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Selective hydroformylation of open-chain conjugated dienes promoted by mesitylene-solvated rhodium atoms to give β,γ unsaturated monoaldehydes

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Abstract

The hydroformylation of 1,3-butadiene, 2-methyl-1,3-butadiene and 1,3-pentadiene using rhodium vapour–mesitylene cocondesates as a catalytic precursor is reported. The reaction gives β,γ-unsaturated monoaldehydes with high chemoselectivity and regioselectivity. η^3-Butenyl complexes, derived from the addition of Rh–H species to the conjugated double-bound system, are likely to be intermediates, as suggested by deuterioformylation experiments.

Keywords: Rhodium vapour; Hydroformylation; Conjugated dienes; Catalysis; Unsaturated aldehydes

1. Introduction

Although the first studies on the hydroformylation of open-chain conjugated dienes appeared several years ago [1], the chemoselectivity and regioselectivity of the reaction with the catalytic precursors employed until now are generally rather low [2]. Only 1,3-butadiene has been hydroformylated to linear saturated monoaldehyde with selectivity over 90%, employing a rhodium diphosphine catalyst obtained in situ by reaction of [Rh(1,5-cyclooctadiene)OAc_2] and bis(diphenylphosphino)ethane [3]. However, under similar experimental conditions the hydroformylation of isoprene and 1,3-pentadiene gaves poor yields and it was not ascertained whether unsaturated aldehydes were formed as intermediates. We reported previously that rhodium vapour–cycloalkene cocondensates were efficient catalytic precursors for the selective hydroformylation of cyclic dienes to cycloalkene-carboxaldehydes under very mild reaction conditions [4]. We now found that rhodium vapour–mesitylene cocondensates in the presence of bis(diphenylphosphino)ethane (DPPE) catalyse the hydroformylation of open-chain conjugated dienes to give linear β,γ-unsaturated monoaldehydes with unusually high chemoselectivity (Scheme 1).

2. Results and discussion

The catalytic precursor was prepared by cocondensation of rhodium vapour with mesitylene in large excess at liquid-nitrogen temperature [5]. The solid matrix obtained was allowed to melt on warming to −40°C and the resulting red–brown solution manipulated at a low temperature under argon. The amount of rhodium in the mesitylene solution was determined by X-ray fluorescene analysis [6]. Portions of the solution were used in catalytic runs after addition of DPPE. 1,3-Butadiene, 2-methyl-1,3-butadiene (isoprene) and 1,3-pentadiene have been hydroformylated at 80°C, starting from $CO–H_2$ (1:1) at 120 atm using a 1:1 Rh:DPPE ratio. The results obtained are in Table 1. Hydroformylation for 4 h of 1,3-butadiene produces, (*E*,*Z*)-3-pentenal (**I**) containing 4% of 4-pentenal (**II**), with yields of about 76%. Only traces of saturated aldehydes have been detected in the reaction mixture. Under the same reaction conditions the hydroformylation for 8 h of isoprene gives (*E*,*Z*)-3-methyl-3-pentenal (**III**) and 4-pentenal (**IV**) in a ratio of 9:1 with yields of

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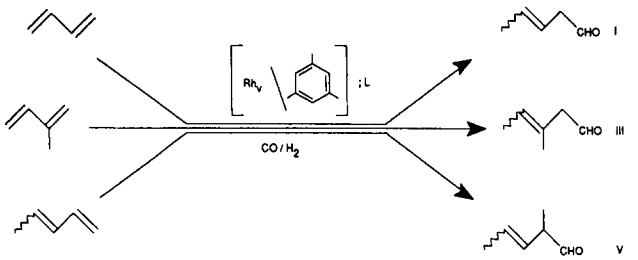
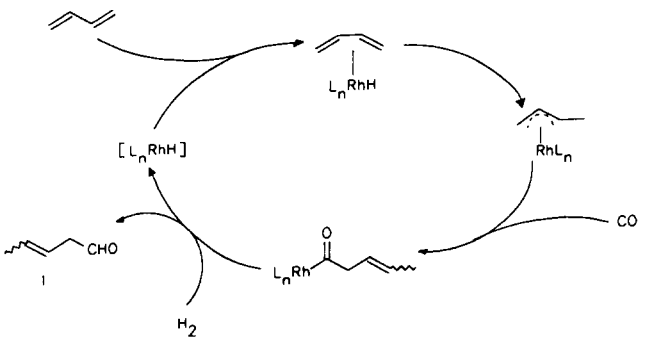


Scheme 1.



Scheme 2.

about 65%. The reaction is slower than the hydroformylation of 1,3-butadiene, where yields of about 80% are reached after 4 h. (*E,Z*)-2-methyl-3-pentenal (**V**) is obtained as the major aldehyde (90%) in the hydroformylation of (*cis–trans*) 1,3-pentadiene. The conjugated aldehyde (*E,Z*)-2-methyl-2-pentenal (**VI**) and other unsaturated aldehydes are present in the reaction mixture, at 6% and 4% respectively.

Longer reaction times result in a complete conversion of the starting dienes and increasing amounts of saturated aldehydes in the hydroformylation of 1,3-butadiene and 1,3-pentadiene. In the case of isoprene the chemoselectivity is not affected by the reaction time and only the unsaturated aldehydes **III** and **IV** are formed in the same 9:1 ratio. If a monophosphine, such as triphenylphosphine is employed additionally ($Rh:PPh_3$, ratio, 1:1) the reaction is very slow, the substrate conversion being about 30% after 24 h; the regioselectivity is poor and saturated aldehydes are the major products in all the cases. Only oligomers are formed if the reaction is performed using condensed rhodium vapour in the absence of phosphines.

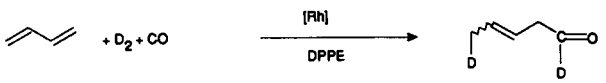
It appears from the results in Table 1 that the main feature of the hydroformylation of 1,3-dienes promoted by rhodium–mesitylene cocondensate is the unusual high chemoselectivity and regioselectivity in β,γ-unsaturated aldehydes, arising formally from 1,4 addition of –H and –CHO groups to the conjugated double bond system. γ,δ-unsaturated aldehydes obtained by 1,2-addition, and α,β-unsaturated aldehydes, probably arising from isomerization of β,γ-aldehyde are always less than 10% of the product.

A possible reaction pathway, using 1,3-butadiene as substrate, is presented in Scheme 2. ^1H NMR analysis of the Rh–toluene and Rh–mesitylene cocondensates in the arene solution at low temperatures shows the presence of Rh-hydrido species as small aggregates. It seems reasonable to suppose that similar Rh-hydrido clusters stabilized by the added phosphine may act as catalytic precursors [7]. On the basis of this observation, coordination and the subsequent addition of a Rh–H species to the conjugated system to give a η^3-butenyl intermediate is likely to occur [8,3]. CO insertion at the less hindered position of the complex follows, affording the corresponding rhodium acyl derivative that is transformed by hydrogenolysis to the β,γ-unsaturated aldehyde (*E,Z*)-3-pentenal (**I**).

Table 1
Hydroformylation of open-chain conjugated dienes by rhodium-vapour-derived catalysts [a]

Substrate	Reaction time (h)	Conversion [b] (%)	Aldehyde [b] yield (%)	Aldehyde distribution (%)		
	4	78	76	CHO (I) [d] 96	CHO (II) 4	CHO Traces
	8	70	65 [c]	CHO (III) [e] 90	CHO (IV) 10	–
	3	70	68	CHO (V) [f] 90	CHO (VI) 6	Others 4

[a] 1,3-diene : Rh : DPPE, 650 : 1 : 1; $T = 80°C$; P = 120 atm ($CO:H_2$, 1:1).
[b] Obtained by gas chromatography analysis using *p*-xylene as the internal standard.
[c] High oligomers were found.
[d] *E/Z* ratio, 75/25.
[e] *E/Z* ratio, 38/62.
[f] *E/Z* ratio, 18/82.



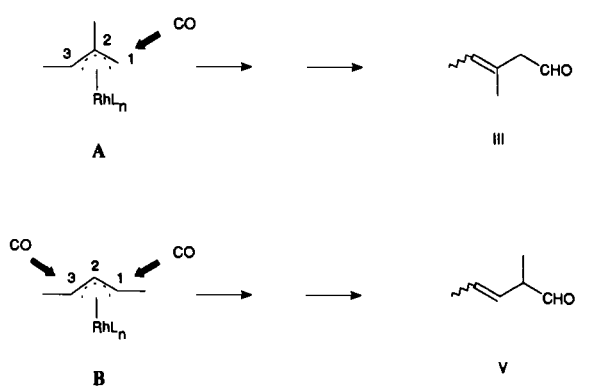
Scheme 3.

Isotope studies are very helpful in the investigation of hydroformylation reactions [9]. To obtain a better insight into the hydroformylation of conjugated dienes, a labelling experiment was performed, replacing dihydrogen by dideuterium. Only one kind of labelled 3-pentenal was formed and was isolated by preparative gas–liquid chromatography (GLC) and identified by ^{1}H NMR, ^{2}H NMR and mass spectroscopy (MS) as pure 1,5-d_2-3-pentenal (Scheme 3). This indicates a 1,4-addition of –H and –CHO to the diene system and makes a pathway involving hydrogen atoms migrations or exchanges improbable.

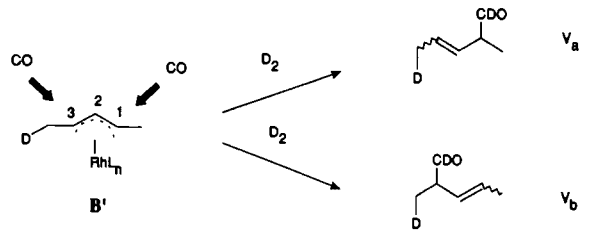
In the case of hydroformylation of isoprene and 1,3-pentadiene, the observed aldehydic products **III** and **V** imply the formation of η^3-butenyl intermediates **A** and **B** respectively (Scheme 4). They could arise from a 1,4- addition of a Rh–H species to the conjugated dienes, the hydrogen atom selectively attacking the less substituted double bond.

The subsequent CO insertion takes place on the less hindered carbon atom C(1) of **A**, leading to (*E*,*Z*)-3-methyl-3-pentenal (**III**). In **B**, two equivalent positions, C(1) and C(3), are available and insertion in either position leads to (*E*,*Z*)-2-methyl-3-pentenal (**V**).

Support for the proposed pathway was provided by deuterioformylation experiments of 1,3-pentadiene. In this case, if the η^3-butenyl intermediate **B′** (Scheme 5) is formed, CO insertion on C(1) or C(3) would give two different aldehydes, namely (*E*,*Z*)-1,5-d_2-2-methyl-3-pentenal (**Va**) or (*E*,*Z*)-1,2-d_2-methyl-3-pentenal (**Vb**). ^{1}H NMR and ^{2}H NMR data showed that equal amounts of these aldehydes are obtained, supporting



Scheme 4.



Scheme 5.

the presence of a symmetrical intermediate such as **B** in the reaction sequence.

In conclusion, the results reported here are a further example of the usefulness of the metal vapour technique in catalysis. The availability of a convenient route to β,γ-unsaturated aldehydes by hydroformylation of conjugated dienes is of real interest; such compounds are useful in organic synthesis and are difficult to obtain [10]. It has been shown by labelling experiments that η^3-butenyl intermediates are likely to be formed in the catalytic process. At the moment it is quite difficult to explain the peculiarity of these rhodium-vapour-derived catalysts compared with the previously employed rhodium compounds. However, the reaction of rhodium–mesitylene cocondesates with DPPE might afford a rhodium-hydrido species in which the phosphine plays an important role in enhancing the chemoselectivity and regioselectivity of the hydroformylation of conjugated dienes, as observed elsewhere [3].

3. Experimental details

GLC analyses were performed on a Perkin–Elmer 8700 gas chromatograph equipped with a 12 m × 0.22 mm fused-silica column filled with dimethylsiloxane (BPI, SG column) and a flame ionization detector. Dinitrogen was used as carried gas. Preparative GLC was carried out on a Perkin–Elmer F21 instrument equipped with 3 m or 5 m × 0.95 cm columns of 5% methyl silicone (SE 30) on 60/80 mesh Chromosorb A-NAW. ^{1}H NMR spectra were recorded in $CDCl_3$ solution on Varian Gemini 200 or Varian VXR 300 spectrometers (chemical shifts in parts per million relative to tetramethylsilane as internal standard) and mass spectra using a VG analytical 70/70E spectrometer.

3.1. Cocondensation reaction

Rhodium metal (82.8 mg, 0.8 mg atom) was evaporated during 40 min and cocondensated with mesitylene (30 ml) at liquid-nitrogen temperature, using a glass metal-atom reactor. The matrix obtained was warmed to about −40°C and the resulting brown solu-

tion syphoned under argon into a Schlenk tube and manipulated at −30°C under argon.

3.2. Hydroformylation reaction (general procedure)

In a typical run, to a portion of the above coconden-sate containing 5.2 mg or rhodium (0.050 mg atom) in 10 ml of mesitylene were added 22 mg (0.05 mmol) of DPPE and 32.5 mmol of 1,3 diene, and the solution so obtained was introduced by suction into an evacuated 80 ml stainless steel autoclave. Carbon monoxide was introduced to the desired pressure, and the autoclave was rocked and heated to 80°C, dihydrogen was rapidly introduced to give a 1:1 gas composition. When the pressure drop reached the theoretical value corre-sponding to the desired conversion, the autoclave was cooled, and depressurized, and the reaction mixture analysed by GLC. The crude product was distilled and pure samples of the various aldehydes were obtained by preparative GLC and characterized by 1H NMR and GC MS analysis.

3.2.1. Hydroformylation of 1,3-butadiene

(*E,Z*)-3-pentenal: ^{1}H NMR (300 MHz): 9,62 (t, J = 2 Hz, 1H, C*H*O, *E*), 9.64 (*t*, J = 1.8 Hz, 1H, C*H*O, *Z*); 5.38–5.90 (m, 2H, C*H*=C*H*, *E* + *Z*); 3.12–3.20 (m, 2H, CH_2, *Z*); 3.05–3.10 (m, 2H, $-CH_2-$, *E*); 1.65–1.78 (m, 3H, CH_3 *E*); 1.55–1.72 (m, 3H, $-CH_3$ *Z*).

GLC MS (*m/e*, *I*%): 84, 25 $(M)^+$; 69, 10 $(M - CH_3)^+$; 55, 100 $(M - CHO)^+$.

4-pentenal: ^{1}H NMR (200 MHz); 9.75 (t, J = 1.5 Hz, 1H, C*H*O); 5.04–5.07 (m, 1H, −C*H*=); 4.94–5.02 (m, 2H, $=CH_2$); 2.45–2.55 (m, 2H, $-CH_2-CHO$); 2.35–2.40 (m, 2H, $-CH_2-CH_2$).

GLC MS (*m/e*, *I*%): 84, 8 $(M)^+$; 83, 30 $(M - H)^+$; 55, 100 $(M - CHO)^+$; 41, 69 $(M - CH_2 - CHO)^+$.

3.2.2. Hydroformylation of isoprene

(*E,Z*)-3-methyl-3-pentenal: ^{1}H NMR (300 MHz): 9.57 (t, J = 2.6 Hz, 1H, C*H*O, *Z*), 9.54 (t, J = 2.6 Hz, 1H, C*H*O, *E*); 5.42–5.60 (m, 1H, CH_3–CH=, *E*); 5.28–5.42 (m, 1H, CH_3–C*H*=, *Z*); 3.07–3.13 (m, 2H, $-CH_2-$ CHO, *E*); 2.96–3.03 (m, 2H, $-CH_2$–CHO, *Z*); 1.73 (s, 3H, CH_3–C=, *E* + *Z*); 1.64 (d, J = 8 Hz, 3H, CH_3–CH=, *Z*); 1.60 (d, J = 8 Hz, 3H, CH_3–CH= *E*).

GLC MS (*m/e*, *I*%): 98, 15 $(M)^+$; 83, 12 $(M - CH_3)^+$; 69, 23 $(M - CHO)^+$; 55, 50 $(M - C_2H_3O)^+$; 41, 100 $(M - C_3H_5O)^+$.

4-methyl-4-pentenal: ^{1}H NMR (200 MHz); 9.74 (t, J = 1.7 Hz, 1H, C*H*O); 4.62–4.76 (m, 2H, CH_2=); 2.50–2.60 (m, 2H, CH_2–CHO); 2.33 (t, J = 8 Hz, 2H, =C–CH_2–); 1.75 (m, 3H, CH_3–C=).

GLC MS (*m/e*, *I*%): 98, 15 $(M)^+$; 83, 5 $(M - CH_3)^+$; 69, 28 $(M - CHO)^+$; 55, 13 $(M - C_2H_3O)^+$; 41, 100 $(M - C_3H_5O)^+$.

3.2.3. Hydroformylation of (E,Z)-1,3-pentadiene

(*E,Z*)-2-methyl-3-pentenal: ^{1}H NMR (200 MHz); 9.52 (d, J = 1.8 Hz, 1H, C*H*O, *Z*); 9.50 (d, J = 1.8 Hz, 1H, C*H*O *E*); 5.51–5.82 (m, 1H, =C*H*–CH *E* + *Z*); 5.14–5.49 (m, 1H, CH_3=C*H*, *E* + *Z*); 3.22–3.48 (m, 1H, −C*H*–CHO, *E*); 2.84–3.12 (m, 1H, −C*H*–CHO, *Z*); 1.75–1.82 (m, 1H, CH_3–C*H*=, *E*); 1.67–1.73 (m, 1H, CH_3–C*H*=, *Z*); 1.14 (d, J = 6.8 Hz, 3H, CH_3–CH–, *Z*) 1.06 (d, J = 6.8 Hz, 3H, CH_3–CH=, *E*).

GLC MS (*m/e*, *I*%): 98, 15 $(M)^+$; 83, 32 $(M - CH_3)^+$; 69, 100 $(M - CHO)^+$; 55, 22 $(M - C_2H_3O)^+$; 41, 99 $(M - C_2H_5O)^+$.

(*E,Z*)-2-methyl-2-pentenal: ^{1}H NMR (200 MHz); 10.1 (s, 1H, C*H*O, *Z*); 9.37 (s, 1H, C*H*O, *E*); 6.40–6.62 (m, 1H, C*H*=, *E* + *Z*); 2.24–2.64 (m, 2H, CH_3–CH_2–, *E* + *Z*); 1.74–178 (m, 3H, CH_3–C=, *E* + *Z*); 1.08 (t, J = 8 Hz, 3H, CH_3–CH_2, *E* + *Z*).

GLC MS (*m/e*, *I*%); 98, 80 $(M)^+$; 83, 25 $(M - CH_3)^+$; 69, 40 $(M - CHO)^+$; 55, 25 $(M - C_2H_3O)^+$; 41, 100 $(M - C_3H_5O)^+$.

3.2.4. Deuterioformylation of 1,3-butadiene

(*E,Z*)-1,5-d_2-3-pentenal: ^{2}H NMR (46 MHz): 9.63 −C*D*O (1D *E* + *Z*); 1.82 $-CH_2D$ (1D *E* + *Z*).

GLC MS (*m/e*, *I*%): 86, 20 $(M)^+$; 70, 5 $(M - CH_2D)^+$; 56, 100 $(M - CDO)^+$.

3.2.5. Deuterioformylation of (E,Z)-1,3-pentadiene

(*E,Z*)-1,5-d_2-2-methyl-3-pentenal: ^{2}H NMR (46 MHz); 9.10 −C*D*O (1D *E* + *Z*); 1.42 DCH_2–CH=(1D *E* + *Z*).

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