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Selective hydroformylation–acetalization of aryl alkenes in methanol catalyzed by $RhCl_3 \cdot 3H_2O$–$P(OPh)_3$ system

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Abstract

Acetals were formed under hydroformylation conditions of alkenes in alcohols as solvents. The hydroformylation process is combined with acetalization in a one-pot reaction leading to acetals as final products. These reactions sequences were catalyzed by the simple rhodium catalyst $RhCl_3 \cdot 3H_2O$. The effects of the addition of different types and amounts of phosphine and phosphite ligands were carefully studied in order to improve the regioselectivity of the reaction.

Keywords: Hydroformylation; Acetalization; Aldehydes; Acetals; Rhodium; Styrene; Phosphine; Phosphite; Syngas

1. Introduction

The product range of hydroformylation reaction (known also as oxo synthesis) has remained unchanged for the past decades. In general, hydroformylation reactions are mainly catalyzed by Co and Rh catalysts. While the industrially relevant product range of hydroformylation has remained more or less unchanged over the past 20 years, the research work has continued actively in this area [1–3]. Hydroformylation–acetalization reactions represent a one-pot synthesis of acetals by the formation of aldehydes followed by the addition reactions of alcohols. Various examples of direct acetal formation under hydroformylation conditions in the presence of alcohols were reported [1–9]. The hydroformylation of 1-hexene in biphasic catalysis using ethylene glycol as co-solvent directly leads to the corresponding acetals of the oxo aldehydes [10]. The intermolecular and intramolecular acetalizations of allylic and homoallylic alcohols take place on zeolite-encapsulated rhodium catalysts [11]. Similar hydroformylations with subsequent acetal formation of the oxo aldehyde with methanol as solvent were achieved with the rhodium complex $[Rh_2(\mu\text{-}S(CH_2)_2NMe_2)_2(cod)]$, which is anchored to a sulfonic exchange resin through protonation of the residual amine groups. With this catalytic system styrene yields 1,1-dimethoxy-2-phenylpropane in 85% selectivity [12]. The conversion of cyano olefins to cyano aldehydes is of great interest because of their potential use as precursors for amino acids. When the reaction of hydroformylation was catalyzed by cobalt in alcohol as a solvent, cyano acetals are isolated. The modification of the cobalt carbonyl catalysts with ligands such as $HN(CH_2CN)_2$, $H_2N(CH_2)_3NHMe$, $Me_2N(CH_2)_2NHMe$, PPh_3, and PCy_3, up to quantitative yields of the acetals are obtained [13–15]. Selective formation of acetals from alkenes under hydroformylation conditions can also be achieved with triethyl orthoformate or 2,2-dimethoxypropane (DMP) instead of alcohols as the reagent. $[Rh_2(\mu\text{-}Ome)_{2-}(cod)_2]$ catalyzes the acetalization only in the presence of acid cocatalysts. The conversion of styrene to corresponding acetals was achieved with pyridinium *p*-toluenesulfonate (PPTS) as co-catalyst [16]. Lower regioselectivities but high enantioselectivities were reported in hydroformylation of styrene with the catalyst system [(−)-BPPM]$Pt(SnCl_3)Cl$ in the presence of triethyl orthoformate. The ratio of the branched acetal and linear is determined as

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1:2 with an enantiomeric excess of >96% for the branched acetal [17]. With $[Rh(\mu\text{-}SCR_2CH(NH_2)(COOH))]_2[Otf]_2$ (R = H, R = Me) as catalysts no additional acid co-catalyst is needed. These catalyst precursors convert terpenoids such as isolimonene with high chemoselectivity [18]. Acetal formation was also employed with functionalized alkenes. The conversion of unsaturated ketones such as 5-methyl-5-hexen-2-one in the presence of 2,2-dimethoxypropane (DMP) exclusively led to acetals with high aldehyde acetalization selectivity [16]. Asymmetric hydroformylation of unsaturated amines offers a pathway towards the synthesis of amino acid derivatives with high ee. To prevent racemization the conversion of *N*-vinylphthalimide to *N*-phthalylalanine can be performed via the acetal with the catalytic system [(−)-BPPM]Pt($SnCl_3$)Cl [17].

The products obtained by this type of tandem hydroformylation offer access to a wide range of interesting compounds. Hydrogenation of the hemiacetal leads to diols, which are important precursors, e.g. for ethers and resins [19,20]. It is also possible to oxidize the lactols to lactones. Other reactions can be performed at the double bond of the enol ether (epoxidation, dihydroxylation, allylic substitution). These reactions enable the synthesis of subunits of naturally occurring products with biological and pharmacological activities [21,22]. The results described in this chapter are ordered according to the type of unsaturated alcohols used as starting material. The acetalization of carbonyl compounds is still a subject that attracts many scientists. Recently, sulfonic acid group-functionalized amorphous silica showed high effectiveness and recyclable catalyst for the acetalization of various carbonyl compounds with methanol as a solvent [23]. Also, the palladium (II) complexes catalyzed efficiently and regioselectively the reaction of addition of alcohols to alkynes [24].

2. Experimental

2.1. General

Styrene, aryl alkenes and anisole were highly pure (>99%) and were purchased from Sigma–Aldrich company. The solvents used in the experiments were all HPLC grade and were stored under nitrogen over activated 3 Å molecular sieves (activated for 3 h at 300 °C) and also purchased from Sigma–Aldrich. The rhodium catalysts such as $RhCl_3{\cdot}3H_2O$, $[Rh(COD)Cl]_2$, $[Rh(CO)_2Cl]_2$, $RhHCO(PPh_3)_3$, $RhCl(PPh_3)_3$, and $Rh_6(CO)_{16}$ were purchased from Strem and used without purification. The triphenylphosphine (PPh_3), 1,4-bis-(diphenylphosphino)butane (dppb), 1,3-bis(diphenylphosphino)propane (dppp), and other phosphine ligands were purchased from Sigma–Aldrich in pure form.

The carbonylation reactions were carried out in 45 ml high-pressure Parr autoclaves. The products of the reaction of hydroformylation and acetalization were characterized using NMR, GC and GC–MS techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on 500 MHz Joel l500 NMR machine. Chemical shifts were reported in ppm (δ) relative to tetramethyl silane (TMS) using $CDCl_3$. Gas chromatography analyses were achieved on HP 6890 equipped with capillary column HP-5 in the presence of anisole as internal standard. The products have been identified on bench GC–MS spectrometer (Varian 3800 equipped with a capillary column HP-5 and coupled with mass spectrometer Saturn 2000).

2.2. General procedure for the hydroformylation–acetalization of aryl alkenes

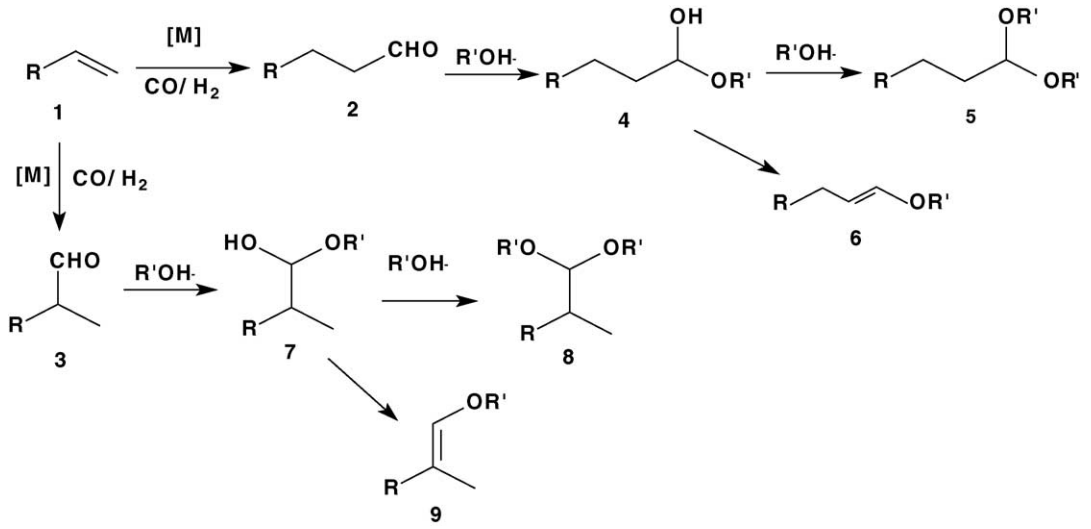
The following general procedure was considered for styrene adopted as a model substrate. A mixture of styrene (5.0 mmol), rhodium catalyst (0.005 mmol), ligand (0.010 mmol if used) was dissolved in 5.0 ml of dry solvent (or 5 ml of alcohol for the acetalization reaction) and placed in the liner of a 45 ml high-pressure Parr autoclave. The autoclave was flushed thoroughly three times with carbon monoxide, subsequently pressurized with carbon monoxide followed by hydrogen. The autoclaves were in oil baths heated on hotplates controlled by temperature sensor to maintain the temperature constant (±0.5 °C). The rate of stirring was maintained 750 rpm. After the reaction time elapsed, the autoclave was cooled down to room temperature and the gas was carefully released (carbon monoxide is a deadly gas) and the autoclave was open. The reaction mixture was filtered on celite to remove the catalyst. Hundred microgram of anisole as internal standard was added to the mixture to determine the conversion of styrene. The products were identified using GC–MS, ^{1}H NMR and ^{13}C NMR techniques and the spectra were compared with authentical samples. The ratio of branched to linear aldehydes or acetals was determined by GC and ^{1}H NMR.

3. Results and discussion

Acetal formation under hydroformylation conditions may be used to modify the aldehyde unit for further synthetic purposes or in order to protect the sensitive aldehyde group. Acetal formation is a typical addition reaction of aldehydes and frequently used in organic synthesis. Acetals 5 and 8 can be formed under the hydroformylation conditions when alcohols (R′OH) are added to oxo aldehydes 2 and 3. Therefore, the hydroformylation process can be combined with acetalization in a single reaction sequence to form hemiacetals 4 and 7, acetals 5 and 8, and enol ethers 6 and 9 (Scheme 1).

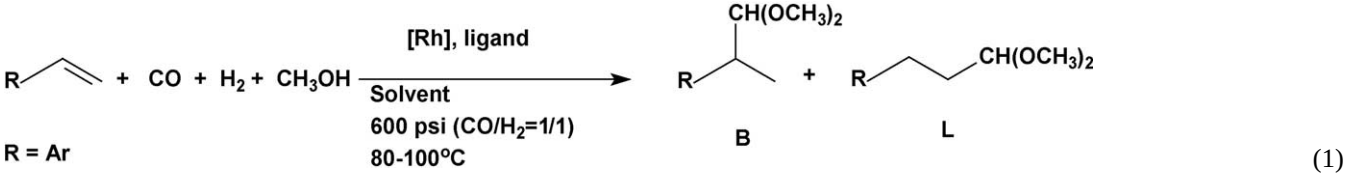
3.1. Hydroformylation–acetalization of styrene by $RhCl_3{\cdot}3H_2O$

In order to optimize the experimental conditions, we have examined the reaction of the acetalization of styrene and 1-octene, adopted as model substrates of aryl and alkyl alkenes (Eq. (1)). We have considered in this study a variety of rhodium catalysts including rhodium (III) and rhodium (I)



Scheme 1.

complexes and different co-catalysts or ligands such as phosphine or phosphite ligand.

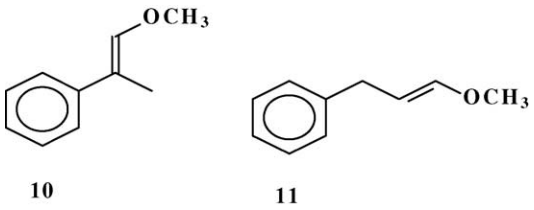


(1)

The acetalization by homogeneous and supported system was carried out in details including the effects of the type of the heteropolyacids and the phosphine–phosphite ligand on the occurrence of the reaction.

3.1.1. Hydroformylation–acetalization of styrene by rhodium catalysts: effect of the type of catalyst, co-catalyst and the ligand

The acetalization of styrene was studied by varying the type of rhodium catalyst in methanol as a solvent. The results are summarized in Table 1. We have started our study by the rhodium cluster $Rh_6(CO)_{16}$. The reaction of acetalization of styrene by $Rh_6(CO)_{16}$ shows very low conversion even at 100 °C with the formation of the aldehydes as major products (Table 1, entries 1, 2), no acetals were detected in the reaction mixture. The addition of $P(OPh)_3$ to $Rh_6(CO)_{16}$ enhanced seriously the conversion of styrene and the selectivity of aldehydes, but again no acetals were formed. Surprisingly the rhodium (III) catalyst, $RhCl_3{\cdot}3H_2O$, known by its low catalytic activity in the hydroformylation of alkenes, showed a relatively good catalytic activity in the reaction of acetalization of styrene in methanol as a solvent (Table 1, entry 4). $RhCl_3{\cdot}3H_2O$ alone gave 51% conversion and excellent selectivity (94%) of acetals with also good selectivity toward the branched acetal B. The most exciting and important result was observed with the rhodium (III) complex, $RhCl_3{\cdot}3H_2O$ associated to $P(OPh)_3$ (Table 1, entry 5). Excellent conversion of styrene (92%) and excellent yield of acetals (90%) were obtained in pure methanol at 80 °C and after 6 h. It is worth noting that the major by-products detected in the mixture were the ethers 10 and 11 with 10 as the major by-product. It is important to note that the yields of acetals and aldehydes were calculated based on GC and by considering the total yield of acetals plus aldehydes equals to 100%.



The rhodium (I) complex, $HRh(CO)(PPh_3)_3$, gave only aldehydes with an average conversion (45%) of styrene in the absence of any additive. The same reaction repeated in the presence of $P(OPh_3)_3$ led to higher conversion (95%) and excellent selectivity of aldehydes (94%) (Table 1, entries 6, 7). The other very important and very exciting results were obtained with $RhCl(PPh_3)_3$ as a catalyst (Table 1, entries 8, 9). $RhCl(PPh_3)_3$ alone gave high conversion of styrene with high selectivity towards acetals. However, when $P(OPh_3)_3$ was added to the system, aldehydes were formed as only products of the reaction and no acetals were observed. Similar results were obtained with $[Rh(COD)Cl]_2$ in methanol as a solvent (Table 1, entries 10–12). The only products of the reaction were aldehydes even at higher temperature

Table 1
Acetalization of styrene by [Rh]-$P(OPh)_3$ system: effect of the type of catalyst

Entry	Catalyst (mmol)	$P(OPh)_3$	Conversion[a] (%)	RCHO[a] (%)	RCHO (%)		Ethers (%)	Acetals[a] (%)	Acetals (%)	
					B	L[b]			B	L[b]
1	$Rh_6(CO)_{16}$ (0.0010)	No	5	100	83	17	0	0	–	–
2[c]	$Rh_6(CO)_{16}$ (0.0010)	No	9	100	69	31	0	0	–	–
3	$Rh_6(CO)_{16}$ (0.0010)	Yes	96	100	92	8	0	0	–	–
4	$RhCl_3{\cdot}3H_2O$ (0.0050)	No	51	2	84	16	4	94	79	21
5	$RhCl_3{\cdot}3H_2O$ (0.0050)	Yes	92	4	92	8	6	90	92	8
6	$HRh(CO)(PPh_3)_3$ (0.0050)	No	45	100	88	12	0	0	–	–
7	$HRh(CO)(PPh_3)_3$ (0.0050)	Yes	95	100	93	7	0	0	–	–
8	$RhCl(PPh_3)_3$ (0.0050)	No	72	20	90	10	2	78	84	16
9	$RhCl(PPh_3)_3$ (0.0050)	Yes	98	100	94	6	0	0	–	–
10	$[Rh(COD)Cl]_2$ (0.0050)	No	58	8	84	16	10	82	80	20
11	$[Rh(COD)Cl]_2$ (0.0050)	Yes	99	100	90	10	0	0	–	–
12[c]	$[Rh(COD)Cl]_2$ (0.0050)	Yes	99	100	82	18	0	0	–	–

Reaction conditions: $P(OPh)_3$ (0.010 mmol), styrene (5.0 mmol), CH_3OH (5 ml), 600 psi (CO/H_2 = 1/1), 80 °C, 6 h.
[a] Determined by GC.
[b] Determined by GC and ^1H NMR.
[c] 100 °C.

(100 °C) with no acetals formed or detected in the reaction mixture.

It seems that the combination of Rh(III) chloride and $P(OPh)_3$ forms the most active catalyst system for the selective acetalization of alkenes. We strongly believe that the active catalytic species for the hydroformylation and acetalization reactions are totally different. It can be observed that rhodium halides gave the highest conversions of styrene towards acetals. We believe that a rhodium intermediate of general formula $Rh_xCl_y[P(OPh)_3]_z$, having Lewis acidity, is the active species in the conversion of alkenes into aldehydes followed by the effective acetalization process.

3.1.2. Hydroformylation–acetalization of styrene by $RhCl_3{\cdot}3H_2O$: effect of the type of ligand

The earlier results obtained with the ligand $P(OPh)_3$ encouraged us to deeply consider the effect of the other mono- and di-phosphine ligands in the acetalization of styrene (Table 2). It is important to note that the use of a mixture of solvents such as THF–methanol, hexane–methanol, toluene–methanol, acetonitrile–methanol inhibited the reaction of hydroformylation–acetalization of styrene. An example of the results obtained with a mixture of THF and CH_3OH (1/1) is shown in Table 2 (entry 2). Similar results also were observed when a mixture of methanol and THF (1/1) was used in the presence of $P(OPh)_3$ (Table 2, entry 2). Furthermore, the reaction carried out in the presence of phosphine ligands such as 1,4-bis(diphenylphosphino)butane (dppb), diphenylphosphino ferrocene (dppf), and triphenyl phosphine (PPh_3) led to no or very low conversion of styrene (Table 2, entries 3–5). Tricylohexylphosphine (PCy_3) gave relatively better results in terms of conversion (49%) and yield of acetals (80%) (Table 2, entry 6). Other phosphite ligands were also used in the study. Trimethyl and triethyl phosphites were active in these reactions with the latest showing almost similar activity to $P(OPh)_3$ (Table 2, entries 8–10). However,

Table 2
Acetalization of styrene $RhCl_3{\cdot}3H_2O$: effect of the type of ligand

Entry	Ligand	Conversion[a] (%)	RCHO[a] (%)	RCHO (%)		Ethers (%)	Acetals[a] (%)	Acetals (%)	
				B	L[b]			B	L[b]
1	–	51	2	84	16	4	94	79	21
2[c]	–	5	42	80	20	5	53	82	18
3	dppb	0	–	–	–	–	–	–	–
4	dppf	9	18	86	14	14	68	84	16
5	PPh_3	0	–	–	–	–	–	–	–
6	PCy_3	49	2	98	2	11	87	82	18
7	$P(OPh)_3$	92	4	92	8	6	90	92	8
8	$P(OMe)_3$	78	4	88	12	11	85	83	17
9	$P(OEt)_3$	94	5	88	12	10	85	91	9
10	$PO(OBu)_3$	48	1	–	–	13	86	84	16
11[c]	$P(OPh)_3$	25	48	95	5	2	50	81	19

Reaction conditions: $RhCl_3{\cdot}3H_2O$ (0.005 mmol), ligand (0.010 mmol), styrene (5.0 mmol), CH_3OH (5 ml), 600 psi (CO/H_2 = 1/1), 80 °C, 6 h.
[a] Determined by GC.
[b] Determined by GC and ^1H NMR.
[c] THF (2.5 ml) and CH_3OH (2.5 ml) were used.

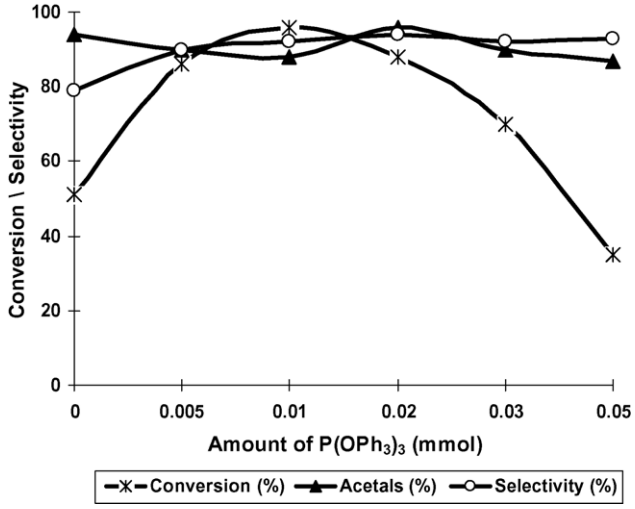


Fig. 1. Acetalization of styrene by $RhCl_3{\cdot}3H_2O$. Effect of the amount of $P(OPh)_3$ on the conversion and the selectivity. Reaction conditions: $RhCl_3{\cdot}3H_2O$ (0.0050 mmol), styrene (5.0 mmol), CH_3OH (5 ml), 600 psi (CO/H_2 = 1/1), 80 °C, 6 h.

the highest activity was maintained with $P(OPh)_3$ as a ligand. The effect of the $P(OPh)_3$ on the catalytic activity of the rhodium catalyst, $RhCl_3{\cdot}3H_2O$, appears to be enormous and this is probably related to an electronic effect of the phosphite ligands.

3.1.3. Hydroformylation–acetalization of styrene by $RhCl_3{\cdot}3H_2O$: effect of the amount of $P(OPh)_3$

The amount of ligand is highly important to the occurrence of the catalytic acetalization of styrene as shown in Fig. 1. The optimum amount of $P(OPh)_3$ was determined as 0.010 mmol, which corresponds to a 2/1 ligand to catalyst molar ratio. The conversion was maintained high at a molar ratio ranging between 1/1 and 4/1. As this ratio increased (>4) the conversion of styrene dropped significantly to reach 35% at a ratio of 10/1. Any addition of a ligand has an effect to stop totally the reaction of hydroformylation–acetalization of styrene. This observation can be explained by the probable formation of a stable and non-active intermediate such as $Rh_x[P(OPh)_3]_y$ in the form of a dimer or a trimer.

3.1.4. Hydroformylation–acetalization of styrene by $RhCl_3{\cdot}3H_2O$: effect of the reaction time

The reaction of acetalization of styrene catalyzed by $RhCl_3{\cdot}3H_2O$ was studied for the reaction time in the absence (Fig. 2) and in the presence (Fig. 3) of $P(OPh)_3$. The simple comparison of the two figures showed clearly the effect of the presence of the $P(OPh)_3$ on the kinetics of the reaction. In the absence of the ligand the reaction is relatively slow and it needs 16 h for completion. In addition, the selectivity toward the branched acetal B is not very high (80–84%).

However, the addition of $P(OPh)_3$ to the mixture enhanced significantly the hydroformylation–acetalization reaction (Fig. 3). The conversion of styrene reached its maximum after 6 h with excellent selectivity (92%) in branched acetals B.

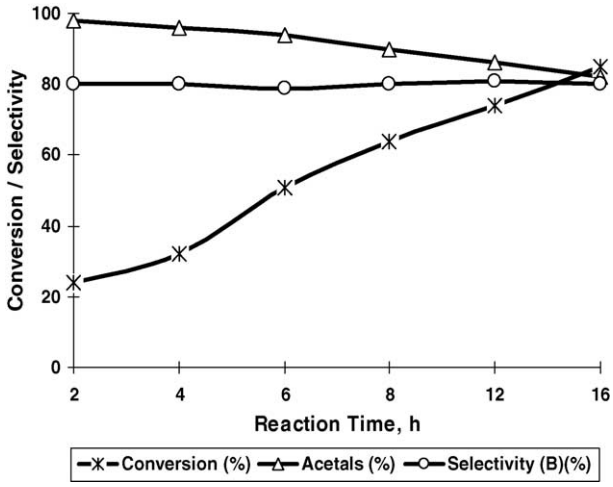


Fig. 2. Acetalization of styrene by $RhCl_3{\cdot}3H_2O$. Effect of the reaction time on the conversion and the selectivity. Reaction conditions: $RhCl_3{\cdot}3H_2O$ (0.0050 mmol), styrene (5.0 mmol), CH_3OH (5 ml), 600 psi (CO/H_2 = 1/1), 80 °C.

These results confirm again the important role of the phosphite ligand in the acetalization process.

3.1.5. Hydroformylation–acetalization of styrene by $RhCl_3{\cdot}3H_2O$: effect of the temperature

The study of the effect of the temperature was important in order to complete our study on the optimization of the experimental conditions toward the fast, complete, and selective reaction of acetalization (Fig. 4). At temperature below 50 °C, the conversion of styrene was very low (<30%). The conversion was doubled (62%) with the increase of the temperature by 10 °C. The conversion reached its maximum (96%) at 80 °C and 6 h with excellent yield and selectivity toward acetals. The further increase of the temperature has a direct effect on the reaction time where at 100 °C the total

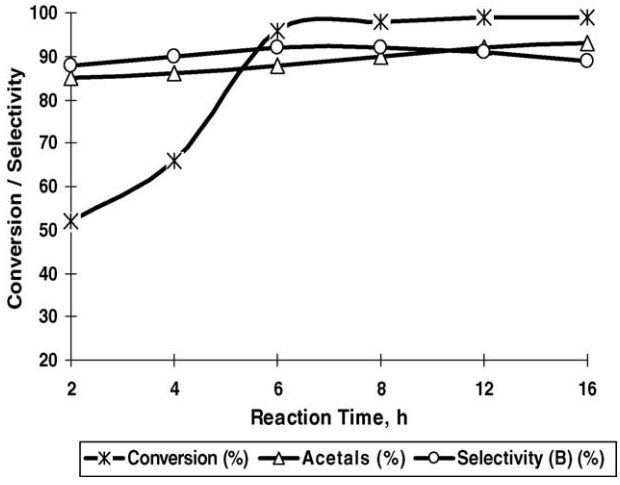


Fig. 3. Acetalization of styrene by $RhCl_3{\cdot}3H_2O$–$P(OPh)_3$. Effect of the reaction time on the conversion and the selectivity. Reaction conditions: $RhCl_3{\cdot}3H_2O$ (0.0050 mmol), $P(OPh)_3$ (0.010 mmol), styrene (5.0 mmol), CH_3OH (5 ml), 600 psi (CO/H_2 = 1/1), 80 °C.

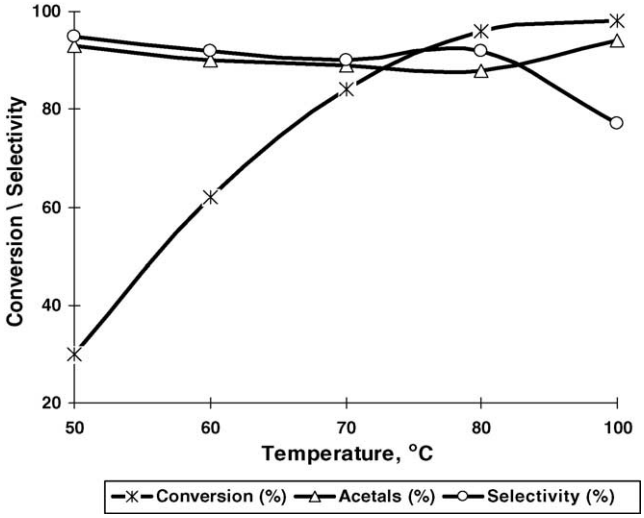
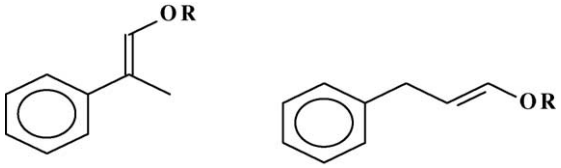


Fig. 4. Acetalization of styrene by $RhCl_3{\cdot}3H_2O$–$P(OPh)_3$. Effect of the temperature on the conversion and the selectivity. Reaction conditions: $RhCl_3{\cdot}3H_2O$ (0.0050 mmol), $P(OPh)_3$ (0.010 mmol), styrene (5.0 mmol), CH_3OH (5 ml), 600 psi (CO/H_2 = 1/1), 6 h.

conversion was observed after only 3 h of reaction but the selectivity toward the branched acetal B dropped to 77%.

3.1.6. Hydroformylation–acetalization of styrene by $RhCl_3{\cdot}3H_2O$: effect of the type of alcohol

The acetalization of styrene has been studied also by varying the type of alcohol. Ethanol, 1-propanol, 2-propanol, 1-buatnol, and 1,2-ethandiol were considered in this reaction (Table 3). The alcohols other than methanol behave differently in the reaction of acetalization of styrene. For example, ethanol at 80 °C gave only 63% conversion after 6 h of reaction with the formation of 13% of unsaturated ethers 12 and 13 (R = Et). The increase of the temperature to 100 °C improves significantly the conversion to 98% with a slight drop in the selectivity toward the branched acetals (Table 3, entries 2, 3). 1-Propanol and 1-butanol were not very reactive even at high temperature (100 °C) and longer reaction time (16 h). The conversions were 35 and 25%, respectively (Table 3, entries 4, 7). The interesting results were obtained with 2-propanol (isopropanol) in the acetalization of styrene. The products of the reaction were a mixture of aldehydes, acetals and ethers. The acetals could not be formed as the major products even at high temperature (100 °C) and longer time (16 h) (Table 3, entries 5, 6). About 31–35% of the ethers 12 and 13 (R = isopropyl) were formed even at high temperature with the 12 as the major by-product. The unsaturated ethers are the products of the decomposition of acetals due to steric hindrance of the isopropyl group – $CH[(OCH(CH)_3]_2$. The 1,2-ethanediol (ethylene glycol) was absolutely not reactive under the present experimental conditions and in some reactions only traces of a mixture of aldehydes and acetals were formed (Table 3, entry 8). The reason of such behavior of the diol is likely due to the complexation of the rhodium ion intermediate and subsequently the inhibition of its catalytic activity.



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3.2. Hydroformylation–acetalization of styrene derivatives by $RhCl_3{\cdot}3H_2O$

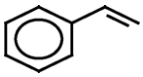
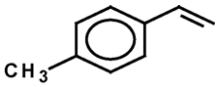
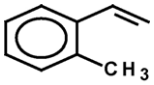
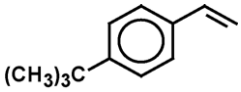
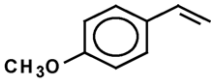
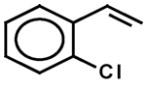
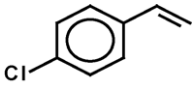
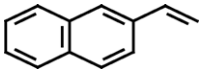
The optimization of the reaction of acetalization of styrene led to define the most active catalyst among the tested systems. This active system is a combination of the simple rhodium (III) complex $RhCl_3{\cdot}3H_2O$ along with phosphite ligand $P(OPh)_3$ in pure methanol as a solvent-reagent at 600 psi of syngas (CO/H_2 = 1/1) and 80 °C for 6 h. This system was applied to various aryl alkenes. The results are summarized

Table 3
Acetalization of styrene $RhCl_3{\cdot}3H_2O$–$P(OPh)_3$: effect of the type of alcohol

Entry	Alcohol	Conversion[a] (%)	RCHO[a] (%)	RCHO (%)		Ether (%)	Acetals[a] (%)	Acetals (%)	
				B	L[b]			B	L[b]
1	CH_3OH	92	4	92	8	6	90	92	8
2	CH_3CH_2OH	63	9	92	8	13	78	91	9
3[c]	CH_3CH_2OH	98	8	90	10	6	86	88	12
4[c,d]	$CH_3CH_2CH_2OH$	35	4	90	10	6	90	85	15
5	$(CH_3)_2CHOH$	73	31	93	7	35	34	96	4
6[d]	$(CH_3)_2CHOH$	98	33	88	12	31	36	86	14
7[c,d]	$CH_3CH_2CH_2CH_2OH$	25	5	89	11	-	95	88	12
8[c]	$HOCH_2CH_2OH$	Traces	–	–	–	–	–	–	–

Reaction conditions: $RhCl_3{\cdot}3H_2O$ (0.005 mmol), $P(OPh)_3$ (0.010 mmol), styrene (5.0 mmol), alcohol (5 ml), 600 psi (CO/H_2 = 1/1), 80 °C, 6 h.
[a] Determined by GC.
[b] Determined by GC and ^1H NMR.
[c] 16 h
[d] 100 °C.

Table 4
Acetalization of styrene derivatives by $RhCl_3{\cdot}3H_2O$–$P(OPh)_3$

Entry	Substrate	Conversion[a] (%)	Acetals[b] (%)	Acetals (%)		By-products[c] (%)
				B	L[b]	
1		92	90	92	8	6
2		90	89	90	10	4
3		86	87	88	12	5
4		91	90	88	12	5
5		89	78	88	12	8
6		86	94	94	6	3
7		88	94	93	7	4
8		85	90	94	6	8

Reaction conditions: $RhCl_3{\cdot}3H_2O$ (0.005 mmol), ligand (0.010 mmol), alkene (5.0 mmol), CH_3OH (5 ml), 600 psi (CO/H_2 = 1/1), 80° C, 6 h.
[a] Determined by GC.
[b] Determined by GC and ^1H NMR.
[c] Unsaturated ethers.

in Table 4. The presence of an electron donating or an electron withdrawing group in the position 4 or 2 on the benzene ring did not affect the reactivity of the aryl alkenes. For example, 2-methyl and 4-methyl styrene or 4-*tert*-butyl styrene undergo the acetalization with extremely high conversions (86–91%) and excellent selectivity toward the branched acetal B (Table 4, entries 2–4). The 4-vinyl anisole was little less reactive due the presence of the methoxy group in the *para* position to the vinyl group (Table 4, entry 5), but this phenomenon was not observed with 2- or 4-chloro styrene (Table 4, entries 6, 7). The conversion and the selectivities toward the branched acetals were among the highest obtained with aryl alkenes systems. 2-Vinyl naphthalene was also converted successfully to the corresponding acetals (Table 4, entry 8).

The importance of these results is related to the fact that, for the first time, these aryl alkenes were converted selectively directly into acetals via one-pot hydroformylation–acetalization by a very simple and easy to use catalytic system involving rhodium (III) and phosphite ligand.

4. Conclusion

The hydroformylation–acetalization of styrene was studied by varying the type of rhodium catalyst in methanol as a solvent. The reaction of acetalization of styrene by $Rh_6(CO)_{16}$ shows very low conversion even at high temperature with the formation of the aldehydes as major products and no acetals were detected in the reaction mixture.

Interesting results showed that the combination of Rh(III) chloride and $P(OPh)_3$ gave rise to the most active catalyst system for the hydroformylation–acetalization of alkenes. We believe that the active catalytic species for the hydroformylation and acetalization reactions are different. The rhodium intermediate, of general formula $Rh_xCl_y[P(OPh)_3]_z$ and having the Lewis acidity and the appropriate ligand, is the probable active species in the conversion of alkenes into aldehydes followed by the acetalization process. It was observed that the use of a large excess a phosphite ligand has an effect to stop totally the reaction of acetalization of alkene. This observation can be explained by the probable formation of a

stable and non-active intermediate such as $Rh_x[P(OPh)_3]_y$ in the form of a dimmer or a trimer.

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