fresh (+)-bromo ester. It was concluded that recovered bromo ester had racemized to the extent of 9% (maximum) during the course of the reaction.

Reaction of Allyl Bromide with Phenylcadmium Reagent.—A solution of 6.05 g (0.05 mol) of allyl bromide in 10 ml of anhydrous ether was added dropwise with stirring to 0.1 mol of phenylcadmium solution diluted with 75 ml of dry ether. After spontaneous refluxing subsided (about 5 min), the mixture was heated to reflux for an additional 4 hr. It was hydrolyzed with 10 ml of water, whereupon the usual precipitate formed. The liquid was decantated from the solid, and the precipitate was washed twice with 25-ml portions of ether. The washings were combined with the decantate, dried with $MgSO_4$, and filtered, and the ether was removed. When a portion of the 2.60 ml of crude residue was injected onto a column (10% Carbowax, 130°), three major peaks besides ether were observed. The one at 2.4 cm had the same retention time as that of allyl bromide. One at 10.7 cm was isolated, and its ir spectrum was identical with that of 3-phenylpropene (Sadtler[10] Spectrum No. 13701). The ir spectrum of the large peak at 16.1 cm was identical with that of bromobenzene. The yield of 3-phenylpropene was 39%, as determined by peak enhancement.

Reaction of Benzyl Bromide with Phenylcadmium Reagent.—To 0.1 mol of phenylcadmium reagent in 75 ml of anhydrous ether, 8.55 g (0.05 mol) of benzyl bromide was added dropwise with stirring at room temperature. The mixture was maintained at reflux for 10 hr, and then hydrolyzed with 10 ml of water. A portion of the crude mixture isolated as above was injected onto the gc (Apiezon L, 150°); three peaks were observed at 1.8, 2.4, and 15.3 cm. The last exhibited an ir spectrum identical with that of diphenylmethane (Sadtler[10] Spectrum No. 3389). Its yield, as determined by the peak enhancement method, was 40%.

Reaction of Phenylcadmium Reagent with 3-Bromocyclohexene.—To 0.1 mol of phenylcadmium reagent in 75 ml of anhydrous ether, 8.05 g (0.05 mol) of 3-bromocyclohexene was added slowly with stirring. After reaction conditions and workup identical with those of allyl bromide, there was obtained 7.0 g (7.40 ml) of crude product. Glpc analysis (10% Carbowax, 150°) gave peaks for ether and starting halide and one at 23.4 cm. Its ir spectrum was that expected for 3-phenylcyclohexene: 3080, 3050 (ArH, C=CH), 1650 cm^{-1} (C=C). The yield (81%) of 3-phenylcyclohexene was established by the method of peak enhancement.

The above reaction of 3-bromocyclohexene with phenylcadmium reagent was repeated, and aliquots of the reaction mixture were removed at various time intervals, placed in a sample tube, and the esr spectrum taken. Aliquots were taken immediately after mixing of the reagents at room temperature, after 5 min of stirring at room temperature, after 0.5 hr of refluxing, and after 4 hr of refluxing. None of the spectra indicated the presence of radicals.

Reaction of Chloromethyl Methyl Ether with Phenylcadmium Reagent.—Reaction as above of a solution of 4.0 g (0.05 mol) of chloromethyl methyl ether in 10 ml of anhydrous ether and phenylcadmium reagent afforded 6.0 ml of crude product. On glpc (Apiezon L, 160°) it exhibited peaks for ether and benzene and one at 7.5 cm. The ir spectrum of the third peak was identical with that of commercial benzyl methyl ether (Sadtler[10] Spectrum No. 17013). The yield, determined by the peak enhancement method, was 34%. No starting material or other by-products were found.

Registry No.—Phenylcadmium reagent, 15924-35-3; ethyl α-bromopropionate, 535-11-5; ethyl α-bromoisobutyrate, 600-00-0; (*R*)-(+)-methyl α-bromopropionate, 20047-41-0; allyl bromide, 106-95-6; benzyl bromide, 100-39-0; 3-bromocyclohexene, 1521-51-3; chloromethyl methyl ether, 107-30-2.

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[15] H. Janssen, *Justus Liebigs Ann. Chem.*, **250**, 125 (1889).

Noble Metal Catalysis. II. Hydratocarbonylation Reaction of Olefins with Carbon Monoxide to Give Saturated Acids

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A process study of the hydratocarbonylation reaction of olefins with carbon monoxide to give saturated acids is described. The catalyst is probably a zero valent palladium–phosphine complex. Effects of changes in temperature, pressure, and concentrations of the three reactants and the complex catalyst system were studied. The rate of reaction depends approximately in a linear manner on the concentration of olefin and the pressure of carbon monoxide, while the rate reaches a maximum with a water concentration of 5–10%. The catalyst system undergoes a complex number of changes between the zero and plus two valence states, probably some involving the carbon moieties attached to the phosphine ligand.

The synthesis of saturated carboxylic acids from olefins, carbon monoxide, and water has been recently described,[1] according to eq 1 using a palladium–phosphine complex as catalyst.

$$RCH{=}CH_2 + CO + H_2O \xrightarrow{\text{cat.}} RCH_2CH_2CO_2H + CH_3CHRCO_2H \quad (1)$$

If alcohols are used in place of water, then esters are produced.[2] These palladium–phosphine catalyzed systems have advantages in rate and selectivity over the earlier palladium complexes without phosphines.[3] However, in those examples involving α olefins the branched-chain isomer was shown to be dominant.[2,4] The purpose of this paper is to describe methods for obtaining increased yields of the straight-chain acids starting from α olefins, since the straight-chain acids find greater utility as surface active agents.

Results

The following variables were studied: temperature and pressure, catalyst and solvent changes, proportions of olefin and water, and oxidation–reduction conditions.

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[1] N. von Kutepow, K. Bittler, and D. Neubauer, U. S. Patent 3,437,676 (1969), to Badische Anilin- and Soda-Fabrik.

[2] K. Bittler, N. von Kutepow, D. Neubauer, and H. Reis, *Angew. Chem., Int. Ed. Engl.*, **7**, 329 (1968).

[3] J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Lett.*, 1937 (1963).

[4] R. Huttel, *Synthesis*, **5**, 225 (1970).

Effect of Olefin.—1-octene was chosen as the olefin component because of its ready availability and purity (over 90% 1-octene) and because it might suitably represent olefins used for fatty acid synthesis. The results are shown in Table I. At both 125 and 150° increases in the 1-octene concentration lead to increases in the production of acids. The small changes in normal to α-methyl acid ratio may be due to small changes in the water concentration and/or catalyst changes (as discussed later). The production of acids is approximately proportional to the concentration of 1-octene.

TABLE I

CONVERSION TO AND RATIO OF ACID PRODUCTS AS A FUNCTION OF WEIGHT OF STARTING OLEFIN

Starting wt 1-Octene, g[a]	Temp, °C	Conversion, %	Ratio normal acid to α-methyl acid
80	125	72	1.7
160	125	80	1.5
40	150	71	0.7
80	150	75	0.5
160	150	74	0.5

[a] Water was added intermittently to keep water percentage around 5%. Otherwise except where noted conditions were as for the "standard run"; see Experimental Section.

Effects of Changes of Carbon Monoxide (and Hydrogen) Pressure.—As might be expected, increases in the carbon monoxide pressure cause increases in the yield of acid products. The increase is approximately linear with increase in carbon monoxide pressure. However, the ratio of normal to α-methyl acid products is effected inversely; *i.e.*, as carbon monoxide pressure increases the ratio decreases; refer to Table II.

TABLE II

CONVERSION TO AND RATIO OF ACID PRODUCTS AS A FUNCTION OF CARBON MONOXIDE (AND HYDROGEN) PRESSURE

Pressure, psig			
Carbon monoxide	Hydrogen	Conversion, %	Ratio normal acid to α-Methyl acid
100	0	14	5.5
200	0	51	3.0
800[a]	0	71	2.0
350	50	76	3.6
750	50	74	2.1
700	100	78	2.5
400	400	33	3.8

[a] Standard run.

The effect of hydrogen is noteworthy.[5] Small partial pressures lead to an increase in yield and also ratio but ultimately the yield drops dramatically, but no aldehydes, esters, or alcohols were discerned as long as carbon monoxide pressures above 400 psig were maintained. At 200 psig carbon monoxide pressure (with no added hydrogen) some *n*-octane was found in the remaining olefin.

Effect of Changes in Water Concentration.—As can be seen from Table III, water has a most pronounced effect on both yield and product ratio. The water percentages listed (by weight) are for the initial water concentrations. A 100% yield of acid products corresponds to about a 4% drop in water concentration. Thus, an initial water concentration of 0% means that anhydrides are the products of reaction. The yield of acid products reaches a maximum between 5 and 15% water both at 125 and 150°, while the ratio of normal acid to α-methyl acid reaches a minimum at slightly higher water levels. At quite high water levels probably a two-phase system exists, so that in the olefin-rich phase the concentration of water may be low, similar to the low water experiments. Thus the ratios of normal to α-methyl acids are similar, though the yields in the high concentration water experiments are low, probably owing to loss of catalyst. On the other hand, high anhydride levels also impede the reaction. It may be that a water molecule is a highly desirable ligand and at high anhydride concentrations it is lost. In a related system for hydratocarbonylation using a platinum–stannous chloride complex as catalyst, Kehoe and Schell[6] showed that small amounts of water were necessary for reaction even in alcoholic systems.

TABLE III

CONVERSION TO AND RATIO OF ACID PRODUCTS AS A FUNCTION OF INITIAL WATER PER CENT

Initial water %[a]	Temp, °C	Conversion, %	Ratio normal acid to α-methyl acid
50	125	38	2.0
12	125	80	0.9
8	125	74	1.5
4[b]	125	71	2.0
0	125	48	2.5
−50[c]	125	0	
75	150	11	0.9
22	150	57	0.8
12	150	64	0.5
8	150	73	1.0
0	150	63	2.0

[a] Standard catalyst and conditions except for water concentration. [b] Standard run. [c] 50% by weight acetic anhydride.

Effect of Temperature Changes.—The maximum yield of acids is obtained around 150° while the maximum ratio occurs around 125°. Yields at temperatures above 150° are complicated by the inverse reaction, *i.e.*, the dehydratocarbonylation reaction. At these temperatures acid products can be converted back to olefin, carbon monoxide, and water so that both the forward reaction (hydratocarbonylation) and the reverse reaction (dehydratocarbonylation) occur at appreciable rates. The resulting ratios and conversion are a function of both reactions; refer to Table IV.

TABLE IV

CONVERSION TO AND RATIO OF ACID PRODUCTS AS A FUNCTION OF TEMPERATURE

Temp, °C	Conversion, %	Ratio normal acid to α-methyl acid
100	47	1.3
125[a]	71	2.0
150	76	1.2
175	71	1.0

[a] Standard run.

Effects of Varying Catalyst Concentrations.—When the standard catalyst (0.5 g of palladium chloride and 3 g of triphenylphosphine, a molar ratio of 1:4) is doubled, the conversion of acid products goes from 71% to 77%

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(5) D. M. Fenton, U. S. Patent 3,641,074 (1972), to Union Oil Company of California.

(6) L. J. Kehoe and R. A. Schell, *J. Org. Chem.*, **35**, 2846 (1970).

but the ratio of acid products remains constant at 2.0. However, if just the triphenylphosphine concentration is increased, then there are effects on both conversion and ratio. At 125° the conversion is lowered by increasing the triphenylphosphine amount to 10 g but the ratio is dramatically increased, while at 150° both the yield and the ratio are increased. However, at 150°, additional increases in triphenylphosphine to 20 g increases the yield but lowers the ratio; refer to Table V.

TABLE V

CONVERSION TO AND RATIO OF ACID PRODUCTS AS A FUNCTION OF WEIGHT OF TRIPHENYLPHOSPHINE

Weight Triphenylphosphine, g	Temp, °C	Conversion, %	Ratio normal acid to α-methyl acid
3[a]	125	71	2.0
6[b]	125	77	2.0
10	125	46	3.5
3	150	75	1.0
10	150	80	3.6
20	150	86	1.5

[a] Standard run. [b] With 1 g of $PdCl_2$, 6 g of triphenylphosphine.

Effect of Phosphine Substituents.—Although all of the listed triarylphosphines are active it appears that electron-donating groups both decrease conversion and lower ratio. Tris-*o*-tolylphosphine is an exception and will be discussed later. *p*-Fluoro substituents give mixed results; refer to Table VI.

TABLE VI

CONVERSION TO AND RATIO OF ACID PRODUCTS AS A FUNCTION OF PHOSPHINE SUBSTITUENTS

Phosphine substituents[a]	Conversion, %	Ratio normal acid to α-methyl acid
Tris-*p*-anisyl	50	1.0
Tris-*p*-tolyl	67	1.2
Tris-*m*-tolyl	69	1.6
Triphenyl[b]	71	2.0
Tris-*o*-tolyl	73	2.4
Triphenyl[c]	77	2.0
Diphenyl-*p*-fluorophenyl[c]	81	1.8
Bis-*p*-fluorophenylphenyl[c]	83	1.7
Tris-*p*-fluorophenyl[c]	53	1.8

[a] 3 g of phosphine used in otherwise standard run. [b] Standard run. [c] 1 g of $PdCl_2$ and 6 g of triarylphosphine.

Effect of Additional Reagents.—Since both hydrochloric acid and lithium chloride reduce the normal to α-methyl ratio by the same amount, it is inferred that the effect on ratio is predominantly due to the chloride ion. Chloride ion (from lithium chloride) increases the conversion but hydrochloric acid decreases the conversion. So it must be that strong acid hydrogen ion is more detrimental to conversion than chloride ion is beneficial. In contrast to lithium chloride, those reagents capable of chloride ion removal, such as iron carbonyls, increase ratio but decrease conversion. Of course, iron carbonyls like ferrous chloride may complex with the palladium.[7] Stearic acid is effective, probably acting on colloidal palladium as a surface-active agent;[8] refer to Table VII.

TABLE VII

CONVERSION TO AND RATIO OF ACID PRODUCTS IN THE PRESENCE OF ADDITIONAL REAGENTS

Reagent	Amount of reagent, g	Conversion, %	Ratio normal acid to α-methyl acid
Concd HCl	2	69	1.6
$LiOAc\cdot 2H_2O$	5	74	2.0
LiCl	5	82	1.6
Stearic acid	10	86	1.0
$FeCl_2\cdot 4H_2O$	5	62	0.9
$Fe(CO)_5$	2	50	3.0
$Fe_2(CO)_9$	2	57	2.6
[a]	0	71	2.0

[a] Standard run.

Effect of Solvents.—Acetic acid was chosen as the paramount solvent because of its convenience. However, in industrial practice the product acids would probably be chosen as solvents. At 150° or lower the reverse reaction is negligible; so other carboxylic acids can be used. Noncarboxylic acid solvents that have a capacity for dissolving water may also be used; refer to Table VIII.

TABLE VIII

CONVERSION TO AND RATIO OF ACID PRODUCTS PRODUCED IN OTHER SOLVENTS

Solvent	Temp, °C	Conversion, %	Ratio normal acid to α-methyl acid
Valeric acid	125	58	2.2
	150	40	1.3
Octanoic acid	125	28	0.5
Tetrahydrofuran	125	28	0.8
Pyridine	150	0	
Acetonitrile	150	~44	0.7

Effect of Oxidative Conditions.—It was found necessary to thoroughly purge the system of oxygen in order to obtain reproducible results, for oxygen dramatically lowered the rate of conversion. Other oxidizing agents, such as benzoquinone and cupric chloride, completely inhibited the reaction. Also it was found that, when triphenylphosphine oxide was substituted for triphenylphosphine while under oxygen-free conditions, the hydratocarbonylation reaction did proceed but at diminished rate. Therefore, the conversion of triphenylphosphine to triphenylphosphine oxide was not the only reason for inhibition. Since hydroquinone, the reduction product of benzoquinone, actually increased the rate of reaction, and since zero-valent palladium complexes were observed as the products of the initial palladium complex added to the reaction, *e.g.*, $PdCl_2[(C_6H_5)_3P]_2$ (I), then it is proposed that the interfering oxidizing agents complex with I and render it inactive.

Effect of Reducing Agents.—Moderate amounts of reducing agents, *e.g.*, hydrogen, hydrazine, and hydroquinone, cause slightly improved conversion, and in the case of hydrogen to slightly higher ratios. The improved conversions may be due to the impedance of the oxidative side reaction leading to the inactive complex I. Previously Tsuji[9] noted that with the nonphosphine complexes hydrogen was beneficial. It was noted that in an open flask at 110° I was stable in acetic acid with 1-octene and that the introduction of carbon monoxide

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[7] D. M. Fenton, U. S. Patent 3,661,949 (1972), to Union Oil Company of California.

[8] D. M. Fenton, U. S. Patent 3,530,155 (1970), to Union Oil Company of California.

[9] J. Tsuji and K. Ohno, *Advan. Chem. Ser.*, **No. 70**, 155 (1968).

TABLE IX

PALLADIUM COMPLEXES ISOLATED FROM HYDRATOCARBONYLATION REACTIONS

Registry no.	Complex	Decomposition range, °C	Carbon, %		Hydrogen, %		Phosphorus, %		Chlorine, %	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
13965-03-2	$PdCl_2[P(C_6H_5)_3]_2$	280–290	61.6	61.1	4.3	4.8	8.8	8.6	10.0	8.7
40691-26-7	$PdCl(O_2CCH_3)[P(C_6H_5)_3]_2$	250–260	63.1	63.4	4.6	5.7	8.5	8.4	4.9	5.5
28516-49-6	$Pd[P(C_6H_5)_3]_3$	90–100	72.7	71.6	5.1	5.6	10.0	10.2	0.0	<0.1
14221-01-3	$Pd[P(C_6H_5)_3]_4$	105–110	74.8	75.2	5.2	5.5	10.7		0.0	
40691-27-8	$Pd[P(C_6H_5)_3]_2[(C_6H_5)_2PC_6H_4Cl]$	120–130	69.0	70.6	4.9	4.9	10.3	10.1	4.0	4.5
40756-38-5	$Pd[P(C_6H_5)_3][(C_6H_5)_2P(C_6H_4Cl)]_2$	120–130	66.6	66.7	4.7	5.0	10.0	9.6	7.6	7.4
40691-28-9	$PdCl_2[(C_6H_5)P(C_6H_4Cl)_2]_2$	200–210	51.5	50.4	3.1	3.9	7.4		25.4	26.7
40691-29-0	$PdCl_2[C_6H_5P(C_6H_4Cl)_2][P(C_6H_4Cl)_3]$	290–300	49.7		2.9		7.1	6.0	28.2	28.1

only very slowly caused catalyst decomposition, while either hydrogen or hydrazine quickly reduced I. Also small amounts of lithium acetate slightly speeded up the decomposition of I.

The slightly increased normal to α-methyl ratio with small amounts of hydrogen may be due to the reaction of hydrogen with complexes such as V (see next section) to give back complex I and thus impede the formation of substituted chlorophenylphosphine complexes which may give ratios more like fluorophenylphosphine complexes, *i.e.*, less than 2. Indeed it was noted for the standard run that in the first 0.5 hr the ratio was 2.4 with subsequent leveling off at 2.0.

Discussion of the Catalyst System.—The palladium catalyst system undergoes many complex reactions. When hydrochloric acid was added to the standard run, the main catalyst component isolated after reaction was I, as was noted earlier.[2] However, in other experiments without the added hydrochloric acid I was not isolated. Several components were isolated and will be discussed.

In those runs deficient in phosphine, colloidal palladium metal was sometimes found. This palladium metal could be redissolved by treating it with hydrochloric acid and triphenylphosphine[10] in acetic acid according to eq 2, and accordingly hydrogen was detected in the gas phase above the reaction. Small amounts of hydrogen were also detected in the gas phase during the hydratocarbonylation reaction, particularly if hydrochloric acid was present. It may also be recalled that with low carbon monoxide concentrations some conversion of octene to octane occurred.

$$Pd^0 + 2HCl + 2(C_6H_5)_3P \longrightarrow I + H_2 \qquad (2)$$

It was also found that heating I to its decomposition point under vacuum gave an equimolar mixture of triphenylphosphine and chlorophenyldiphenylphosphine. This is germane, for, particularly from experiments conducted above 150° and in the presence of excess chloride ion, there were isolated type II complexes where

$$PdCl_2[P(C_6H_{5-x}Cl_x)_3]_2 \qquad Pd[P(C_6H_{5-x}Cl_x)_3]_3$$

II III

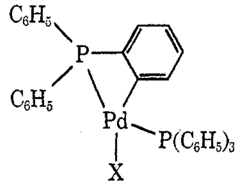
$x = 0$ and/or 1. The infrared spectrum of some of these yellow-orange complexes showed aromatic ortho disubstitution, indicating that the chlorine was ortho to the phosphorus. Some of these complexes are listed in Table IX.

The known complex[11] $Pd[P(C_6H_5)_3]_3$ was frequently isolated, particularly at high triphenylphosphine concentrations. Also $Pd[P(C_6H_5)_3]_4$ was once isolated.[12] The corresponding chlorophenylphosphine complexes III were isolated, where $x = 0$ and/or 1. These light yellow complexes slowly turned green on standing and were probably picking up oxygen.[13] In addition, small amounts of triphenylphosphine oxide and, under strongly acidic conditions, some diphenylphosphinic acid were found.

With a lithium acetate cocatalyst IV and V were found.

$$PdCl(O_2CCH_3)[P(C_6H_5)_3]_2$$

IV



V, X = Cl, OH, O_2CCH_3

V is quite labile and was not isolated in satisfactory condition from hydratocarbonylation runs, but can be made independently (see Experimental Section). The addition of hydrochloric acid to V gives I. Also it was shown that $Pd[P(C_6H_5)_3]_4$ reacts with chloride to give V (X = Cl). Also V in the presence of excess triphenylphosphine goes to type III complexes. Furthermore, Coulson[14] reported that the decomposition of a mixture of palladium chloride and $Pd[P(C_6H_5)_3]_4$ gave VI, which might arise from still another decomposition mode of V. Scheme I shows some of the interrelationships proposed for the complex catalyst system. Although the analogous platinum complexes to V are known, apparently V cannot be recovered by simple heating of I; so bases are necessary (however, see Shaw[15]). The addition of hydrogen effects reduction while that of hydrogen chloride causes oxidation (dehydrogenation). Also base hinders oxidation. The insertion of palladium into a carbon–chlorine bond effects oxidation and the reverse reaction causes reduction of the palladium.

Tris-*o*-tolylphosphine is a special case. The palladium complex of this ligand does not give V complexes but instead VII is formed. The results of these various effects are summarized in Table X.

Dehydratocarbonylation and Reversible Reactions.—An important adjunct to the hydratocarbonylation reaction is the dehydratocarbonylation, which involves the

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[10] J. Tsuji and K. Ohno, *J. Amer. Chem. Soc.*, **90**, 94 (1968).

[11] L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

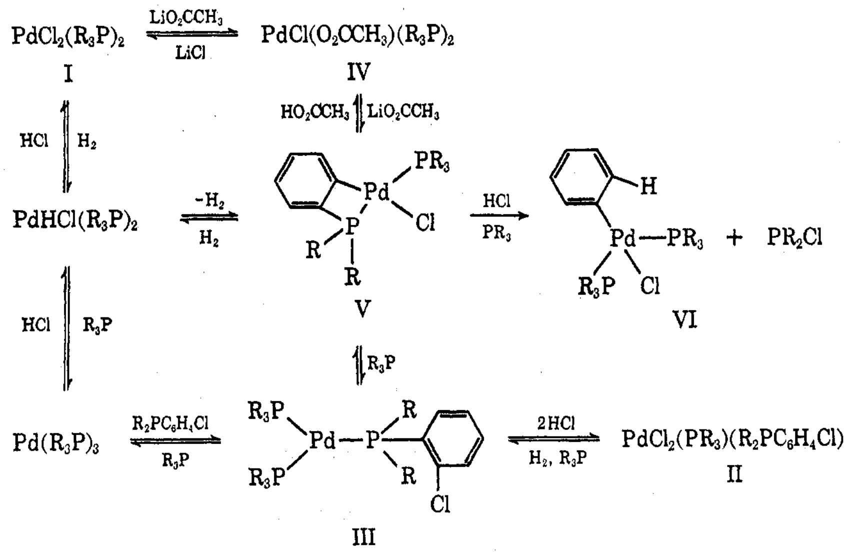
[12] P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, **1**, 6 (1968).

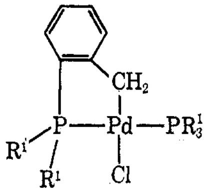
[13] C. J. Nyman, C. T. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 561 (1968).

[14] D. R. Coulson, *Chem. Commun.*, **23**, 1530 (1968).

[15] A. J. Cheney and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 860 (1972).

SCHEME I





VII, R^1 = *o*-tolyl

TABLE X

Effect[a]	Change made by increasing the effect: Rate changes	Ratio changes
HCl	Minor decrease	Lower
LiO_2CCH_3	Minor increase	None
LiCl	Increase	Lower
Low chloride	Decrease	Higher
Carboxylic acid solvent	Increase	Higher
Water	Maximum at initial concn around 8%	Maximum at initial concn around 4%
Temperature	Maximum at 150°	Maximum at 125°
1-Octene	Increase	None
Carbon monoxide	Increase	Lower
Hydrogen	Maximum at 50 psig	Higher
Triphenylphosphine	Reaches maximum	Possible maximum
Other phosphines	Complex, generally lower	Complex, generally lower

[a] As compared to standard run.

decomposition of acids back to olefins, carbon monoxide, and water.[16] Under certain conditions both of these reactions are significant so that products are based on thermodynamic control, and equilibrium conditions dominate. On the other hand, conditions are easily found where only one of the two reactions is occurring to any significant extent, so that kinetic control is achieved. Further, if only one acid isomer is desired, the other can be separated by distillation, crystallization, clathration, etc., and submitted to dehydratocarbonylation conditions to give back the olefin starting material. In this way, by-products are eliminated and essentially only the desired product is synthesized.[17]

Proposed General Mechanism.—Since the rate of formation of acid products near standard reaction conditions depends on the concentration of all three of the reactants, *i.e.*, 1-octene, carbon monoxide, and water, as well as the complex catalyst system, then the catalyst system must accommodate all three of the reactants before the rate-determining step. It will be recalled that acid production varies linearly with both 1-octene and carbon monoxide concentrations but that only carbon monoxide has an effect on ratio. Similarly, near standard conditions acid synthesis is approximately proportional to water concentration, and, like carbon monoxide, water also effects the acid ratio. Thus it is inferred that, in addition to the three reacting molecules, the active complex also includes other ligands, which list includes carbon monoxide and water, but not 1-octene. It should be emphasized that the competition of nonreactive ligands for the remaining sites of the palladium complex is equilibrium controlled and depends not only on ligand concentration but also on the stability of the palladium–ligand bond. In particular, since quite small amounts of both water (or hydroxide ligand) and chloride have such pronounced effects, it is evident that they form exceptionally stable ligand–palladium bonds. However, chloride, like 1-octene, does not effect ratio (except for a slight initial drop). On the other hand, the effect of triphenylphosphine is complex and ratios vary dramatically. It is concluded that the list of important ligands filling nonreactive sites on the active palladium complex includes chloride, water (or hydroxide), carbon monoxide, and triphenylphosphine, but it is only the last three that significantly affect ratio and particularly the last two. Since increases in the triphenylphosphine concentration lead first to an increase in ratio and then to a decrease, this implies that at high triphenylphosphine concentrations two triphenylphosphines are complexed at one time.

The transition state might look more like the product than like the starting materials. That this is true can be deduced from the following. The reaction of olefins, carbon monoxide, and ROH for the production of esters, acids, and anhydrides has shown to be reversible,[16] and also the production of esters occurs at lower temperatures than does the production of acids, while the for-

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[16] D. Fenton, U. S. Patents 3,530,198 (1970), 3,578,688 (1971), and 3,592,849 (1971), to Union Oil Company of California.

[17] D. Fenton, U. S. Patent 3,668,249 (1972), to Union Oil Company of California.

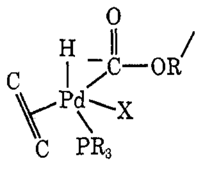
mation of anhydrides at practical conversions is difficult. Vice versa, the decomposition of anhydrides is facile at 150° while acids need temperatures around 200° and esters demand still higher temperatures. Thus the nature of R in VIII and IX is important. If the degree of ionization is important, then the formation of products should decrease in the order of acids > esters, but such is not the case. Also, if the production of the oxygen–hydrogen bond in ROH is important in the decomposition reactions then the decomposition series should be esters > anhydrides > acids, and again such is not the case. Therefore, the nature of R in ROH is not so important as the nature of R in RO_2CR', or, in other words, the transition state more closely resembles the acid derivative product than it does olefin, carbon monoxide, and ROH. While this fact does not rule out a concerted mechanism, it does imply that a stepwise mechanism is possible.

There are several candidates for the first step in the stepwise mechanism. Palladium–olefin[18] and palladium–carbonyl[19] complexes are known as well as alkyl,[12,19,20] acyl, and carboalkoxyl[12,21] complexes. Tsuji[22] and Chatt[23] have discussed mechanisms in which first-formed alkyl complexes are converted next to acyl complexes and finally to product. Heck[24] and the author[25] have considered the addition of carboalkoxyl or carboxyl complexes to olefins.

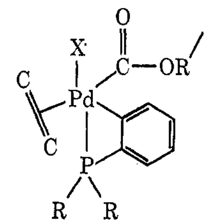
Mitigating against alkyl complexes is the fact that neither in the presence or absence of carbon monoxide were any alcohols (olefin plus water) or esters (olefin plus carboxylic acid) found, except under very acidic conditions with mineral acid. This is in contrast to palladium(II) chemistry, where acetaldehyde and vinyl carboxylates are prepared. Recently McKeon[26] has emphasized this difference between Pd(II) and Pd(0) where Pd(II) will cause transesterification and transetherification reactions while reduced palladium will not, thus indicating that reduced palladium will not form alkyl–palladium bonds by addition to olefins[27] under non-strong-acid conditions. Also, in the presence of hydrogen no aldehydes are produced, thus mitigating against acyl complexes although at still higher hydrogen (and lower carbon monoxide) pressures some alkane is produced. If then we have eliminated, as the first step, the attachment of H to olefin as well as the attachment of carbon monoxide to olefin, then we have left to consider only the attack of ROH on the palladium–carbonyl complex. This complex could look like VIII.

Here pentacoordinate complexes are drawn, because although three ligands are donating two electrons each, the H and COR are donating only two electrons altogether.[28] The olefin may be coplanar with the ring.[29]

The nature of R′ in type VIII complexes is important and it might be anticipated that esters would give more stable complexes than acids and acids more stable complexes than anhydrides. In particular, carboxyl complexes can undergo the shift reaction to give carbon dioxide and hydrogen. This may also account for the small amounts of hydrogen found. That carboalkoxyl complexes are stable was shown for Pd(II) complexes when oxalates[30] were prepared from carbon monoxide and alcohols, but in an aqueous environment oxalic acid could not be, and only carbon dioxide was produced. Thus Pd(II) can tolerate two carbonyl groups, at least one of which is a carboalkoxyl group.



VIII, X = Cl



IX, X = Cl, H

The hydride ligand in type VIII complexes may be relatively unstable. It has been shown that other palladium hydrides are unstable either under acidic or basic conditions,[31] and only moderately thermally stable.[32]

Under these conditions reactions like those discussed in Scheme I are probably occurring. In particular, complexes like IX could occur. This might account for the interesting effects of mixed phosphines. With the phenyl-substituted phenylphosphines it may be that the phenyl group is the preferred "second" ligand and thus exerts an extraordinary influence.

The second step would then be the attack of the olefin on the carboxyl group to give β-carboxyalkyl–palladium complexes. The ultimate formation of either the straight-chain acid of the branched-chain acid is determined in this step. Steric effects would dictate the formation of the straight-chain acid, and this is the general result as long as large amounts of free mineral acid are absent (in the presence of free mineral acid alkyl–palladium complexes are probably formed from alkyl groups which, in turn, are formed by the addition of a proton to the olefin so that the direction of proton addition determines the ratio).

That intermediates have some lifetime was indicated when it was shown that in competitive experiments the rate of isomerization of butyric anhydride to isobutyric anhydride was faster than the rate of reaction of butyric anhydride with 1-octene to give nonanoic and α-methyloctanoic acids (anhydrides). The reverse reaction with nonanoic anhydride and propylene also showed that isomerization was faster than olefin exchange.[33]

Finally, the addition of the olefin to the carboxyl

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(25) D. M. Fenton and K. L. Olivier, *Chemtech*, 220 (1972).

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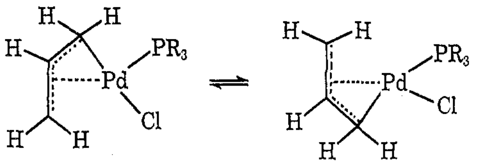
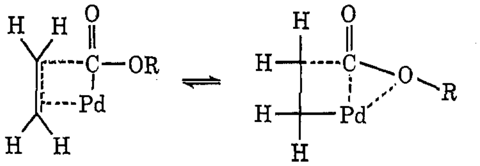
(32) K. Kudo, M. Midai, T. Murayama, and Y. Uchida, *Chem. Commun.*, 1701 (1970).

(33) D. M. Fenton, U. S. Patent 3,654,322 (1972), to Union Oil Company of California.

group can be linked to the π–σ complex shifts of allyl palladium complexes,[34] where eq 3 shows the π–σ



(3)



(4)

shifts and eq 4 shows the corresponding form for the reversible hydratocarbonylation reaction.

Experimental Section

A one-half gallon stainless steel stirred autoclave equipped with a cooling coil and condenser was used for the hydratocarbonylation reactions. The catalyst system, solvent, water, and olefin were placed in the autoclave, which was then purged twice with nitrogen. Carbon monoxide was added to the desired pressure. Heating and stirring were started. Pressure drops were noted. The autoclave was cooled and depressured, and any gain or loss of liquid weight was noted. The contents were analyzed by gas chromotography on a FFAP (free fatty acid phase) coated column. Each sample was run twice to reduce problems associated with "memory" effects. When acetic acid was used as solvent, additional information was obtained by either concentration by partial evaporation or by water washing. The recipe for the standard run is as follows: palladium chloride·$2H_2O$, 0.5 g; triphenylphosphine, 3 g; acetic acid, 400 ml; water, 15 g; 1-octene, 80 g; carbon monoxide, 800 psig. The conditions for the standard run are as follows: temperature, 125°; pressure, 800 psig (initial); time, 2 hr. In addition to the production of straight-chain and α-methyl acids there were also obtained small amounts of two other isomeric acids. Without additional hydrochloric acid the total of these other acids (α-ethylheptanoic and α-propylhexanoic) was less than 20% of the α-methyloctanoic acid production.

Preparation of V (R = C_6H_5).—To a 100-ml saturated solution of palladium chloride bis(triphenylphosphine) in *N*,*N*-dimethylformamide (the filtrate from 2.5 g of palladium chlorine bis(triphenylphosphine) in 100 ml of *N*,*N*-dimethylformamide), all protected by a nitrogen atmosphere, was added a 10-ml solution of 0.5 g of lithium acetate in 20 ml of water. Quickly a light yellow solid precipitated, decomposition range 80–100°. *Anal.* Calcd for $C_{36}H_{29}ClP_2Pd$: C, 65.5; H, 3.7; P, 9.4; Cl, 5.4. Found: C, 65.7; H, 4.4; P, 9.4; Cl, 5.3. The infrared spectrum showed ortho substitution and the compound could be reduced polarographically.

Conversion of V to Pd[P(C_6H_5)$_3$]$_3$.—To 1.5 g of V (R = C_6H_5) and 3 g of triphenylphosphine was added 200 ml of ethanol. The mixture was stirred for 6 hr at room temperature in a closed container. A white solid appeared. *Anal.* Calcd for $C_{54}H_{45}P_3Pd$: C, 72.6; H, 5.1; P, 10.4; Cl, 0.0. Found: C, 71.3; H, 5.2; P, 10.2; Cl, 0.3.

Reaction of V with Carbon Tetrachloride. Formation of II (Where Only 1 X = 1, Other X = 0).—To a solution of 1.5 g of V (R = C_6H_5) in 50 ml of carbon tetrachloride was added heat to reflux for 5 min. A yellow solid formed. *Anal.* Calcd for $C_{36}H_{29}Cl_3P_2Pd$: C, 58.7; H, 4.0; Cl, 14.4. Found: C, 59.2; H, 4.6; Cl, 13.0.

Reaction of V with Bromine.—Bromine (0.7 g) was slowly added to a solution of V (1.5 g) in benzene (50 ml). At first the color was rapidly discharged but after about half of the bromine was added the color persisted. The solution was refluxed for 5 min. To the cooled solution was added 50 ml of methanol, which caused the precipitation of 0.5 g of $PdBr_2[P(C_6H_5)_3]_2$, decomposition range 300–305°. The filtrate was concentrated on the steam bath to give brick red solid, 0.7 g, analyzing for either $PdBr_2[P(C_6H_5)_2(C_6H_4Br)]_2$ (*Anal.* Calcd for $C_{36}H_{28}Br_4P_2Pd$: C, 45.6; H, 3.0; P, 6.5.) or $PdBr_2[P(C_6H_5)(C_6H_4Br)_2][P(C_6H_5)_2C_6H_4Br]$ (*Anal.* Calcd for $C_{36}H_{27}Br_5P_2Pd$: C, 42.1; H, 2.7; P, 6.0. Found: C, 43.1; H, 3.4; P, 5.9).

Conversion of Pd[P(C_6H_5)$_3$]$_3$ to Pd[P(C_6H_5)$_3$]$_2$[P(C_6H_5)$_2$$C_6H_4$Cl].—To 2 g of $PdCl_2[(C_6H_5)_3P]_2$, 2 g of triphenylphosphine, and 200 ml of 1-butanol was added 5 ml of hydrazine hydrate. The mixture was magnetically stirred and heated to 90°, whereupon the white $Pd[P(C_6H_5)_3]_3$ formed. Heating was continued until a greenish-yellow precipitate had formed, decomposition range 125–130°. *Anal.* Calcd for $Pd[(C_6H_5)_3P]_2[(C_6H_5)_2PC_6H_4Cl]$: C, 67.4; H, 5.2; P, 10.9; Cl, 4.1. Found: C, 69.1; H, 5.2; P, 10.6; Cl, 2.0.

Conversion of V to I (R = C_6H_5).—To 0.8 g of V (R = C_6H_5), 5 ml of concentrated hydrochloric acid, and 1 g of triphenylphosphine in a 250-ml flask was added 100 ml of acetic acid. The mixture was refluxed for 16 hr to give a yellow precipitate identified as I, decomposition range 300–310°. *Anal.* Calcd for $C_{36}H_{30}Cl_2P_2Pd$: Cl, 10.1. Found: Cl, 9.8.

Preparation of IV (R = C_6H_5).—To 4 g of I (R = C_6H_5) dispersed in 200 ml of acetic acid was added 5 ml of hydrazine hydrate. The mixture was refluxed for 30 min. A light yellow solid was filtered away from the blackish filtrate, decomposition range 260–270°. *Anal.* Calcd for IV, $C_{38}H_{33}O_2ClP_2Pd$: C, 62.9; H, 4.6. Found: C, 63.8; H, 4.7.

Decomposition of I (R = C_6H_5).—To 3.5 g of I (R = C_6H_5) in 50 ml of acetic acid and 50 ml of acetic anhydride in a 250-ml flask was bubbled nitrogen while the mixture was heated to reflux for 6 hr. The palladium was removed and the filtrate was distilled to give 0.5 g of an oil, bp 220–240° (1 mm). The infrared spectrum of this distillate showed triphenylphosphine and an ortho-disubstituted phenyldiphenylphosphine. *Anal.* Calcd for 50% triphenylphosphine and 50% chlorophenyldiphenylphosphine: Cl, 6.0. Found: Cl, 5.2.

Preparation of VII.—To 3.5 g of palladium chloride bis(tri-*o*-tolylphosphine), 100 ml of acetic acid, and 5 g of lithium acetate in a 250-ml flask was added hydrogen while the mixture was heated for 2 hr at reflux. An orange-yellow precipitate was filtered which gave an infrared spectrum that indicated the presence of methylene groups (not present in the starting material). *Anal.* Calcd for VII, $C_{42}H_{41}P_2ClPd$: Cl, 4.7. Found: Cl, 5.7.

Registry No.—II, 40691-30-3; V, 35917-41-0; VII, 35917-43-2; 1-octene, 111-66-0; carbon monoxide, 630-08-0; triphenylphosphine, 603-35-0; carbon tetrachloride, 56-23-5; bromine, 7726-95-6; $PdBr_2[P(C_6H_5)_3]_2$, 23523-33-3; $PdBr_2[P(C_6H_5)_2(C_6H_4Br)]_2$, 40691-31-4; $PdBr_2[P(C_6H_5)(C_6H_4Br)_2][P(C_6H_5)_2(C_6H_4Br)]$, 40691-32-5; palladium chloride bis(tri-*o*-tolylphosphine), 40691-33-6.

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