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Hydroformylation of acrolein acetal

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Abstract

Acrolein acetals were hydroformylated by the rhodium–triarylphosphine system. Excellent rates and selectivity to succinaldehyde monoacetal were obtained by using 4,4,6-trimethyl-2-vinyl-1,3-dioxane and tris(3,5-dichlorophenyl)phosphine as the acrolein acetal and phosphine ligand, respectively. Key roles of substituents of the phosphine and the acrolein acetal to promote the reaction are also discussed.

Keywords: Acetal; Acrolein; Hydroformylation; Phosphine; Rhodium; Succinaldehyde

1. Introduction

The hydroformylation of alkenes is one of the most important reaction for manufacturing aldehydes and alcohols in industry [1,2]. 1,4-Butanediol (BDO) is an important precursor for the polybutylene terephthalate (PBT), which has much interesting properties for the high performance engineering plastics. BDO is now mainly manufactured by the reaction of acetylene and formaldehyde, followed by catalytic hydrogenation of the resulting 1,4-butyndiol. However, this method has some serious problems:

(1) price of acetylene is predicted to be rising; (2) the BDO manufacturing process carries the risk of acetylene detonation. In this context, other routes to produce BDO have been proposed substituting acetylene by the other possible raw materials [3]. Among these routes, much of the patent literature describes that BDO can be obtained by the following three-step processes using acrolein as the starting material [4,5].

(1) Acetalization reaction of acrolein with appropriate diol to form acrolein acetal.
(2) Hydroformylation reaction of the acrolein acetal to succinaldehyde monoacetal (linear aldehyde).
(3) Hydrolysis of the hydroformylated acetal, followed by subsequent hydrogenation of the resulting succinaldehyde.

The key to realizing industrial application consists in improvement of selectivity to the linear aldehyde in the hydroformylation step.

Selective hydroformylation of the acrolein acetal toward the desired linear aldehyde can be achieved by the use of the $Rh_6(CO)_{16}$–trialkyl or triarylphosphite systems [6–8] or the $Rh_6(CO)_{16}$–triphenylphosphine system [9]. However, the phosphite ligands in the former systems are bearing instability under the reaction conditions, and the latter system indicates that the rate and selectivity to the linear aldehyde tend to

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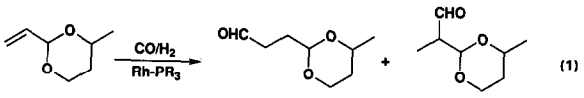
decrease with reducing the catalyst concentrations. From industrial point of view, catalyst must be not only stable, but also active and selective to the linear aldehyde even at relatively low catalyst concentrations.

2. Results and discussion

2.1. Effect of phosphine ligand

It is well known that selective linear hydroformylation of conventional 1-alkenes can be achieved by the rhodium–phosphine system [10]. We have examined the effect of a wide variety of triarylphosphines (PR_3) to improve the catalytic activity and selectivity in the following reaction using 4-methyl-2-vinyl-1,3-dioxane as the acrolein acetal (Eq. 1).



(1)

Results are summarized in Table 1. Steric hindrance of the phosphine molecule toward the acrolein acetal in the η^2- (4-methyl- 2-vinyl-1,3-dioxane) hydrido rhodium intermediates may act to form predominantly a linear alkyl rhodium intermediate rather than a branch one. However, no correlations are found between selectivity and electronic (δ ^{13}CO [11] or χ [12] or ^{31}P-NMR chemical shifts for the corresponding phosphine oxides [13]) or steric (θ) [12] parameters for the phosphine ligand. Phosphines, possessing substituents at *ortho*-positions of the aryl rings, provide very low active catalysts. It seems that these phosphines cannot coordinate to rhodium because of the much steric bulk. Actually, rhodium catalysts, which are not modified by any kind of phosphine ligands, exhibited no catalytic activities under our reaction conditions. Meanwhile, a similar steric effect can be expected by reducing the Rh–P bond length of the η^2-complexes. Catalysts should be designed by the following circumstances:

(1) Steric bulkiness of the phosphine ligand should be appropriate to coordinate to rhodium metal.
(2) Decrease in the Rh–P bond length may be effective to improve the selectivity because of the steric effect of the phosphine to acrolein acetal, which coordinates to the rhodium–phosphine complex.

We have examined the effect of triarylphosphines, of which aryl groups possess a wide variety of the substituents, and the results are summarized in Table 1. The selectivity increases with increase in the electron-withdrawing nature of the substituent (Hammett σ value), except for the *ortho*-substituted phosphines (runs 6, 10, and 11). The Rh–P bond length is strongly affected by the electron donating and back-donating ability of the phosphine in the rhodium–phosphine complex. The Rh–P bond length can be estimated by J(Rh–P) value of ^{31}P-NMR spectra for the rhodium–phosphine complexes. Correlation between the Pt–P bond length and J(Pt–P) value has been reported for platinum–phosphine complexes [14]. We have chosen $Rh_4(CO)_{11}L$ (L = phosphine) as the rhodium–phosphine complex for determining J(Rh–P). The reason for this choice is that the stable complex, $Rh_4(CO)_{11}L$, is easily prepared and the J(Rh–P) value varies to a great extent depending on the nature of phosphine ligand. Results show that the electron withdrawing nature of the substituent causes to increase in the J(Rh–P) value, which is ascribed to decrease in the Rh–P bond length. Phosphine, possessing such groups, decreases the electron donating ability toward rhodium metal, however, the back-donating ability from the rhodium increases by the electron accepting character of the substituted aryl groups. Sum of these abilities determined the Rh–P bond length. To the best of our knowledge, this is a novel conception to improve selectivity for hydroformylation catalyzed by the rhodium–phosphine complexes. Rate of conversion does not correlate with such substituent property. Higher rates are observed in **1h** and **1g**, however, the reason is not yet clear.

Table 1
Effect of various triarylphosphines [a]

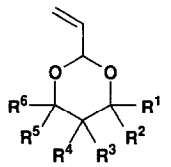
Expt.	Acrolein acetal	PR_3: R =	δ ^{13}CO [b]	χ [c]	θ [c]	$\Sigma\sigma$ [d]	J(Rh–P) [e] Hz	Conversion %	Selectivity [f] %
1	**1a**	C_6H_3-3,5-F_2	–	–	–	+0.68	126.5	32.6	85.1
2	**1b**	C_6H_3-3,5-Cl_2	–	–	–	+0.74	126.1	31.8	82.6
3	**1c**	C_6H_4-4-CF_3	–	–	–	+0.54	126.1	25.6	80.5
4	**1d**	C_6H_4-3-CF_3	–	–	–	+0.43	126.1	29.4	80.4
5	**1e**	C_6H_4-3-Cl	–	–	–	+0.37	126.0	33.7	79.7
6	**1f**	C_6H_4-2-CH_3	3.67	3.5	194	−0.17	–	3.3	77.5
7	**1g**	C_6H_4-3-F	–	6.0	145	+0.34	122.4	73.0	76.7
8	**1h**	C_6H_4-4-Cl	–	5.6	–	+0.23	122.8	81.9	73.5
9	**1i**	C_6H_3-3,4-F_2	–	–	–	+0.40	–	23.0	73.0
10	**1j**	C_6H_3-2-CH_3-4-Cl	–	–	–	+0.06	–	3.6	71.4
11	**1k**	C_6H_4-2-Cl	–	–	–	+0.23	–	12.1	65.0
12	**1l**	C_6H_5	4.30	4.3	145	0	120.4	23.7	62.3
13	**1m**	C_6H_4-4-F	3.77	5.0	–	+0.06	–	35.4	61.5
14	**1n**	C_6H_4-3-CH_3	4.48	3.7	–	−0.07	119.8	34.5	57.1

[a] Reaction conditions: 4-methyl-2-vinyl-1,3-dioxane, 80 mmol; $Rh(CO)_2(acac)$, 8×10^{-3} mmol; PR_3, 0.4 mmol; CO/H_2(1/1), 1 MPa; 100°C; 4 h.
[b] Ref. [11].
[c] Ref. [12].
[d] Sum of the Hammett σ value for substituents on one aryl ring.
[e] Coupling constants, observed in ^{31}P-NMR spectra of $Rh_4(CO)_{11}(PR_3)$.
[f] (Linear aldehyde/linear and branch aldehydes) × 100.

2.2. *Effect of substituents of acrolein acetal*

As described above, we have found effective phosphine ligands to improve selectivity toward succinaldehyde monoacetal in the hydroformylation of 4-methyl-2-vinyl-1,3-dioxane. The other possible method to improve selectivity concerns optimization of the structure of the acrolein acetal. Matsumoto et al. reported hydroformylation of alkenes, consisting with CH_2=CH–CH_2–O– moiety, catalyzed by the rhodium–triphenylphosphine (**1l**) system [15]. They observed a thermodynamically stable six-membered acyl rhodium intermediate, in which the original oxygen atom coordinates to rhodium. The six-membered intermediate converts into a linear product. A linear/branch ratio is determined by the thermodynamic stability of the intermediate, so that improvement of the ratio has not been successful under a variety of the reaction conditions so long as triphenylphosphine is used.

We have examined a series of 2-vinyl-1,3-dioxanes as acrolein acetals, of which dioxane rings are substituted by some methyl groups.



R^n: n=	1	2	3	4	5	6
2a	H	H	H	Me	H	H
2b	H	H	Me	Me	H	H
2c	Me	H	H	H	H	H
2d	Me	Me	H	H	H	H
2e	Me	Me	H	H	H	Me

formulae of acrolein acetals

Results using various phosphine ligands are shown in Table 2 and Fig. 1. The substituents at 4- or 6-positions of a dioxane ring are thought to avoid adjacent oxygen atoms to coordinate to rhodium because of the steric effect of the substituents. In the case of **1l**, improvement of selectivity is observed in the following order: **2a** ≈ **2b** < **2c** ≈ **2d** < **2e**. The steric effect of the methyl groups is considered to increase in the same order. Acrolein acetals shown above can be classified into three groups. Acrolein acetals **2a**

Table 2
Effect of substituents in acrolein acetal [a]

Acrolein acetal	n[b]	Selectivity[c] (conversion) (%)			
		PR_3 ($\Sigma\sigma$)			
		1l(0)	**1h**(+0.23)	**1d**(+0.43)	**1b**(+0.74)
2a	2	56.1 (43.5)	67.5 (46.4)	78.5 (45.1)	82.6 (52.0)
2b	2	55.9 (64.1)	64.6 (94.2)	75.0 (59.7)	–
2c	1	62.3 (23.7)	73.5 (81.9)	80.4 (29.4)	82.6 (31.8)
2d	1	62.5 (64.4)	69.6 (57.2)	75.1 (44.6)	–
2e	0	72.7 (64.9)	76.9 (92.6)	84.5 (75.0)	88.6 (99.8)[d]

[a] Reaction conditions: acrolein acetal, 80 mmol; $Rh(CO)_2(acac)$, 8×10^{-3} mmol; PR_3, 0.4 mmol; CO/H_2(1/1), 1 MPa; 100°C; 4 h.
[b] Number of carbon atoms at 4- and 6-positions, not substituted by methyl groups in dioxane ring.
[c] (Linear aldehyde/linear and branch aldehydes) × 100.
[d] $Rh(CO)_2(acac)$, 4×10^{-3} mmol.

and **2b** are not substituted by methyl groups at either the 4- or the 6-positions of the dioxane ring, and **2c** and **2d** have no methyl groups at the 6-position. However, it is noted that **2e** has methyl groups at not only 4- but also 6-positions. Possible reaction pathway is shown in Scheme 1, which is based upon Wilkinson's results for alkene hydroformylation catalyzed by the rhodium–triphenylphosphine system. [16]. Methyl substituents of acrolein acetal shift the equilibria between **7e** and **4e** toward the **4e** direction because of sterically crowded structure of **7e** compared to **4e**. On the other hand, not so significant difference in the selectivity is seen for **2a–2d** in the case of **1h**, **1d**, and **1b**. This indicates that change in effect of the methyl substituents for **2a–2d** does not significantly affect to the selectivity. These acrolein acetals have at least one acetal oxygen atom, of which the adjacent carbon is not substituted by methyl groups. Higher selectivity is found for **2e** by all phosphines, we examined. It is concluded that selectivity depends on the equilibria between **7** and **4**. Decrease in the Rh–P bond length and the methyl substituent of acrolein acetal shift the equilibria to **4**.

Remaining problem is how to accelerate the reaction rate with keeping the high selectivity. At first, we describe mechanistic considerations concerning **2a–2d**. As mentioned by Matsumoto et al., predominant formation of the similar acyl rhodium intermediates **5a–5d** can be considered rather than **6a–6d** formation. The rate determining step of the hydroformylation reaction is considered to be oxidative addition of H_2 to the acyl rhodium intermediate, such as **6a–6d** [16]. Coordination of acetal oxygen atom to rhodium in **5a–5d** opposes the oxidative addition of H_2 because of lack of coordination sites to react with H_2. On the other hand, methyl groups of **5e** at 4,4,6-positions (R^1, R^2, and R^6) are supposed to avoid coordination of both of the two acetal oxygen atoms to rhodium because of steric hindrance of the methyl groups. Thus, the effect of the methyl substituents shifts the equilibrium between **5e** and **6e** to the right, which rapidly converts into succinaldehyde monoacetal. Improvement of reaction rate of **2e** can be understood in this context. In combination of **2e** and **1b**, much high rate of conversion and selectivity are found, which are ascribed to thee synergistic effect of the structure of acrolein acetal and the electronic effect of the phosphine ligand.

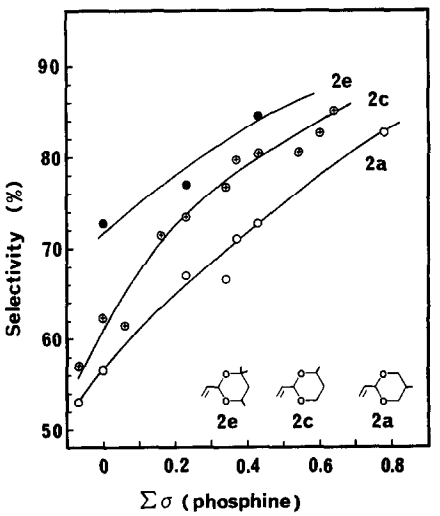
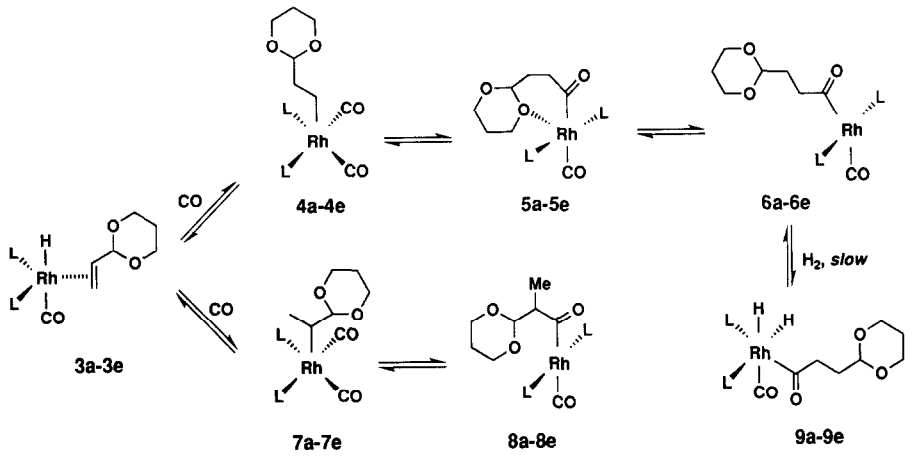


Fig. 1. Relation between selectivity and the electronic properties of phosphine ligand. Reaction conditions as in Table 2.



Scheme 1. Equilibria of acyl rhodium intermediates. Positions of methyl groups of **a–e** as in formula of acrolein acetal. Methyl substituents at dioxane rings are omitted. L: phosphine ligand.

2.3. *Improved hydroformylation of 2e*

We have tried to optimize the reaction conditions for hydroformylation of **2e**. Results are summarized in Table 3. Using a large excess of **1h** results in a relatively higher rate and selectivity. Surprisingly, **1b** exhibits much higher rate and selectivity even in lower rhodium concentrations so long as the concentration of **1b** is more than ca. 30 mM. To conclude, we have realized the excellent reaction system consisting of **2e** as the acrolein acetal, and **1b** as the ligand for the stable rhodium–phosphine catalyst. For example, expt. 21 shows that **2e** can be readily converted into succinaldehyde monoacetal in high yield catalyzed by the rhodium–**1b** system under very low rhodium concentration (1.13×10^{-3} mol%) and mild reaction conditions.

Table 3
Hydroformylation of **2e** [a]

Expt.	Rh		PR_3			Conversion[b] %	Selectivity %
	2eRh	mM		PR_3/Rh	mM		
15	9327	0.64	**1h**	50	32.1	92.6	76.9
16	20000	0.30	**1h**	100	29.9	85.3	84.3
17	19164	0.31	**1h**	49	15.3	53.6	69.4
18	19908	0.30	**1b**	98	29.7	99.8	88.6
19	40154	0.15	**1b**	201	30.2	99.8	88.2
20	39349	0.15	**1b**	150	22.9	88.2	87.8
21[c]	90575	0.06	**1b**	502	33.5	98.4	88.5

[a] Reaction conditions: **2e**, 65 mmol; CO/H_2(1/1), 1 MPa; 100°C; 3 h.
[b] (Linear aldehyde/linear and branch aldehydes) × 100.
[c] CO/H_2(1/1), 1.2 MPa.

3. Experimental

3.1. *Materials*

Acetylacetonatodicarbonylrhodium, $Rh(CO)_2(acac)$, (purchased from Johnson Matthey) was used as the catalyst precursor. Phosphines were synthesized by the reaction of phosphorus trichloride and the corresponding Grignard reagents in diethyl ether solvent. The complex $Rh_4(CO)_{11}L$ was prepared by the reaction of $Rh_4(CO)_{12}$ (purchased from N.E. Chemcat, Japan) and an equimolar amount of phosphine [17]. Acrolein acetals were prepared by the acetalization reaction of acrolein with corresponding diols catalyzed by ion exchange resin, followed by distillation, and stored under nitrogen in a freezer. Compounds **2a**, **2c**, and **2e** were composed of the stereoisomers (*cis*/*trans*): **2a** (27/73); **2c** (98/2); **2e** (98/2).

3.2. *Analytical methods*

Phosphorus-31 NMR spectra were recorded on a Varian Gemini 300 FT-NMR spectrometer.

Analyses of the reaction products were obtained on a Hewlett Packard HP-5880 gas chromatograph, using a 0.32 mm × 100 m methyl silicon fused capillary column. Identities of major products were determined by ^{1}H-NMR and GC/MS.

3.3. Hydroformylation reaction

Hydroformylation reactions were conducted in a 30 cm^3 autoclave constructed of SUS-316 stainless steel, fitted with heating and efficient agitation means. Typical procedure was as follows. A dodecane solution of $Rh(CO)_2(acac)$, phosphine, and acrolein acetal were mixed in a Schlenk tube under an N_2 atmosphere to form a homogeneous solution, and this was transferred into the autoclave under an N_2 atmosphere. The reactor was sealed, flushed with CO/H_2 (1/1) several times, charged with CO/H_2 pressures of 1 MPa at the room temperature and heating commenced. The reactor was connected to a CO/H_2 bomb through a pressure control valve to maintain the pressure during reaction. After the appropriate reaction time, the reactor was cooled, vented to atmospheric pressure and opened. The liquids were collected and analyzed. Identified products were succinaldehyde monoacetal, 2-methylmalonaldehyde monoacetal, and propionaldehyde acetal (less than 2%).

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