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Regioselective hydroformylation of allyl acetates catalyzed by rhodium–montmorillonite

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Abstract

The rhodium(I) complex, $[Rh(COD)Cl]_2$, intercalated into montmorillonite, is an effective catalyst for the selective hydroformylation of allyl acetate derivatives to produce the corresponding linear or branched aldehydes. The catalytic reaction of allyl acetates gave linear aldehydes with high selectivity at temperatures > 130°C, while the branched aldehyde could be obtained as the major product, at lower temperature (< 50°C), and in excellent yield.

Keywords: Regioselectivity; hydroformylation; Allyl acetates; Rhodium; Montmorillonite

1. Introduction

The transition metal catalyzed hydroformylation of unsaturated organic compounds is one of the most important reactions in industry as well as in organic synthesis [1]. The selective carbonylation of unsaturated esters is a good method to synthesize difunctional organic compounds. Specifically, the selective hydroformylation of allyl acetate has been achieved by the zwitterionic and cationic rhodium complexes, $Rh(COD)(\eta^6\text{-}PhBPh_3)$ and $[Rh(COD)(PPh_3)_2]BPh_4$ in the presence of dppb (dppb = 1,4-bis(diphenylphosphino)butane) to give 4-acetoxybutanal as the major product which can be converted to an industrially important chemical, 1,4-butanediol, via hydrolysis and hydrogenation [2]. Generally, the regioselectivity in homogeneous processes strongly depends on the catalytic system employed [3]. Heterogeneous methods can sometimes enhance selectivities, and with more facile catalyst recovery in transition metal catalyzed reactions. Clays can be used as solid supports, and among them, montmorillonite has been widely investigated due to its natural abundance and swelling ability [4–8].Recently, it has been reported that a Rh–clay (**2**) compound could be easily prepared by intercalation of $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) complexes into montmorillonite, and that it is catalytically active for the regioselective hydroformylation of vinylsilanes [9]. We now describe the regioselective hydroformylation of allyl acetate derivatives cat-

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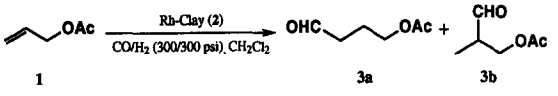
alyzed by rhodium–montmorillonite to produce aldehydes containing the ester unit.

2. Results and discussion

The hydroformylation of allyl acetate (**1**) proceeded in the presence of Rh–clay (**2**) (667/1 ratio of **1**/**2**) in CH_2Cl_2 using a 1:1 ratio of CO/H_2, to give the corresponding linear (**3a**) and branched aldehydes (**3b**) (Eq. 1).



(1)

Previous studies demonstrated that the product ratio in the hydroformylation reaction of olefins was affected by the temperature, partial and total pressure of gases (CO and H_2), and the nature of the added ligand [2,10]. The temperature effect on the regiochemistry in the hydroformylation of **1** with **2** was investigated, and the results are summarized in Table 1. As the temperature was increased, the reaction rate became faster with greater selectivity for the linear aldehyde (**3a**). The linear aldehyde, **3a**, could be obtained without **3b**, when the hydroformylation reaction was run at 145°C (Table 1, entry 1). This is, to our knowledge, the first example of the selective synthesis of the linear aldehyde, **3a**, from the hydroformylation of **1**: it was previously reported that only a mixture of **3a** and **3b** was obtained from the hydroformylation of **1** although **3a** was the major product [2,11]. It should be noted that at high temperatures (> 130°C), some oligomerization of the formed aldehyde was observed (Table 1, entries 1 and 2). The branched aldehyde **3b** was formed as the major product (**3b**/**3a** = 7/3) by the reaction of **1** at 65°C. The yield of aldehydes was excellent (Table 1, entry 4) and no oligomerization product was detected in this reaction. A similar ratio of **3b**/**3a** (7/3) resulted when a homogeneous rhodium complex, $Rh(PPh_3)_2(NO)$, was employed as the catalyst for the hydroformylation of **1** in the presence of excess PPh_3 ($PPh_3/Rh = 10$) [12]. The hydroformylation of **1** did not occur at room temperature during 9 days (Table 1, entry 5). It should be noted that no hydrogenation product of **1**, **3a** or **3b** was detected by GC and ^1H NMR (Table 1, entries 1–5).

The influence of the pressure of the gases, and an added ligand, dppb (dppb = 1,4-bis(diphenylphosphino)butane) was examined for the hydroformylation of **1** catalyzed by **2**, and the results are listed in Table 2. The high pressure of gases accelerated the hydroformylation reaction (see Table 1, entries 3 and 4, and Table 2, entries 1–5). The aldehyde selectivity, **3a**/**3b** is slightly reduced at > 100°C under a high pressure of hydrogen or carbon monoxide (see Table 1, entries 2 and 3, and Table 2, entries 1–4). It seems that the change of pressure did not affect the ratio of **3a**/**3b** at low

Table 1
Effect of temperature on the Rh–clay (**2**) catalyzed hydroformylation of allyl acetate (**1**) [a]

Entry	Temp. (°C)	Time (h)	Conversion (%)	Product(s) [b]	Isolated yield (%)
1	145	36	100	**3a** [c]	56
2	130	36	100	**3a**/**3b** = 86/14 [c]	82
3	100	48	100	**3a**/**3b** = 47/53	92
4	65	60	100	**3a**/**3b** = 30/70	92
5	rt	216	0		

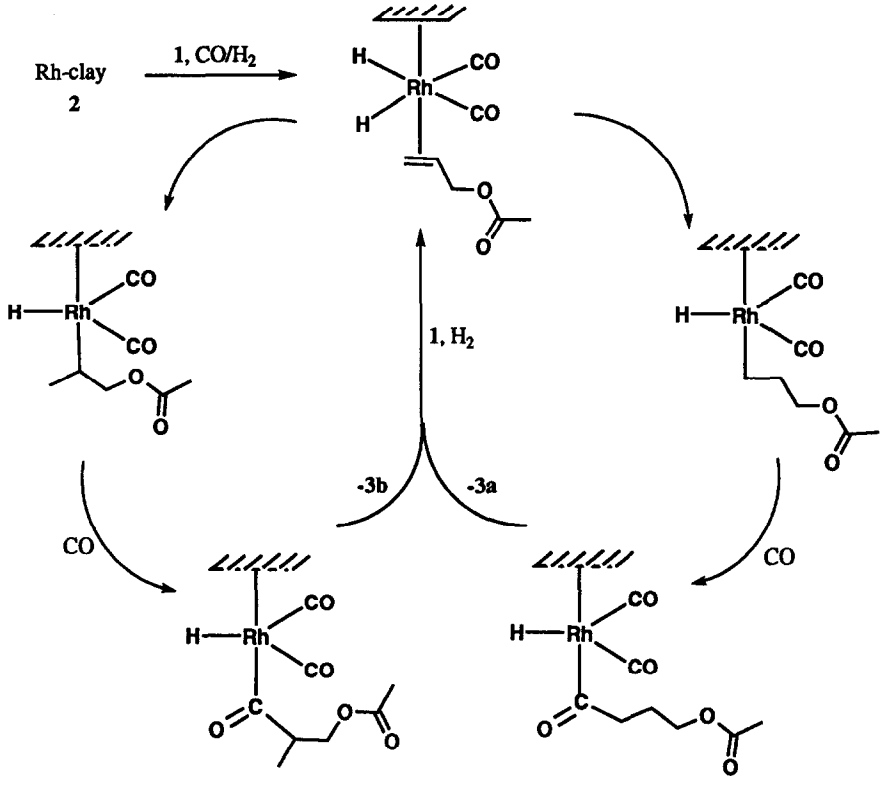
[a] Reaction conditions: **1**, 2.0 mmol; Rh–clay (2) [100 mg (0.003 mmol Rh)]; CH_2Cl_2, 10 ml; CO/H_2 = 300/300 psi.
[b] The product ratio was determined by ^1H NMR.
[c] Aldehyde oligomers were detected in the ^1H NMR spectrum of the crude mixture.

Table 2
Effect of pressure and dppb for the hydroformylation of 1 catalyzed by **2** [a]

Entry	Pressure (psig)		Time (h)	Conversion (%)	Product(s) [b]	Isolated yield (%)
	CO	H_2				
1	100	1,000	36	100	**3a**/**3b** = 35/65	90
2	250	750	45	100	**3a**/**3b** = 38/62	91
3	750	250	30	100	**3a**/**3b** = 38/62	90
4 [c]	1,000	100	24 [d]	85	**3a**/**3b** = 77/23	81
5 [e]	100	1,000	48 [d]	100	**3a**/**3b** = 25/75	93
6 [f]	300	300	72	100	**3a**/**3b** = 48/52	93
7 [g]	300	300	96	100	**3a**/**3b** = 42/58	92

[a] Reaction conditions: **1**, 2.0 mmol; Rh–clay (**2**) [100 mg (0.003 mmol Rh)]; CH_2Cl_2, 10 ml; temp. = 100°C.
[b] The product ratio was determined by ^1H NMR.
[c] Reaction temp. of 130°C.
[d] Gases were recharged after 20 h.
[e] Reaction temp. of 55°C.
[f] The reaction was carried out in the presence of 0.01 mmol of dppb.
[g] 0.02 mmol of dppb was added to the reaction mixture.

temperature (Table 1, entry 4 and Table 2, entry 5). 1,4-Bis(diphenylphosphino)butane (dppb) significantly retarded the Rh–clay (**2**) catalyzed hydroformylation of **1**, but the product ratio was almost the same as that obtained in the absence of dppb (Table 2, entries 6 and 7). This behav-



Scheme 1. Possible mechanism for the hydroformylation of allyl acetate (**1**) with Rh–clay (**2**).

ior is very different from the results obtained with the zwitterionic and cationic rhodium complexes, $Rh(COD)(\eta^6\text{-}PhBPh_3)$ and $[Rh(COD)(PPh_3)_2]BPh_4$: the selective reaction of **1** with the Rh complexes proceeds well in the presence of dppb to give linear aldehyde, **3a** as the major product (**3a**/**3b** = 95/5) [2]. A possible mechanism for these Rh–clay (**2**) catalyzed hydroformylation of allyl acetate **1** is given in Scheme 1, analogous to the pathway proposed for the homogeneous reaction [13]. The product ratio which mainly depends on the reaction temperature, can be modestly affected by the pressure of gases at high temperature, and is not influenced by the solvent at room temperature (vide infra). It is noteworthy that the Rh–clay, recovered from a mixture of the hydroformylation reaction of **1** catalyzed by **2**, showed similar catalytic activity (i.e. yields within 7% of those of the initial run) and the same product ratio for three different hydroformylation runs of **1**.

The hydroformylation of allyl butyrate (**4**) was also carried out with Rh–clay (**2**) under similar reaction conditions to that of allyl acetate (**1**) to produce the related linear aldehyde, **5a** and the branched isomer, **5b**. The results of the influence of temperature, pressure and solvent for the hydroformylation of **4** are given in Table 3. Only **5a** (no **5b**) was obtained from the reaction of **4** with **2** under CO and H_2 at 155°C (Table 3, entry 1). The proportion of **5b** increased as the temperature was lowered (Table 3, entries 2 and 3). The product ratio, **5a**/**5b** (19/81) is essentially independent of the ratio of the pressure of CO and hydrogen (Table 3, entries 2–4), and no significant solvent effect was observed on the product distribution (Table 3, entries 5 and 6). Note that the reaction does not proceed in DMF even at 150°C for 5 days (Table 3, entry 7).

The hydroformylation of other allyl acetate derivatives was investigated at various temperatures in methylene chloride, and the results are summarized in Table 4. Allyl benzoate, **6**, reacted at 140°C under CO and H_2 in the presence of **2** to give the linear and branched aldehyde, **7a** and **7b**, but the cleavage product, benzoic acid was the major product (**7a**/**7b**/PhCOOH = 33/17/50). Benzoic acid was not formed when the reaction of **6** was run at room temperature (Table 4, entry 1). The product ratio of **7a**/**7b** was also reduced at lower temperatures.

The Rh–clay (**2**) catalyzed hydroformylation reaction of 2-methylallyl acetate, **8**, gave only the linear aldehyde, **9a**, even at room temperature (Table 4, entry 2), and this may be due to the steric effect of the methyl substituent at the unsaturated carbon. When 3-butenyl acetate, **10**, was employed as the reactant, three hydroformylation products were observed at 100°C:

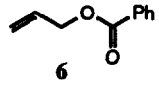
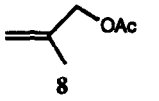
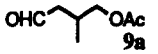
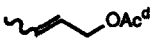
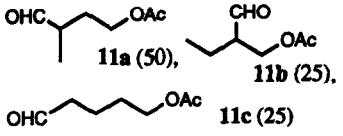
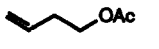
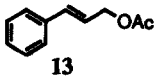
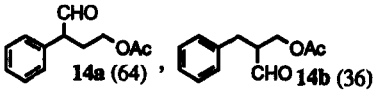
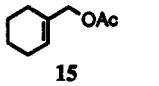
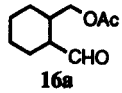
Table 3
Temperature, pressure and solvent effects for the hydroformylation of **4** catalyzed by **2** [a]

Entry	Solvent	Pressure (psig)		Temp. (°C)	Time (h)	Conversion (%)	Product(s) [b]	Isolated yield (%)
		CO	H_2					
1	CH_2Cl_2	300	300	155	15	100	**5a** [c]	32
2	CH_2Cl_2	300	300	60	20	100	**5a**/**5b** = 25/75	96
3	CH_2Cl_2	300	300	rt	216	60	**5a**/**5b** = 20/80	53
4	CH_2Cl_2	100	900	rt	192	100	**5a**/**5b** = 19/81	88
5	DME	100	900	rt	144	89	**5a**/**5b** = 22/78	81
6	benzene	100	900	rt	168	100	**5a**/**5b** = 23/77	89
7	DMF	100	900	150	120	0		

[a] Reaction conditions: **4**, 2.0 mmol; Rh–clay (**2**) [100 mg (0.003 mmol Rh)]; solvent = 10 ml.
[b] The product ratio was determined by ^1H NMR.
[c] A significant of aldehyde oligomers was detected in the ^1H NMR spectrum.

4-acetoxy-2-methylbutan-1-al (**11a**), 3-acetoxy-2-ethylpropan-1-al (**11b**), and 5-acetoxypentan-1-al (**11c**). It should be mentioned that hydroformylation of **8** and **9** did not occur using the zwitterionic rhodium complex, Rh(COD)(η^6-$PhBPh_3$) as the catalyst [2]. The compounds, **11a** and **11b**, could be obtained by the direct hydroformylation of **10**. The double bond migration of **10** may proceed before hydroformylation to give compound **11c** (*via* **12**), although

Table 4
Hydroformylation of allyl acetate derivatives catalyzed by Rh–clay (**2**) [a]

entry	substrate	temp.(°C)	time(h)	conv.(%)	product(s) (%)[b]	isolated yield(%)
1	 **6**	150	4	100	**7a/7b** = 33/17, PhCOOH = 50	27[c]
		rt	264	83	**7a/7b** = 18/82	61
2	 **8**	150	20	100	 **9a**	97
		rt	216	83	**9a**	79
3	 **10**	100	24	100	 **11a** (50), **11b** (25), **11c** (25)	93
		50	96	100	**11a/11b** = 30/70	93
4	 **12**	140	16	100	**11c/11a** = 55/43[e]	76
		50	30	70	**11c/11a** = 39/61	66
5	 **13**	110	20	100	 **14a** (64), **14b** (36)	89[f]
		rt	216	62	**14a/14b** = 17/83	58[g]
6	 **15**	130	120	75	 **16a**	43[h]

[a] Reaction conditions: substrate, 2.0 mmol; Rh–clay (**2**) [100 mg (0.003 mmol Rh)]; solvent = CH_2Cl_2, 10 ml.

[b] The structures of all of the starting materials and products were established by comparison of spectral data (NMR, (^{1}H, ^{13}C), MS, IR) with those for known compounds. The product ratio was determined by ^{1}H NMR.

[c] Yield of **7a** after isolation by preparative thin layer chromatography using hexanes/ethyl acetate (10/1) as the eluant.

[d] A 10/1 *trans/cis* mixture.

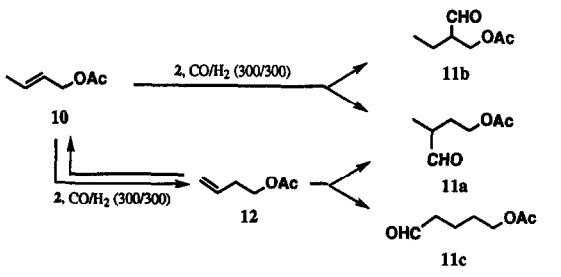
[e] A trace amount of **11b** was detected in the crude mixture by ^{1}H NMR.

[f] A small amount of unknown compound(s) was detected by ^{1}H NMR, and removed by column chromatography using hexanes/ethyl acetate (5/1) as the eluant.

[g] The starting material was recovered by column chromatography using hexanes/ethyl acetate (10/1) as the eluant.

[h] A significant amount of aldehyde oligomers was detected in the crude mixture by ^{1}H NMR, and removed by column chromatography using hexanes/ethyl acetate (10/1) as the eluant.

compound **12** was not detected during the reaction of **10** (Eq. 2).



(2)

The contrathermodynamic isomerization of an internal to a terminal olefin is unusual, while the double bond migration of a terminal olefin to an internal olefin is readily catalyzed by a number of transition metal complexes [14]. The isomerization of **10** was not observed at 50°C (Table 4, entry 3). The hydroformylation of **10** was compared with that of **12**. Olefin isomerization was not observed in the Rh–clay (**2**) catalyzed reaction of **12** under the same reaction conditions (up to 140°C) (Table 4, entry 4). The homoallylic acetate, **12** showed poor regioselectivity in the hydroformylation reaction. Cinnamyl acetate, **13**, in the hydroformylation gave similar results to those obtained from the reactions of other allylic acetates with **2** to afford the corresponding aldehydes, **14a** and **14b** (Table 4, entry 5), and the hydroformylation of (cyclohex-1-enyl)methyl acetate, **15**, occurs only at the less hindered position to give **16a** (Table 4, entry 6).

3. Conclusions

The regioselectivity of the hydroformylation of allyl acetate derivatives with Rh–montmorillonite, **2** mainly depends on the reaction temperature, and is not significantly affected by the pressures of carbon monoxide and hydrogen at high temperature (> 100°C). The catalytic reaction of allyl acetates produces linear aldehydes with high selectivity at high temperatures (> 130°C), while the branched aldehyde is formed in excellent yield as the major product at low temperature (< 50°C). The hydroformylation reaction of allyl acetates is retarded by the presence of the added ligand, dppb. The catalytic activity of Rh–clay recovered from the catalytic reaction of **1** with **2** was maintained for three different runs.

4. Experimental

4.1. General

All solvents were purified by standard methods before use. The Rh–clay, **2**, was prepared according to the literature method [9]. Allyl acetate, allyl butyrate, and cinnamyl acetate were purchased from Aldrich Chemical Co., and were used as received. The other substrates were synthesized by literature methods, using the required allylic alcohol, with acetic anhydride in the presence of anhydrous zinc chloride in ether as the solvent [15]. Proton and carbon-13 NMR spectra were recorded on a Varian Gemini 200 spectrometer using $CDCl_3$ as the solvent. A Bomem MB 100-C15 (FT-IR) and a Varian 3400 instrument were used for IR and GC analyses, respectively.

4.2. General procedure for the hydroformylation reactions

A mixture of 1 (2.0 mmol) and Rh–clay, **2** (100 mg, 0.003 mmol Rh), in CH_2Cl_2 (10 ml) was placed in a 45 ml autoclave. The autoclave was flushed thoroughly with carbon monoxide, pressurized with carbon monoxide and hydrogen, and then heated in an oil bath to the desired temperature. After the time indicated in the Tables, the reaction mixture was cooled to room temperature, and the products were isolated by removal of the catalyst by filtration (except **4a**, **4b**, **14a**, **14b** and **16a**, see Table 4), followed by Kugelrohr distillation.

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