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Rhodium complex catalyzed hydroformylation reactions of linear and cyclic mono- and diolefins

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Abstract

The hydroformylation reactions of cyclopentene, cyclohexene, 4-vinylcyclohexene, cycloheptene and cyclooctene, catalyzed with a Rh(acac){$P(OPh)_3$}$_2$/$P(OPh)_3$ (I) system at 80°C and 10 atm ($CO + H_2$), have been studied. Only cyclopentene and 4-vinylcyclohexene undergo hydroformylation at 1 atm and 40°C. The hydroformylation of some cyclic dienes; (1,3- and 1,4-cyclohexadienes, 1,3- and 1,5-cyclooctadienes and 1,3-cyclopentadiene), at 10 atm and 80°C, was investigated in two catalytic systems: (I) and Rh(acac) (CO) (PPh_3)/PPh_3 (II). The main reaction products of cyclohexadienes and pentadiene (at 80°C, 10 atm) are unsaturated monoaldehydes. In hydroformylation of 1,5-cyclooctadiene the main product is formylcyclooctane.

Key words: Rhodium; Olefins; Hydroformylation

1. Introduction

Hydroformylation reactions of cyclic mono- and diolefins have been particular interest for many years [1–5], mainly because the products are used in the perfume and pharmaceutical industries [6]. Some show biological activity [7] and may be used as substrates for the synthesis of naturally occurring substances [8]. The hydroformylation reactions of heterocyclic olefins have also been frequently studied [8–10].

Generally, the reactivity of cyclic olefins in hydroformylation is lower than that of terminal olefins [1,2] and reaction, therefore, requires much higher temperatures and pressures as well as more active catalysts. Secondly, hydroformylation reactions of cyclic olefins are usually less selective and lead to a mixture of products [4,5,11]. In very few cases, for example hydroformylation of cyclohexadienes [12], cyclooctadienes [12] and dicyclopentadiene [6], and after careful selection of catalyst precursor [12] and optimization of reaction parameters (temperature and pressure, [6]) higher yields of unsaturated monoaldehydes have been obtained.

In this paper we present our studies of the hydroformylation reactions of mono- and diolefins catalyzed with two different rhodium systems modified with phosphite, $P(OPh)_3$ (I) and phosphine, PPh_3 (II) ligands. Rh(acac){$P(OPh)_3$}$_2$ + 3$P(OPh)_3$, (I); Rh(acac)(CO)(PPh_3) + 3PPh_3, (II).

Previous studies of the hydroformylation of hex-1-ene [13,14] and 1,5-hexadiene [15] have shown that the systems have quite different levels of activity. The phosphite system (I) was found to be an effective isomerization catalyst. It catalyzed the isomerization of hex-1-ene to hex-2-ene, and 6-heptenal (the hydroformylation product of 1,5-hexadiene) to 4-heptenal [13,15]. In contrast with the phosphine system (II) the isomerization reaction of olefins is practically negligible [15]. In this paper, we examine such relations as they are shown in the hydroformylation reactions of cyclic mono- and diolefins.

2. Results and discussion

2.1. *Hydroformylation of cyclic monoolefins*

The reactivities of cyclic olefins depend strongly on their structure (Table 1). Among the olefins under study only cyclopentene can be hydroformylated with 100% yield at 1 atm, in 4–6 h with the phosphite

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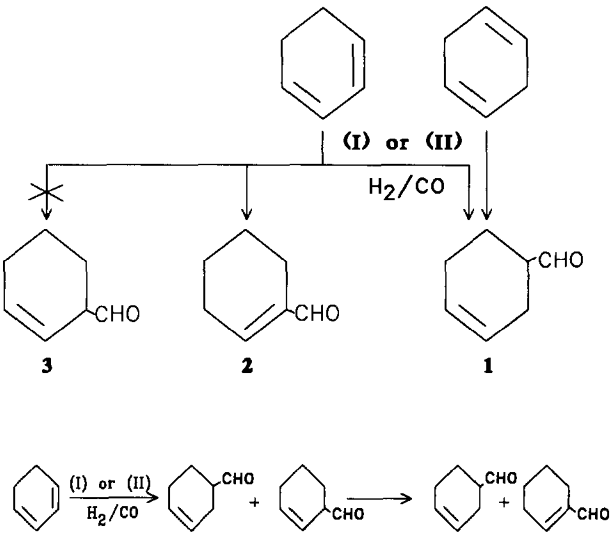
system (**I**). Other olefins like cyclohexene, react much more slowly (Table 1). In cyclopentene hydroformylation *ca.* 3 h induction time is observed, whereas hydroformylation of hex-1-ene is already started after 40 min. IR studies of cyclopentene hydroformylation reaction mixture have proved the gradual conversion of catalyst precursor (I) into $HRh(CO)\{P(OPh)_3\}_3$ (ν(CO) 2065 cm^{-1}), its catalytically active form. The initially colourless solution of catalyst precursor turns red and next $Rh_4(CO)_8\{P(OPh)_3\}_4$ is formed (IR: ν(CO) 2004, 2012, 1840 cm^{-1}). In our earlier studies [16] we found that the polynuclear rhodium complex is catalytically inactive.

Recently, a report of hydroformylation of cyclohexene with $Rh_4(CO)_8\{P(OPh)_3\}_4$ at 50°C and at 1 atm has been published [17]. After 48–90 hours of reaction *ca.* 90% conversion has been obtained. In contrast to the phosphite system (I), the phosphine system (II) is not effective under mild conditions, probably because reactive monohydride species cannot be formed at pressures under 1 atm. Some activity has been observed when a mixed system containing $Rh(acac)\{P(OPh)_3\}_2$ and PPh_3 was used for cyclopentene hydroformylation. After quite a long induction time (*ca.* 7 h) the reaction rate was comparable to that of the catalytic system (I). However, when $Rh(acac)\{P(OPh)_3\}_2$ was modified with pyridine, hydroformylation of cyclopentene did not occur. It is worthwhile noting that hex-1-ene is effectively hydroformylized in such conditions [16]. In 4-vinylcyclohexene only the terminal double bond undergoes selective hydroformylation (40 or 80°C, 1 or 10 atm) while cyclohexene undergoes hydroformylation with *ca.* 40% yield in comparable conditions (Table 1). Generally the yield of hydroformylation reaction products decreases with enlargement of the cyclic olefin ring (Table 1) which may be explained by the steric hindrance effect of the larger olefin in coordination to the catalyst.



Scheme 1.

2.2. *Hydroformylation of cyclic dienes; 1,3- and 1,4-cyclohexadiene*

Hydroformylation of 1,4-cyclohexadiene leads, as expected, to only one product—cyclohex-3-enecarboxyaldehyde (Scheme 1, **1**) whereas 1,3-cyclohexadiene produces cyclohex-3-enecarboxyaldehyde and cyclohex-1-enecarboxyaldehyde in nearly 1 : 1 ratio (Scheme 1, **2**). Although expected, there was no cyclohex-2-enecarboxyaldehyde (Scheme 1, **3**) among the hydroformylation reaction products of 1,3-cyclohexadiene. Probably it undergoes fast isomerization to cyclohex-1-enecarboxyaldehyde (with conjugated system of double bonds) (Scheme 1, **2**). The composition of the reaction products is very similar in both the catalytic systems under study (Table 2). Quite different products—90% of cyclohex-2-enecarboxyaldehyde and 10% of cyclohex-1-enecarboxyaldehyde—were obtained in hydroformy-

TABLE 1. Products of hydroformylation of cyclic olefins catalyzed by $Rh(acac)\{P(OPh)_3\}_2/P(OPh)_3$ (I) system

Substrate	Reaction conditions *p*(atm)/*t* (°C)	Time (h)	Product	Yield (%)
Cyclopentene	1/40	7 [a]	Cyclopentane-carboxyaldehyde	100
	10/80	1		100
Cyclohexene	1/40	6	Cyclohexane-carboxyaldehyde	20
	10/80	2		36
	10/80	4.5		44
	10/80 [b]	3		31
4-Vinylcyclohexene	1/40	6	3-(Cyclohex-3-ene)-propanal	100
	10/80	2		95
Cycloheptene	10/80	3	Cycloheptane-carboxylaldehyde	24
Cyclooctene	10/80	3	Cyclooctane-carboxyaldehyde	20

[a] Induction time 3 h; [b] catalytic system (II). (I), (II) [Rh] = $2.1 \cdot 10^{-5}$ mol, [$P(OPh)_3$] or [PPh_3] = $3.3 \cdot 10^{-5}$ mol [substrate]: [Rh] = 215.

TABLE 2. Products of hydroformylation of 1,3- and 1,4-cyclohexadiene with catalytic system Rh(acac){P(OPh)$_3$}$_2$/P(OPh)$_3$ (I) and Rh(acac)(CO)(PPh$_3$)/PPh$_3$ (II) at 80°C, 10 atm, after 3 h

Substrate	Catalytic system	Yield of products (%)	
		1	**2**
1,4-Cyclohexadiene	(I)	55	–
	(II)	71	–
1,3-Cyclohexadiene	(I)	42	31
	(II)	30	43

1, cyclohex-2-enecarboxyaldehyde; **2**, cyclohex-1-enecarboxyaldehyde. (I), (II) [Rh] = 2.1·10^{-5} mol, [P(OPh)$_3$] or [PPh$_3$] = 3.2·10^{-5} mol, [substrate]: [Rh] = 200.

lation of 1,3-cyclohexadiene with catalyst produced by the condensation of rhodium vapour with excess of diene [12].

Cyclohex-3-enecarboxyaldehyde was obtained as one of the products of 1,3- and 1,4-cyclohexadiene hydroformylation at 100 atm with Rh(CO$_2$Me)(CO)(PPh$_3$)$_2$ [11].

In all our experiments the only products obtained were the unsaturated aldehydes mentioned above and shown in Scheme 1. Neither formylcyclohexane (the possible hydrogenation product of unsaturated aldehydes) nor dialdehydes were analytically detected. Analyses of the post-reaction mixtures allow us also to exclude the isomerization of substrates during hydroformylation. That the yields of aldehydes obtained in the hydroformylation of 1,3- and 1,4-cyclohexadienes were comparable suggests that the location of double bonds in the six-membered ring has no significant consequences for its reactivity.

A quite different picture is observed for cyclooctadienes.

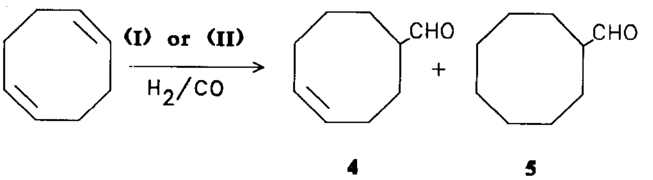
2.3. *Hydroformylation of 1,5- and 1,3-cyclooctadiene*

The conversion of 1,5-cyclooctadiene in the hydroformylation reaction is *ca.* 90% after 3 h whereas that of 1,3-cyclooctadiene is only 20% after 5 h. Similar reactivity has been observed by other authors [12]. The main hydroformylation reaction product of 1,5-cyclooctadiene is formylcyclooctane, the saturated aldehyde formed by hydrogenation of 5-formylcyclooctene (Scheme 2, **5**). The hydrogenation reaction can be restrained by increasing the CO/H$_2$ ratio (Table 3). During hydroformylation, 1,5-cyclooctadiene undergoes fast isomerization to 1,3-cyclooctadiene which is hydroformylated much more slowly and therefore remains in the reaction mixture. This problem appears first of all in the phosphite system (I) in which isomerization is about 30% and is practically uninfluenced by increase of CO concentration. The formylcyclooctane is a typical 1,5-cyclooctadiene hydroformylation reaction product, obtained also for other catalytic systems [1,2,11] although sometimes unsaturated aldehydes are selectively produced [12].

TABLE 3. Products of hydroformylation of 1,5- and 1,3-cyclooctadiene with catalystic system Rh(acac){P(OPh)$_3$}$_2$/P(OPh)$_3$ (I) and Rh(acac)(CO)(PPh$_3$)/PPh$_3$ (II) at 80°C, 10 atm, after 3 h

Substrate	Catalytic system	CO:H$_2$	Yield of products (%)		
			4	**5**	1,3-cyclo-octadiene
1,5-Cyclooctadiene	(I)	1:1	0	67	33
	(I)	3:2	25	50	25
	(II)	1:1	16	72	12
	(II)	3:2	33	63	1
1,3-Cyclooctadiene	(II)	1:1	–	20 [a]	80

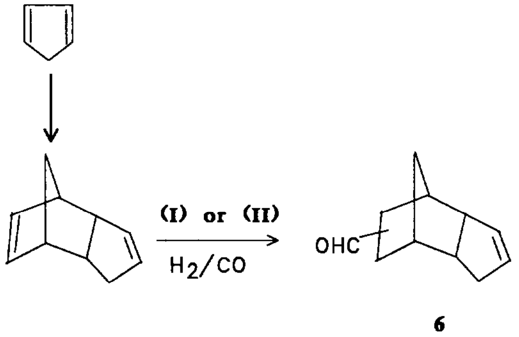
4, Cyclooct-4-enecarboxyaldehyde; **5**, cyclooctanecarboxyaldehyde. [a] Reaction time 5 h. (I), (II) [Rh] = 2.1·10^{-5} mol, [P(OPh)$_3$] or [PPh$_3$] = 3.2·10^{-5} mol, [substrate]: [Rh] = 160.



Scheme 2.

2.4. *Hydroformylation of 1,3-cyclopentadiene*

According to NMR and MS spectra in hydroformylation reaction conditions 1,3-cyclopentadiene is present only in the dimeric form. In the reaction under study dimerization occurs quite fast, so any changes in hydroformylation rate during the reaction were observed. The induction period was also comparable with that noted in reactions of other cycloolefins. However other authors have distinguished different reaction rates for both forms of cyclopentadiene [18]. The only product of hydroformylation of dicyclopentadiene in



Scheme 3.

TABLE 4. Products of 1,5-cyclopentadiene hydroformylation with catalytic system Rh(acac){$P(OPh)_3$}$_2$/$P(OPh)_3$ (I) and Rh(acac)(CO)(PPh_3)/PPh_3 (II) at 10 atm, after 3 h

Catalytic system	t (°C)	Yield of products (%) **6**
(I)	60	57
(I)	80	81
(II)	60	69
(II)	80	89

6, 8- or 9-Formyltricyclodec-4-ene. (I), (II) [Rh] = $2.1 \cdot 10^{-5}$ mol, [$P(OPh)_3$] or [PPh_3] = $3.22 \cdot 10^{-5}$ mol, [substrate]: [Rh] = 140.

both catalytic systems (I) and (II) are two isomers of unsaturated aldehyde, formyltricyclodec-4-ene, with different aldehyde group positions in the norbornenyl ring (Scheme 3, **6**). The products were distinguished chromatographically, though not fully characterized (the MS spectra are given in the Experimental section). Hydroformylation reaction occurs selectively in the norbornenyl ring, which is more reactive than the cyclopentene one [3,6].

The hydroformylation reaction yield for phosphine catalyst (II) is rather higher than that for phosphite catalyst (I) and in both cases, increases with temperature (Table 4).

3. Conclusions

Both catalytic systems under study, Rh(acac){P-$(OPh)_3$}$_2$/$P(OPh)_3$ (I) and Rh(acac)(CO)(PPh_3)/PPh_3 (II) show similar activity in hydroformylation of cyclic dienes. At *ca.* 200-fold excess of cyclic diene concentration vs. catalyst concentration, the average substrate conversion is 70% for cyclohexadienes but 80%–100% for cyclooctadienes and dicyclopentadiene under rather mild reaction conditions, 10 atm and 80°C. The reaction products are unsaturated aldehydes. Only in the case of 1,5-cyclooctadiene, is the saturated monoaldehyde a main reaction product.

During hydroformylation of 1,5-cyclooctadiene with catalyst (I), quite significant isomerization of the substrate (*ca.* 30%) and formation of less reactive, 1,3-cyclooctadiene is observed. The results obtained allow postulation that the structure of the diene rather than that of the catalyst used determines the yield and selectivity of the hydroformylation reaction.

4. Experimental section

Rhodium complexes were obtained according to methods described in the literature: Rh(acac)(CO)(PPh_3) [19], Rh(acac){$P(OPh)_3$}$_2$ [20].

Toluene (benzene) and olefin were carefully distilled before use. Hydroformylation reactions at 10 atm were carried out in a thermostated autoclave of 40 ml volume with magnetic stirrer. Reactions at 1 atm were performed in a thermostated glass reactor.

For each experiment amounts used were $2.1 \cdot 10^{-5}$ mol of catalyst (Rh(acac){$P(OPh)_3$}$_2$ or Rh(acac)(CO)(PPh_3)), $3.2\text{–}3.3 \cdot 10^{-5}$ mol of free ligand ($P(OPh)_3$ or PPh_3) and $3.0\text{–}4.5 \cdot 10^{-3}$ mol of olefin in 0.6 ml of toluene or benzene.

The reagents were introduced to the autoclave in nitrogen atmosphere and next filled with CO/H_2 mixture to required pressure. The reaction products were analyzed using ^1H NMR (Tesla BS 567A, 100 MHz) and GC-MS (Hewlett-Packard) instruments. Mass spectra of 8- 9-formyltricyclodec-4-ene (relative intensities in parentheses): isomer I: 162(M^+, 17), 144(4), 133(9), 121(3), 105(10), 96(28), 95(39), 91(22), 79(17), 78(15), 67(100), 66(90); isomer II: 162(M^+, 10), 144(2), 133(9), 131(9), 117(2), 105(6), 96(19), 95(42), 91(19), 79(13), 77(15), 67(100), 66(62).

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