

Headline Articles

Direct Hydrogenation of Carboxylic Acids to Corresponding Aldehydes Catalyzed by Palladium Complexes

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A variety of carboxylic acids can be directly hydrogenated into the corresponding aldehydes in high yields by using homogeneous catalysts such as $[Pd(PPh_3)_4]$ or combination of $Pd(OAc)_2$ with tertiary phosphines in the presence of an excess amount of 2,2-dimethylpropionic anhydride (pivalic anhydride). As a typical example, octanoic acid can be converted into octanal in 99% yield in 3 h at 80 °C under 3.0 MPa of H_2 in acetone in the presence of pivalic anhydride and a catalyst system composed of $Pd(OAc)_2$ + 5P(*p*-tol)$_3$. Such hydrogenation is widely applicable to various aliphatic, aromatic, and heterocyclic carboxylic acids as well as to di- and tribasic carboxylic acids. The process allows the presence of other functional groups such as ketonic carbonyl, nitrile, and ester groups and even internal C=C bonds. Heterogeneous palladium catalyst such as palladium on carbon also showed some catalytic activities.

Because of the pivotal importance of aldehydes as reagents and intermediates in organic synthesis and as final products for pharmaceutical, cosmetic, and agricultural uses, quite a variety of methods have been developed for preparation of various aldehydes. Hydroformylation of olefins, partial oxidation of primary alcohols, ozonolysis of olefins, and partial reduction of carboxylic acid derivatives can be named among other methods.[1] However, most of the currently available methods entail some problems and limitations in the choice of starting materials and/or in selectivity of the products. In industrial hydroformylation process, for example, applicable olefins are limited and regioselection for obtaining a desired aldehyde sometimes involves problems. Many useful reactions are known in partial oxidation of primary alcohols to aldehydes such as the Swern oxidation, the Dess–Martin oxidation, and oxidation by PCC or MnO_2. However, in these processes stoichiometric amounts of oxidizing agents are required with parallel formation of undesirable by-product(s) which must be discarded.

Reduction of carboxylic acid derivatives such as acid chlorides, anhydrides, and esters with metal hydrides provides a convenient laboratory method, but the reactions require stoichiometric amounts of metal hydrides and have to be carried out at low temperature to avoid reduction of other functional groups. Particularly, over-reduction of the produced aldehydes further to corresponding alcohols presents a considerable problem, since the produced aldehydes are more reactive than the starting compounds.

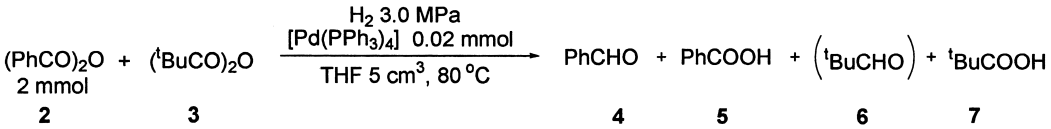
The catalytic Rosenmund reduction of various acid chlorides into aldehydes, performed by palladium on carbon catalyst with atmospheric pressure of hydrogen, is widely used because of high yields and convenient experimental conditions.[2] The process can be carried out at room temperature and under atmospheric pressure of H_2.

However, the Rosenmund reaction involves the necessity of preparing acid chlorides in the first place and is not applicable to unstable acid chlorides. It requires also addition of a stoichiometric amount of a base to neutralize the hydrogen chloride. As another type of convenient synthesis of aldehydes, Fukuyama developed a catalytic hydrogenation of thioesters in combination with triethylsilane catalyzed by Pd/C. The process provides a convenient means of aldehyde synthesis, but the prior synthesis of thioesters is required.[3]

Efficient preparative methods of aldehydes directly from carboxylic acids are rare.[4] Reaction of carboxylic acids with metal hydrides gives inert salts of carboxylic acids with liberation of H_2 and does not yield aldehydes. Catalytic hydrogenation of carboxylic acids by metal catalysts such as ruthenium usually yields the corresponding alcohols because of higher reactivity of aldehydes toward hydrogenation than that of carboxylic acids.[5]

Recently, a direct, vapor phase hydrogenation of carboxylic acids into aldehydes catalyzed by chromia catalyst has been successfully commercialized by Mitsubishi Chemical.[6] The hydrogenation reaction can convert various carboxylic acids into aldehydes in high yields and selectivities with formation of only water. A disadvantage of the process, however, is the requirement of high reaction temperature (350 °C) to vaporize the starting carboxylic acids, excluding applications of the pro-

Table 1. Competitive Hydrogenation of Benzoic Anhydride and Pivalic Anhydride



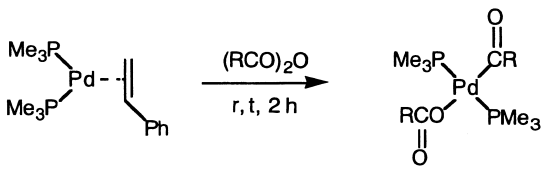
2 3 4 5 6 7

Entry	(tBuCO)$_2$O /mmol	Time/h	Recovered[a]/mmol		Yield[a]/mmol		
			2	**3**	**4**	**5**	**7**
1	2	48	0.26	0.62	2.52	0.72	2.30
2[b]	2	48	0.60	0.82	1.80	0.44	1.68
3	6	120	0.60	3.96	2.80	0	1.62

a) GLC yields. b) [Pd(dba)$_2$]/DPPB 0.02 mmol was used as a catalyst.

cess to thermally unstable compounds and making the process inconvenient in laboratory synthesis of aldehydes.

We have been interested in activation of carbon-oxygen bonds in oxygen-containing organic compounds by transition metal complexes[7] with an objective of developing a new process where use of organic halides can be avoided. As we have reported previously, carboxylic anhydrides were found to oxidatively add to Pd(0) complexes to give acyl(carboxylato)bis(tertiary phosphine)palladium(II) complexes (1) with cleavage of the C–O bond in the carboxylic anhydrides. The acyl(carboxylato)bis(tertiary phosphine)palladium complexes thus formed react with molecular hydrogen to liberate aldehydes and carboxylic acids accompanied by some alcohols produced by hydrogenation of the aldehydes formed (Eq. 1).[8]



1

$$\xrightarrow{H_2} \quad RCHO + RCOOH \qquad (1)$$

Based on the results a new catalytic process was developed to hydrogenate carboxylic anhydrides into aldehydes and carboxylic acids under mild conditions (Eq. 2).

$$(RCO)_2O + H_2 \xrightarrow{[Pd\ cat]} RCHO + RCOOH \qquad (2)$$

The catalytic process provides a convenient means to produce aldehydes from carboxylic anhydrides without using acyl halides under neutral mild conditions, making the process halide-free without liberation of a salt to be discarded. Remaining problems of the process are that preparation of the carboxylic anhydrides is required first and the half of the anhydride molecule is converted into carboxylic acid which must be released.

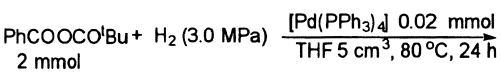
The present paper describes our effort to surmount the disadvantages through fundamental studies on the reactivities of carboxylic anhydrides with Pd(0) complexes. The attempt led to a novel synthetic method to convert carboxylic acids directly into aldehydes in the presence of a less reactive carboxylic anhydride.[9] We summarize in the present paper the results of catalytic hydrogenation of a variety of carboxylic acids and discuss the scope and limitations of the process.

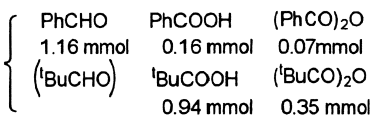
Results

Study of Competitive Hydrogenation of a Pair of Carboxylic Anhydrides into Aldehydes Catalyzed by a Pd(0) Complex. In a previous study of oxidative addition of various carboxylic anhydrides with Pd(0) complexes, we observed that the carboxylic anhydrides having more bulky carboxyl entities such as isobutyric anhydride (pivalic anhydride) and dimethylacetic anhydride, were hydrogenated less rapidly with [Pd(PPh$_3$)$_4$] than the less bulky anhydrides. The result of competitive hydrogenation of benzoic anhydride and pivalic anhydride is shown in Table 1.

When 2 mmol each of benzoic anhydride (**2**) and pivalic anhydride (**3**) were subjected to hydrogenation under hydrogen pressure of 3.0 MPa in THF at 80 °C, benzaldehyde (**4**) and benzoic acid (**5**) were produced, whereas only a negligible amount of pivalaldehyde (**6**) was formed, accompanied by pivalic acid (**7**) that was produced in an amount comparable to that of benzaldehyde. When 6 mmol of pivalic anhydride and 2 mmol of benzoyl anhydride were used, formation of benzoic acid (**5**) became negligible, with benzaldehyde formed as the only aldehyde. Use of a bidentate ditertiary bisphosphine, 1,4-bis(diphenylphosphino)butane (dppb), gave similar results with somewhat less effectiveness (entry 2). The results suggest that the bulkier entity in the anhydride is less reactive to the hydrogenation.

For comparing the reactivities of the acyl entities in the carboxylic anhydrides, we prepared a mixed anhydride, benzoic pivalic anhydride, having bulkier and less bulky acyl groups as shown below, and we examined its behavior toward palladium-catalyzed hydrogenation (Eq. 3).





(3)

The mixed anhydride containing the benzoyl and pivaloyl enti-

ties was prepared by treating silver benzoate with pivaloyl chloride. The mixed anhydrides produced were found to contain minor amounts of benzoic acid, together with benzoic and pivalic anhydrides as revealed by NMR, but the mixture was subjected to the catalytic hydrogenation without distillation to avoid the disproportionation process. The catalytic hydrogenation of the benzoic pivalic anhydride sample gave benzaldehyde as the major product on hydrogenation at 80 °C for 1 day (Eq. 3). Pivalic acid was formed preferentially, with a minor amount of benzoic acid. The reaction system examined after the hydrogenation contained pivalic anhydride and benzoic anhydride generated on disproportionation of the mixed anhydride.

The result indicates that the less bulky acyl part in the benzoic pivalic anhydride is preferentially hydrogenated.

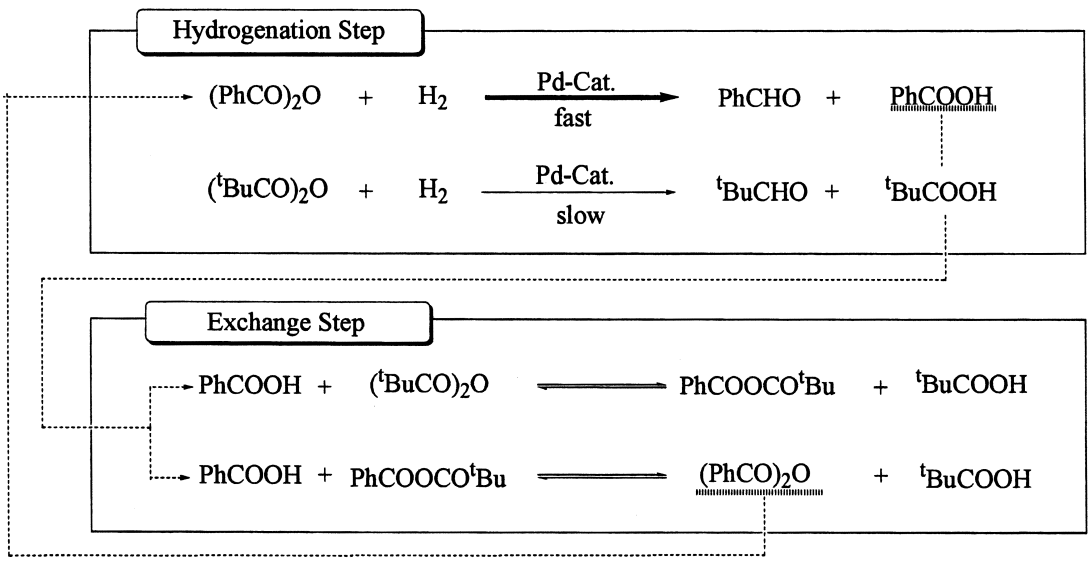
Design of a Catalytic Process to Directly Hydrogenate a Carboxylic Acid. Examination of the result shown in Eq. 3 led us to the idea of employing a mixture of a carboxylic acid and a less reactive, bulky, carboxylic anhydride such as pivalic anhydride as an additive for realizing a direct catalytic hydrogenation of the carboxylic acid into aldehydes. Scheme 1 illustrates the idea.

In the upper part of the Scheme, the competitive hydrogenation of benzoic anhydride and pivalic anhydride is shown. The palladium-catalyzed hydrogenation of benzoic anhydride proceeds much faster than the hydrogenation of pivalic anhydride, yielding corresponding aldehydes and carboxylic acids, respectively. The carboxylic acids produced would then react with the carboxylic anhydrides, as shown in the lower part of Scheme 1, generating a mixture of the mixed anhydride and the two kinds of symmetric anhydrides. The carboxylic anhydrides would then react with molecular hydrogen in the presence of a palladium catalyst, as shown in the upper part of the scheme, with the more reactive benzoic anhydride reacting faster with H_2. It is thus expected that addition of the less reactive bulky pivalic anhydride would lead to the preferential hydrogenation of benzoic acid into benzaldehyde at the cost of pivalic anhydride, which is converted into pivalic acid with formation of a minor amount of pivalaldehyde. Not shown in Scheme 1 for simplicity is the hydrogenation of benzoic pivalic anhydride that gives a mixture of the two aldehydes and the two carboxylic acids. The carboxylic acids produced there would be likewise converted into the mixture of carboxylic anhydrides in the exchange step shown in the lower part of Scheme 1 so as to be involved in the catalytic hydrogenation.

In fact, various types of carboxylic acids were successfully converted into the corresponding aldehydes under H_2 pressure at the cost of pivalic anhydride as shown in Tables 2–7. In these Tables, the experiments are standardized for the sake of comparison by a protocol using $[Pd(PPh_3)_4]$ in THF at 80 °C with hydrogen pressure of 3.0 MPa. We later found that employment of more polar solvents such as acetone and DMF was more favorable to increase the yield, but Tables 2, 3, and 5–8 show the results performed in THF.

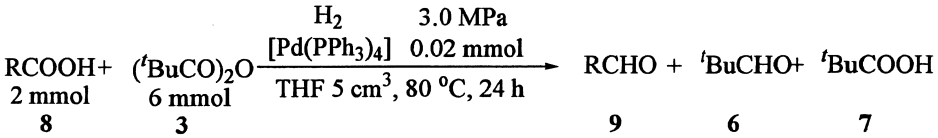
Table 2 summarizes the results of hydrogenation of various aliphatic carboxylic acids in the presence of pivalic anhydride and $[Pd(PPh_3)_4]$.

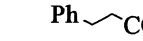
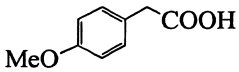
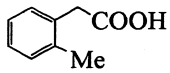
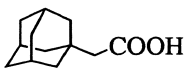
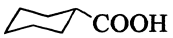
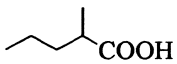
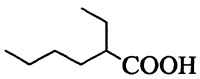
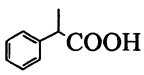
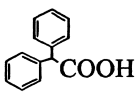
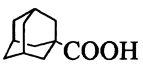
Most carboxylic acids without a substituent at the α-carbon were converted into the corresponding aldehydes in high yields (Table 2, entries 1–6). In the case of more hindered carboxylic acids, the yields of the aldehydes were decreased (entries 7–13). Hydrogenation of cyclohexanecarboxylic acid required a longer reaction time for obtaining a good yield (entries 7, 8). Hydrogenation of α-phenylpropionic acid (entry 11) gave styrene as the major product, indicating that decarbonylation of the acylpalladium intermediate occurred to give α-phenylethylpalladium intermediate that subsequently underwent β-hydrogen elimination to produce styrene. On the other hand, diphenylacetic acid (entry 12) yielded diphenylmethane. Its formation may be accounted for by hydrogenation of the putative intermediate, (diphenylmethyl)palladium species, produced by oxidative addition of the carboxylic anhydride followed by decarbonylation.[10] Highly hindered 1-adamantanecarboxylic acid showed a poor reactivity toward the hydrogenation and the recovery of the starting material was confirmed (entry 13).



Scheme 1. Proposed reaction mechanism of hydrogenation of two anhydrides catalyzed by a palladium complex.

Table 2. Catalytic Hydrogenation of Aliphatic Carboxylic Acids[a)]



Entry	Carboxylic Acids	Yield[b)]/%	Yield/mmol		Recovery/mmol	Other Products
		9[c)]	**6**[c)]	**7**[d)]	**3**[d)]	
1	$^{n}C_7H_{15}COOH$	98	0.46	5.20	2.96	
2[e)]	$^{n}C_7H_{15}COOH$	90	0.14	4.04	0.78	$(^{n}C_7H_{15}CO)_2O$[f]
3		99	0.50	5.64	3.08	
4		70	0.40	4.64	3.32	
5		92	0.54	4.88	3.22	
6		89	0.42	4.62	3.48	
7		63	0.52	5.84	3.34	
8[f)]		82	0.70	5.58	3.04	
9		64	0.70	4.08	3.10	
10		23	0.68	3.22	3.82	
11		< 3	0.40	< 4.80	3.58	 53%
12		13	0.42	5.38	3.12	 17%
13		8	0.64	3.00	3.22	

a) Reaction conditions are shown in the text. b) Yields are based on the starting carboxylic acids. c) Determined by ^{1}H NMR using $(CHCl_2)_2$ as an internal standard. d) Determined by GLC using $^{n}C_{17}H_{36}$ as an internal standard. e) $(^{t}BuCO)_2O$, 3 mmol. f) Reaction time, 48 h.

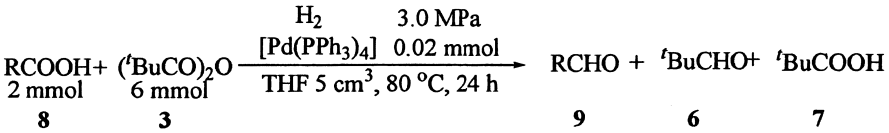
The results of the catalytic hydrogenation of aliphatic acids having functional groups are summarized in Table 3.

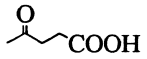
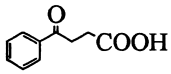
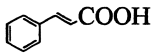
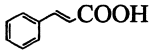
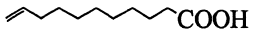
The C=O bonds in esters (entries 14, 15) and ketones (entries 16, 17), and internal C=C bonds (entries 18 and 19) remained unchanged throughout the hydrogenation reactions. In the case of hydrogenation of *trans*-cinnamic acid which has an α,β-unsaturated C=C bond, the yield of *trans*-cinnamaldehyde was low when $[Pd(PPh_3)_4]$ was used as the catalyst (Pd/P ratio = 1/4, entry 20), while a higher yield was achieved by usage of $[Pd(OAc)_2] + 2PPh_3$ catalyst system (Pd/P = 1/2, entry 21). The results of the high yields and quite high selectivities (formation of pivalaldehyde was < 1%.) in this case may be accounted for by assuming pre-coordination of a bis(triphenylphosphine)palladium(0) complex to the C=C bonds[11] in the reaction media, followed by the activation of C–O bond of *trans*-cinnamic acid.

In the case of hydrogenation of 10-undecenoic acid having a terminal C=C bond, isomerization of the terminal C=C bond to an internal bond and partial hydrogenation of the terminal C=C bond also occurred (entry 22). Attempts to hydrogenate 10-undecenoic acid to unsaturated aldehyde without causing terminal-to-internal isomerization and the hydrogenation of the olefinic double bond are summarized in Table 4.

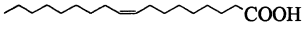
Occurrence of isomerization was found to be suppressed by

Table 3. Catalytic Hydrogenation of Aliphatic Carboxylic Acid Having Functional Groups[a)]

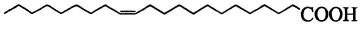


Entry	Carboxylic Acids	Yield[b)]/%	Yield/mmol		Recovery/mmol	Other Products
		9[c)]	**6**[c)]	**7**[d)]	**3**[d)]	
14	$EtOCO(CH_2)_4COOH$	99	0.60	5.12	3.30	
15	$EtOCO(CH_2)_{10}COOH$	99	0.60	4.76	3.28	
16		97	0.38	—	3.40	
17		85	0.14	3.98	3.54	
18	oleic acid[e)]	99[g)]	0.52	5.80	2.84	
19	erucic acid[f)]	96[g)]	0.42	5.52	3.08	
20		30	0.02	3.96	3.82	
21[g)]		84	0.02	3.68	3.80	
22		87[h)]	0.26	4.38	3.50	olefin[c)] external 48% internal 38% hydrogenated (14%)

a) Typical conditions are given in the text. b) Yields are based on the starting carboxylic acids. c) Determined by ^{1}H NMR using $(CHCl_2)_2$ as an internal standard. d) Determined by GLC using $^nC_{17}H_{36}$ as an internal standard.
e) Oleic acid = *cis*-9-octadecenoic acid.



f) Erucic acid = *cis*-13-docosenoic acid.



g) $Pd(OAc)_2/_2PPh_3$ was used as a catalyst.
h) Total aldehyde yield.

using polar solvents such as *N*,*N*-dimethylformamide and 1,2-dimethoxyethane.

Most aromatic acids are reduced in high yields into the corresponding aldehydes as shown in Table 5.

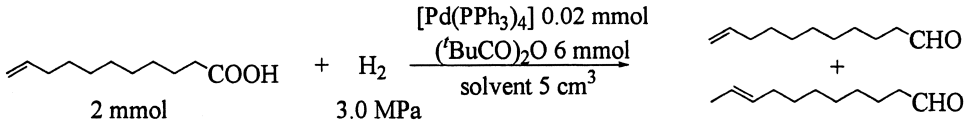
The *meta*- and *para*-substituted benzoic acid derivatives having electron-withdrawing as well as electron-releasing groups were successfully hydrogenated into aldehydes in excellent yields (entries 23–27). In the case of 4-methoxybenzoic acid bearing the electron-donating group at the *para*-position, a longer reaction time was required to complete the reaction (entry 26). On the other hand, *o*-methylbenzoic acid was resistant to reduction to *o*-tolualdehyde owing to the steric hindrance of the methyl group around the carbonyl carbon in the carboxyl group. In hydrogenation of monofluorobenzoic acids (entries 30–32), conversion of the starting carboxylic acids into the corresponding aldehydes occurred in excellent yields for *meta*- and *para*-substituted fluorobenzoic acids, whereas *o*-fluorobenzaldehyde was obtained in a moderate yield. *m*-Chlorobenzoic acid was hydrogenated selectively into *m*-chlorobenzaldehyde without causing the C–Cl bond cleavage (entry 33), whereas chloro-substituted benzoic acids at *para*- and *ortho*-positions gave complicated mixtures. 1- and 2-Naphtoic acids were hydrogenated into the corresponding aldehydes in moderate yields with formation of naphthalene as the decarboxylation product (entries 34–35).

The present catalytic hydrogenation process can be applied to heterocyclic carboxylic acids, as summarized in Table 6.

Among pyridinecarboxylic acids, only nicotinic acid having the carboxyl group at the β-position was hydrogenated to produce the corresponding aldehyde quantitatively. 2-Pyridinecarboxylic acid was not hydrogenated, whereas only a small amount of 4-pyridinecarboxylic acid was hydrogenated. The reason for the poor reactivity of 4-pyridinecarboxylic acid is not clear. Furancarboxylic acids and thiophenecarboxylic acids were hydrogenated in moderate to good yields into the corresponding aldehydes (entries 39–42), although the hydrogenation proceeded slowly.

Aliphatic and aromatic dicarboxylic acids were also converted into corresponding dialdehydes in excellent yields, as shown in Table 7 (entries 43, 44, and 47, 48), exceptions being

Table 4. Attempts of Chemoselective Hydrogenation of 10-Undecenoic Acid



Conditions	Total aldehyde yield/%	Olefin isomerization[a] terminal:internal	Yield of 10-Undecenal/%
acetone, 80 °C, 5 h	68	86:14	58
$MeO(CH_2)_2OMe$, 80 °C, 3.5 h	90	91:9	82
MeCN, 80 °C, 3 h	45	80:20	36
DMF 80 °C, 5 h	69	98:2	68
DMF 2.5 cm^3, H_2 6.0 MPa, $(^tBuCO)_2O$ 3 mmol 80 °C, 5 h	83	96:4	80

a) The amount of hydrogenated product was negligible as determined by ^1H NMR.

those which easily form cyclic carboxylic anhydrides.

Glutaric acid (entry 45), and succinic acid (entry 46) were converted into six- and five-membered cyclic anhydrides, whereas phthalic acid (entry 49) was quantitatively converted into phthalic anhydride. Aromatic tribasic acid, 1,3,5-benzenetricarboxylic acid, was hydrogenated to tricarbaldehyde in a high yield, accompanied by formation of a small amount of isophthalaldehyde as a byproduct formed by removal of one carboxyl group (entry 50).

Table 8 shows the effects of variation of experimental conditions on the yield of octanal by hydrogenation of octanoic acid in the presence of 0.02 mmol of $[Pd(PPh_3)_4]$ under 3.0 MPa of H_2 in THF at 80 °C. When the amount of pivalic anhydride was increased from 2 mmol/2 mmol of octanoic acid to 3, 4, and 6 mmol, the yield of octanal produced increased from 78% to 90, 92, and 98%.

Increase in the yield of pivalaldehyde as by-product was also noted when the higher ratio of the pivalic anhydride to octanoic acid was employed.

Lowering the hydrogen pressure to 0.5 MPa caused a decrease in the yield of octanal down to 47%. Lowering the reaction temperature to 50 °C from 80 °C also caused the decrease in the aldehyde yield under otherwise similar conditions.

Since pivalic anhydride can be considered in a sense as a dehydrating agent, the effects of various dehydrating agents were also examined (Table 9).

Adamantanecarboxylic anhydride, another bulky carboxylic anhydride similar to pivalic anhydride, was effective as an additive in the hydrogenation reaction of octanoic acid. Other dehydrating agents such as acetic anhydride used in excess, dibutyl dicarbonate, and dicyclohexylcarbodiimide showed some effects to enhance the hydrogenation activity, whereas *o*-sulfobenzoic anhydride and diphenylphosphinic anhydride were ineffective in promoting the hydrogenation.

Table 10 shows the effect of solvents in the hydrogenation reaction. In general, the hydrogenation proceeds faster in polar solvents such as acetone and DMF than in THF, dioxane, and toluene.

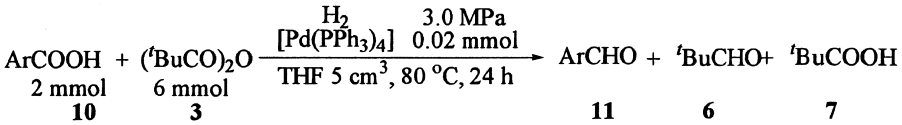
In Table 11 are summarized the effects of catalysts and catalyst precursors on the yield of octanal by hydrogenation of octanoic acid.

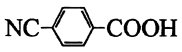
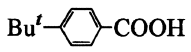
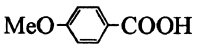
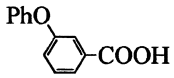
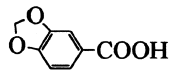
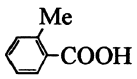
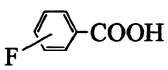
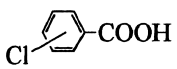
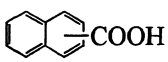
The hydrogenation of octanoic acid with $[Pd(PPh_3)_4]$ in acetone under 3.0 MPa of H_2 at 80 °C for 5 h in the presence of pivalic anhydride gives octanal in 91% yield. Addition of an extra molar amount of PPh_3 to $[Pd(PPh_3)_4]$ suppressed the aldehyde formation to less than half. The effect of addition of PPh_3 ligand in varying molar amounts to a Pd(0) complex was examined next using $[Pd(dba)_2]$. The result showed that use of $[Pd(dba)_2]$ in combination with 4 molar amounts of PPh_3 showed much less activity than the case when $[Pd(PPh_3)_4]$ was used. The results imply that the dba ligand attached to Pd(0) may hinder the reaction of the Pd(0) complex in reaction with the substrate. Further increase in the extra amount of PPh_3 caused further suppression in the catalytic activity.

Although a Pd(0) species is believed to be involved in the catalytic system, it is not necessary to use a Pd(0) complex itself as the catalyst. Use of palladium(II) acetate in combination with a phosphine ligand[12] was found to be effective as well in the hydrogenation. Addition of 4 molar amounts of PPh_3 ligand was effective to give the octanal in a high yield, whereas addition of more PPh_3 had an inhibition effect. Addition of 5 molar amounts of P(*o*-tol)$_3$, which is known as a very bulky ligand, severely hindered the hydrogenation, whereas addition of PPh_2(*p*-tol) had a similar effect to that of PPh_3. The highest aldehyde yield was obtained with use of $Pd(OAc)_2$ with five molar amounts of P(*p*-tol)$_3$.

Effects of other tertiary phosphine and phosphite ligands which showed poor promotion effects are also included in Table 11. Among the catalyst precursors examined, the system containing $Pd(OAc)_2$ and $PMePh_2$ showed a different behavior, giving more pivalaldehyde than octanal. The reason for such abnormal behavior was not pursued further.

Table 5. Catalytic Hydrogenation of Aromatic Carboxylic Acids[a)]



Entry	Carboxylic Acids	Yield[b)]/%	Yield/mmol		Recovery/mmol	Other Products
		11[c)]	6[c)]	7[d)]	3[d)]	
23	PhCOOH	91	0.62	5.20	2.84	$(PhCO)_2O$[f)] 5%[d)]
24		99	0.52	5.38	2.86	
25		99	0.54	5.30	3.22	
26[e)]		95	0.76	5.38	4.52	
27		97	0.42	5.02	2.86	Ph_2O[f)]
28		84	0.64	4.46	3.22	
29[e)]		30	0.40	4.04	3.74	
						
30	*ortho*	78	0.74	4.62	3.14	
31	*meta*	99	0.68	5.08	3.14	
32	*para*	93	0.96	4.80	2.68	
						
33	*meta*	99	0.52	4.40	3.36	
						
34	1-	50	0.32	3.84	3.68	 [f)] 27%[d)]
35[g)]	2-	60	0.26	3.16	3.96	 [f)] 10%[d)]

a) Typical conditions are shown in the text. b) Yields are based on the starting carboxylic acids. c) Determined by ^{1}H NMR using $(CHCl_2)_2$ as an internal standard. d) Determined by GLC using $^nC_{17}H_{36}$ as an internal standard. e) Reaction time, 48 h. f) Detected with GC-MS. g) H_2 6.0 MPa.

Other divalent palladium complexes such as *trans*-$[PdCl_2(PPh_3)_2]$, $[Pd(\eta^3\text{-allyl})Cl]_2$ without and with phosphines showed no or poor catalytic activity. Pd/C also catalyzed the hydrogenation, giving the aldehyde in a yield over 50%,[13] but the yield of pivalaldehyde dominated over that of octanal.

Figure 1 shows the time course of the hydrogenation of octanoic acid with $[Pd(PPh_3)_4]$ and $Pd(OAc)_2$ + 5P(*p*-tol)$_3$ systems. Usage of $Pd(OAc)_2$ + 5P(*p*-tol)$_3$ combination as a catalyst precursor afforded almost quantitative conversion of octanoic acid to octanal within 3 h.

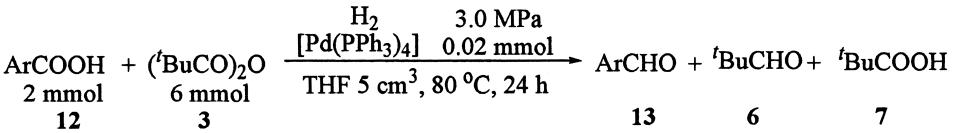
Discussion

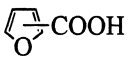
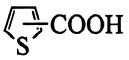
Scope and Limitations. The catalytic hydrogenation process found in the present study provides a new and convenient means to prepare quite a variety of aldehydes directly from free carboxylic acids in one pot. The present process is applicable to various aliphatic acids and is tolerant of the presence of carbonyl groups and does not hydrogenate the inner C=C bond. Various aromatic and heterocyclic carboxylic acids can be smoothly hydrogenated in a reasonable reaction time under mild experimental conditions. Application of the present hydrogenation method to dibasic and tribasic carboxylic acids may be of considerable potential interest to produce di- and tricarbaldehydes. Furthermore, it is possible to protect one of the carboxylic groups by converting it into an ester that is not susceptible to the hydrogenation. That part can be later hydrolyzed, after the first step of hydrogenation, to regenerate the carboxylic part.

The present process is regarded as complementary to the known Mitsubishi Chemical process of direct hydrogenation of carboxylic acids using chromia. One advantage of the present process is that the reaction can be performed under mild conditions, whereas the Mitsubishi Chemical process requires the high temperature of 350 °C and its scope is thus somewhat limited.

The present method does not need to start from acyl halide,

Table 6. Catalytic Hydrogenation of Heterocyclic Carboxylic Acids[a)]



Entry	Carboxylic Acids	Yield[b)]/%	Yield/mmol		Recovery/mmol
		13[c)]	**6**[c)]	**7**[d)]	**3**[d)]
					
36	α	0	0	1.98	4.48
37	β	99	1.06	5.38	2.52
38	γ	4	0.94	5.68	2.48
					
39[e)]	2-	87	0.84	4.90	2.80
40[e)]	3-	90	0.72	4.68	3.18
					
41[e)]	2-	72	1.10	5.42	2.90
42[e)]	3-	73	0.78	4.84	3.06

a) Typical conditions are shown in the text. b) Yields are based on the starting carboxylic acids. c) Determined by ^{1}H NMR using $(CHCl_2)_2$ as an internal standard. d) Determined by GLC using $^n C_{17}H_{36}$ as an internal standard. e) Reaction time, 48 h.

nor does it need use of any extra base, and it produces no extra byproducts that should be discarded. Thus the method can be regarded as an environmentally benign process and may be suitable for laboratory synthesis of various aldehydes. As a limitation, the present process requires addition of pivalic anhydride, posing a cost problem and limiting the commercial applications to production of somewhat expensive products.

Mechanism. In our preliminary communication, we have proposed the reaction mechanism as shown in Scheme 2 to account for the conversion of a carboxylic acid in the presence of pivalic anhydride into an aldehyde catalyzed by a palladium catalyst under pressurized H_2.

Since $[PdL_2(styrene)]$ type complexes having tertiary phosphine ligands such as PMe_3 and PMe_2Ph are known to undergo the oxidative addition of carboxylic anhydride to give the acyl(carboxylato)bis(tertiary phosphine)palladium(II) **1**, as shown in Eq. 1, and complex **1** reacts with H_2 to release the aldehyde and carboxylic acid (Eq. 2), the reaction mechanism shown in Scheme 3 accommodates the known experimental results. The number of ligands L attached to the active Pd species in Scheme 2 is tentative and in certain cases the number may be smaller than 2. The configuration of the acyl(carboxylato)(tertiary phosphine)palladium obtained in the stoichiometric process was in the trans form, but it may have a cis form in the catalytic process depending on the tertiary phosphine ligand employed, since ditertiary phosphine ligand also showed some catalytic activity.

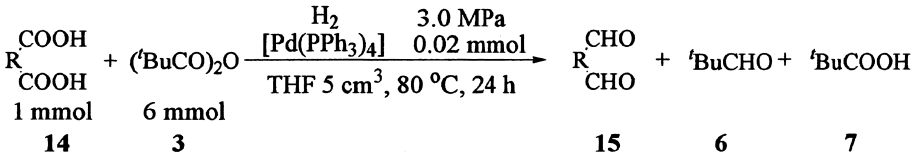
Outside the main catalytic cycle are shown the secondary cycles to convert the carboxylic acid released in the hydrogenation of the acyl(carboxylato)palladium(II) into a mixture of anhydrides on reaction with pivalic anhydride added to the system. On interaction with pivalic anhydride, the carboxylic acid RCOOH would be converted into a mixture of the carboxylic anhydrides: $(RCOOCO^tBu)$, $(RCO)_2O$, and $(^tBuCO)_2O$ as shown in Scheme 2.[14] The palladium(0) complex will attack the less bulky carboxyl carbon preferentially to form an acyl(carboxylato)palladium intermediate that carries the catalytic cycle. Limited amounts of pivalaldehyde are generated in all runs due to occurrence of the hydrogenolysis of pivalic anhydride by the palladium complex.

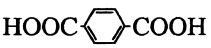
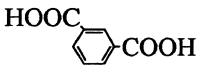
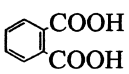
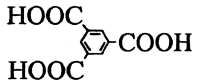
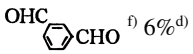
Although the main cycle in Scheme 2 accommodates the results of stoichiometric reactions of the isolated acyl(carboxylato)palladium(II) to release the aldehyde and carboxylic acid, the exact course of catalytic processes requires further validation.

A theoretical study with a DFT calculation[15] suggested that hydrogenation of *trans*-$[Pd(Ac)(OAc)(PMe_3)_2]$ gives acetaldehyde and a acetato(hydrido)palladium species, *trans*-$[PdH(OAc)(PMe_3)_2]$, as shown on the left hand cycle in Scheme 3. The result suggested the possibility of reaction of the carboxylato(hydrido)palladium species with carboxylic anhydride, as shown on the right hand of Scheme 3 to liberate carboxylic acid with formation of acyl(carboxylato)palladium complex as shown at the bottom in Scheme 3. The acyl(carboxylato)palladium complex may carry the catalytic cycle to react with hydrogen. The intermediate species are shown in Scheme 3 as trans forms to be consistent with the experimental results carried out on stoichiometric processes, but the catalytic process may proceed through cis complexes.

The proposed mechanism is novel and involves intermediacy of only Pd(II) species. Scheme 3 stands in contrast to the well accepted mechanism operating through the catalytic cycle composed of Pd(0) and Pd(II) species or with the recently argued catalytic cycle involving Pd(II) and Pd(IV).[16]

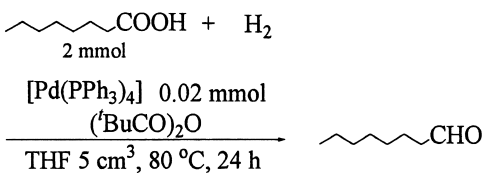
Table 7. Catalytic Hydrogenation of Di- and Tricarboxylic Acids[a)]



Entry	Carboxylic Acids	Yield[b)]/%	Yield/mmol		Recovery/mmol	Other Products
		15[c)]	**6**[c)]	**7**[d)]	**3**[d)]	
	$HOOC(CH_2)_nCOOH$					
43	**n = 10**	99	0.48	5.44	2.92	
44	**7**	98	0.74	4.62	3.12	
45	**3**	—[e)]	0.70	3.52	3.82	 79%[d)]
46	**2**	0	0.64	3.40	4.04	 99%[d)]
47		99	0.36	4.66	3.22	
48		94	0.26	4.60	3.38	
49		0	0.72	3.04	4.04	 [f)] quant.[d)]
50[g)]		86[h)]	0.34	4.56	3.06	 [f)] 6%[d)]

a) Typical conditions are shown in the text. b) Yields are based on the starting carboxylic acids. c) Determined by ^{1}H NMR using $(CHCl_2)_2$ as an internal standard. d) Determined by GLC using $^nC_{17}H_{36}$ as an internal standard. e) The aldehyde signal was observed by ^{1}H NMR at δ 9.35 ($CDCl_3$) in 12% yield. f) Detected with GC-MS. g) Carboxylic acid, 0.67 mmol. h) Trialdehyde yield.

Table 8. Effect of Experimental Conditions in Catalytic Hydrogenation of Octanoic Acid



$(^tBuCO)_2O$ /mmol	H_2 Pressure /MPa	Temperature /°C	$C_7H_{15}CHO$ Yield[a)]/%	^{t}BuCHO[a)] /mmol
6	3.0	80	98	0.46
4	3.0	80	92	0.26
3	3.0	80	90	0.14
2	3.0	80	78	0.08
6	0.5	80	47	0.36
6	3.0	50	68	0.14

a) Determined by ^{1}H NMR.

Our preliminary study on the reaction of *trans*-$[PdH(OCOCF_3)(PMe_3)_2]$ with propionic anhydride gave evidence supporting the formation of propionic acid and of *trans*-$[Pd(COEt)(OCOCF_3)(PMe_3)_2]$ that liberates propionaldehyde on treatment with H_2 in agreement with Scheme 3. Currently we are trying to clarify the mechanism of the catalytic hydrogenation of carboxylic anhydride, examining the feasibility of the mechanisms shown in Scheme 2 or Scheme 3 by experimental and theoretical studies. The results will be reported separately.

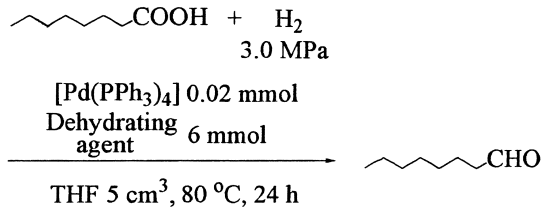
Conclusion

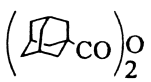
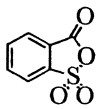
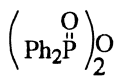
Since the useful methodologies to directly convert carboxylic acids into aldehydes are quite limited, the present method provides a convenient general route to selective production of aldehydes under mild and simple conditions from carboxylic acids. The process is based on the previous studies about release of aldehyde from acyl(carboxylato)palladium complexes on treatment with hydrogen. The direct hydrogenation of carboxylic acids was realized by combining the catalytic hydrogenation process for conversion of carboxylic anhydrides into aldehyde and carboxylic acid with auxiliary cycles involving the exchange processes between the carboxylic acid and bulky carboxylic anhydride.

Experimental

All manipulations were carried out under argon. Solvents were purified by usual methods under argon. Tetrakis(triphenylphos-

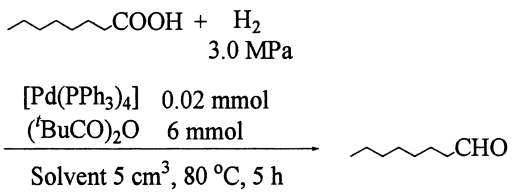
Table 9. Effect of Dehydrating Agent in Catalytic Hydrogenation of Octanoic Acid



Dehydrating agent	$C_7H_{15}CHO$ Yield[a]/%	RCHO[a] /mmol
$(^tBuCO)_2O$	98	0.46 (R = ^{t}Bu)
	99	1.12 (R = adamantyl)
	0	—
Ac_2O (1.1 cm^3),[b] 48 h	40[c]	—
$(^tBuOCO)_2O$	54	—
	0	—
	31	—

a) Determined by ^{1}H NMR unless otherwise noted. b) The reaction mixture was stirred at 80 °C for 1 h before introduction of H_2. c) GLC yield.

Table 10. Effect of Solvent in Hydrogenation of Octanoic Acid

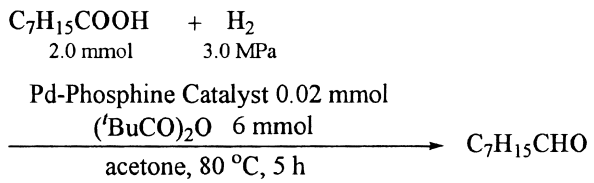


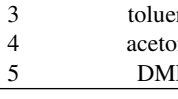
Run	Solvent	$C_7H_{15}CHO$ Yield[a]/%	^{t}BuCHO[a] /mmol
1	THF	78	0.26
2	dioxane	69	0.26
3	toluene	66	0.14
4	acetone	91	0.34
5	DMF	93	0.22

a) Deterrmined by ^{1}H NMR.

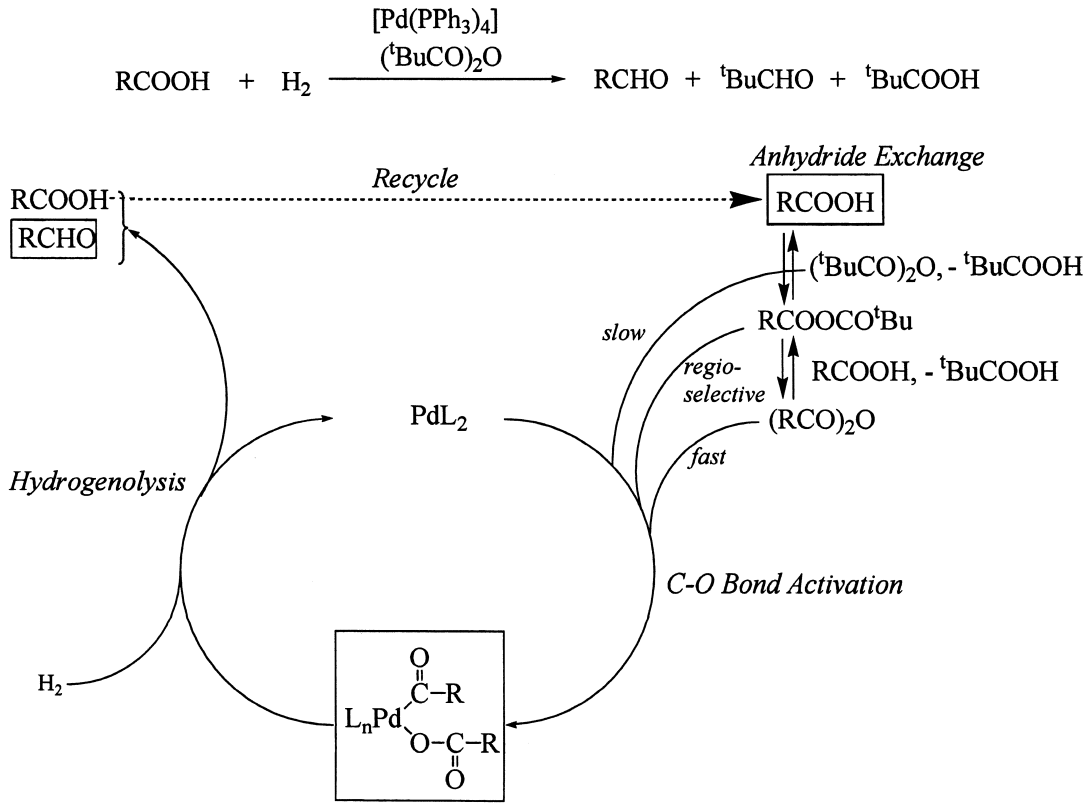
phine)palladium(0),[17] bis(dibenzilydeneacetone)palladium(0),[18] (η^3-allyl)chloropalladium(II),[19] and adamantanecarboxylic anhydride[20] were synthesized by the reported methods. All carboxylic acids and anhydrides were commercial products and were used without further purification. NMR data were obtained with JEOL AL300 in $CDCl_3$ as a solvent at room temperature. Gas

Table 11. Effect of Palladium–Phosphine Catalyst



Pd–Phosphine Cat.		$C_7H_{15}CHO$ Yield[a]/%	tBuCHO[a] /mmol
$[Pd(PPh_3)_4]$		91	0.34
$[Pd(PPh_3)_4]$	+ PPh_3	41	0.12
$[Pd(dba)_2]$	+ $4PPh_3$	13	0.02
	+ $5PPh_3$	7	< 0.01
	+ $6PPh_3$	5	0.02
$[Pd(OAc)_2]$	+ $4PPh_3$	79	0.20
	+ $5PPh_3$	50	0.14
	+ $6PPh_3$	24	0.06
	+ $2P(o\text{-tol})_3$	4	0.02
	+ $3P(o\text{-tol})_3$	7	0.04
	+ $4P(o\text{-tol})_3$	5	0.02
	+ $5P(o\text{-tol})_3$	8	0.02
	+ $4PPh_2(p\text{-tol})$	74	0.18
	+ $5PPh_2(p\text{-tol})$	62	0.12
	+ $3P(p\text{-tol})_3$	67	0.18
	+ $4P(p\text{-tol})_3$	90	0.38
	+ $5P(p\text{-tol})_3$	96	0.48
	+ $6P(p\text{-tol})_3$	33	0.16
	+ 5P(2-furyl)$_3$	0	0
	+ $4PMePh_2$	20	1.18
	+ $5PMePh_2$	12	0.70
	+ 2P(^{t}Bu)3	0	0
	+ $4P(OPh)_3$	2	0.10
	+ $5P(OPh)_3$	< 1	< 0.01
	+ $5P(NMe_2)_3$	0	0
	+ 2DPPE	2	0.04
	+ 2DPPP	15	0.22
	+ $4PPh_3$	14	0.04
	+ $5PPh_3$	11	0.04
	+ $6PPh_3$	8	0
$[PdCl_2(PPh_3)_2]$		0	< 0.01
$[PdCl_2(PPh_3)_2]$ + $3PPh_3$		0	< 0.01
10% Pd/C (30.7 mg)[b]		15	1.26

a) Yields were determined with ^{1}H NMR using $(CHCl_2)_2$ as an internal standard. b) THF (5 cm^3) was used as a solvent.



Scheme 2. Proposed mechanism of catalytic hydrogenolysis of carboxylic acid with a Pd complex.

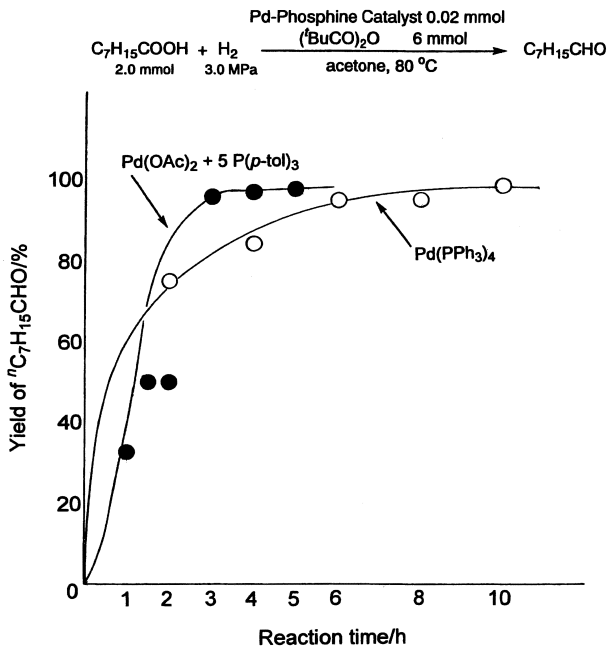


Fig. 1. Time-yield curves in catalytic hydrogenation of octanoic acid to octanal.

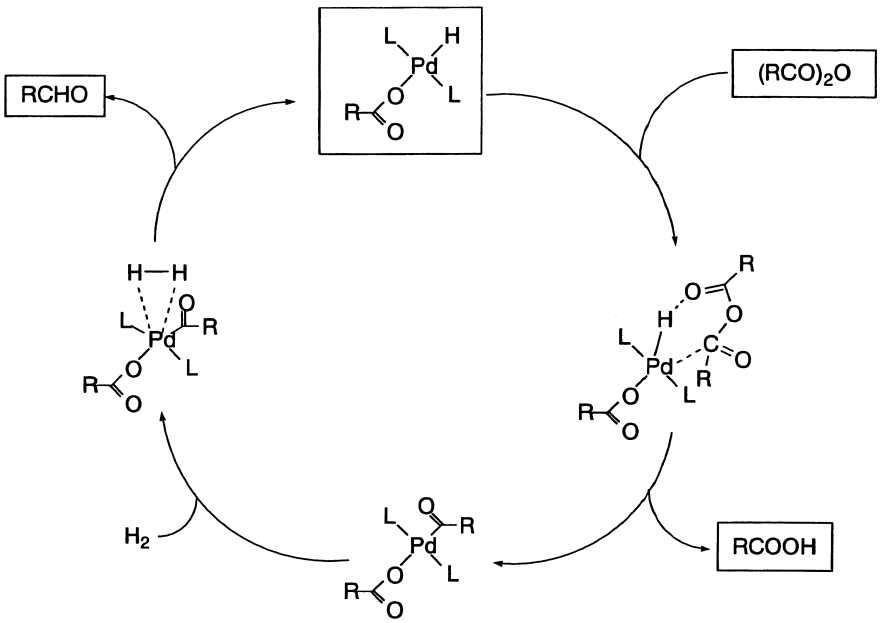
chromatography was carried out on a Hitachi 263-30 equipped with 5%-SE30. Low-resolution mass spectra combined with gas chromatograph were obtained with JEOL JMS-SX102A. FAB analysis and elemental analysis were performed by the Material Characterization Central Laboratory of Waseda University. Stainless autoclave (100 cm^3) was purchased from Taiatsu Glass Co.

General Procedure of Hydrogenation of Carboxylic Acids: A THF (5 cm^3) solution of $[Pd(PPh_3)_4]$ (0.02 mmol), carboxylic acid (2 mmol, monobasic), and pivalic anhydride (6 mmol) was placed in a 100 cm^3 stainless autoclave purged with argon. The autoclave was flushed with dihydrogen (ca. 5 MPa, twice), and pressurized with dihydrogen (3.0 MPa at room temperature). The mixture was stirred at 80 °C for 24 h. The products were analyzed by GC-MS and ^1H NMR ($CDCl_3$, r.t.) by comparison with authentic samples. Some aldehydes as shown below were isolated by the usual silica-gel chromatography (hexane/EtOAc) and were identified by spectroscopic means and elemental analysis.

***cis*-9-Octanal:** Yield 396 mg (74%). ^1H NMR δ 9.73 (1H, t, J = 1.7 Hz), 5.26–5.36 (2H, m), 2.38 (2H, dt, J = 7.3, 1.7 Hz), 1.92–1.99 (4H, m), 1.55–1.64 (2H, m), 1.22–1.28 (20 H, m), 0.85 (3H, t, J = 6.8 Hz); $^{13}C\{^1H\}$ NMR δ 202.9, 130.0, 129.7, 43.9, 31.9, 29.75, 29.65, 29.50, 29.31 (overlapping of two carbon signals), 29.23, 29.12, 29.03, 27.20, 27.13, 22.67, 22.06, 14.09. IR (neat) 2715 ($\nu_{C(=O)H}$), 1729 ($\nu_{HC=O}$) cm^{-1}; FAB-MS: Found m/z 267.2704 (M+H), Calcd for $C_{18}H_{34}O$: 266.26097 (M).

EtOC(=O)$(CH_2)_{10}$CHO: Yield 357 mg (74%). ^1H NMR δ 9.68 (1H, t, J = 1.7 Hz), 4.02 (2H, q, J = 7.1 Hz), 2.35 (2H, tq, J = 7.2, 1.7 Hz), 1.55 (4H, m), 1.15–1.21 (17H, m); $^{13}C\{^1H\}$ NMR δ 202.2, 173.4, 59.8, 43.7, 34.1, 29.15, 29.14, 29.12, 29.02, 28.94, 28.90, 24.8, 2.9, 14.1. IR (neat) 2717 ($\nu_{C(=O)H}$), 1736 ($\nu_{HC=O}$) cm^{-1}; Found: C 69.19, H 11.14%. Calcd for $C_{14}H_{26}O_3$: C 69.38, H 10.81%; FAB-MS: Found m/z 243.1926 (M+H), Calcd for $C_{14}H_{26}O_3$: 242.18819 (M).

PhC(=O)$(CH_2)_2$CHO: Yield 296 mg (91%). ^1H NMR δ 9.75 (1H, t, J = 0.7 Hz), 7.81–7.90 (2H, m), 7.30–7.47 (3H, m), 3.19 (2H, t, J = 6.4 Hz), 2.78 (2H, t, J = 6.4 Hz); $^{13}C\{^1H\}$ NMR



Scheme 3. Proposed mechanism of catalytic hydrogenation of carboxylic anhydride involving a palladium hydride intermediate.

δ 200.3, 197.5, 136.0, 132.9, 128.3, 127.7, 37.4, 30.8; IR (neat) 2831 and 2729 ($\nu_{C(=O)H}$, separated by the Fermi resonance), 1716 ($\nu_{HC=O}$) cm^{-1}; Found: C 73.83, H 6.59%. Calcd for $C_{10}H_{10}O_2$: C 74.06, H 6.21%; FAB-MS: Found *m/z* 163.0726 (M+H), Calcd for $C_{10}H_{10}O_2$: 162.06808 (M).

***p*-Cyanobenzaldehyde:** Yield 241 mg (92%). ^{1}H NMR δ 10.1 (s, 1H), 7.91–7.95 (m, 2H), 7.76–7.80 (m, 2H); $^{13}C\{^1H\}$ NMR δ 190.6, 138.7, 132.9, 129.9, 117.67, 117.61; IR (KBr disc) 2754 ($\nu_{C(=O)H}$), 1722 ($\nu_{HC=O}$) cm^{-1}, Found: C 73.26, H 3.72, N 10.83%, Calcd for C_8H_5NO: C 73.27, H 3.84, N 10.68%; MS (EI, 70 eV): Found *m/z* 131.0337 (M), Calcd for C_8H_5NO: 131.03711 (M).

$CHO(CH_2)_{10}CHO$: Yield 147 mg (75%). ^{1}H NMR δ 9.74 (2H, J = 1.8 Hz), 2.40 (4H, J = 7.3, 1.8 Hz), 1.52–1.66 (4H, m), 1.22–1.34 (12H, m); $^{13}C\{^1H\}$ NMR δ 202.9, 43.8, 29.19 and 29.18 (overlapping), 29.0, 21.9; IR (neat) 2750 ($\nu_{C(=O)H}$), 1713 ($\nu_{HC=O}$) cm^{-1}; Found: C 73.08, H 11.39%. Calcd for $C_{12}H_{22}O_2$: C 72.68, H 11.18%; FAB-MS: Found *m/z* 199.1715 (M+H), Calcd for $C_{12}H_{22}O_2$: 198.16186 (M).

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