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FACTORS AFFECTING THE REGIOSELECTIVITY IN THE RHODIUM-CATALYSED HYDROFORMYLATION OF VINYL ETHERS

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Summary

The rhodium catalysed hydroformylation of vinyl ethers $ROCH{=}CH_2$, where R is an alkyl, a benzyl or a phenyl group, has been investigated over the 20–100°C temperature range in the presence of $Rh_4(CO)_{12}$ or $[Rh(CO)_2Cl]_2/PPh_3$ (1/6) as catalytic precursors. A mixture of 2-alkoxy-(or phenoxy)propanal (the α-isomer) and 3-alkoxy-(or phenoxy)propanal (the β-isomer) is obtained in good yield. The isomeric composition of the aldehydes depends on the structure of the substrate, on the catalytic precursor employed, and on the reaction temperature. The α-isomer predominates in all the cases, its predominance being greater (i) at low temperatures, (ii) in the presence of $Rh_4(CO)_{12}$ as catalyst precursor, and (iii) when a phenyl group is present in the β or γ position with respect to the double bond in the substrate. Electronic factors arising from the presence in the substrate of the oxygen atom and a phenyl group are more important than the steric hindrance of the R group in determining the regioselectivity of the reaction.

Introduction

Rhodium catalysed hydroformylation of functional olefins is of considerable interest because of its wide potential application in organic syntheses [1,2]. Of oxygenated unsaturated compounds [3], vinyl ethers, which have received little attention [4–7], appear to be interesting substrates. Since the oxygen atom is directly bonded to the vinyl group, isomerization, often observed with simple olefins [8], is avoided and only two isomeric aldehydes are obtained as products of the reaction. The structural features of vinyl ethers make these substrates useful in studies of the influence of steric and electronic factors on the regioselectivity of hydroformylation. We describe below the results obtained in hydroformylation of simple vinyl ethers $ROCH{=}CH_2$, where R is a phenyl or a benzyl group or one of the alkyl groups from a series involving increasing steric hindrance, viz. Me, Et, n-Bu, i-Pr and t-Bu.

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Results and discussion

The hydroformylation was usually carried out at 100°C and 100 atm. of CO/H_2 (1/1) in benzene, using $Rh_4(CO)_{12}$ or $[Rh(CO)_2Cl]_2/PPh_3$ (1/6) as catalytic precursor. With alkyl vinyl ethers the reaction was also carried out in the absence of solvent. In all the cases the reaction takes place with a complete conversion of the substrates to give a mixture of two isomeric aldehydes in high yield (eq. 1).

$$ROCH{=}CH_2 + CO + H_2 \begin{cases} \rightarrow ROCHCHO \\ \quad\quad\quad | \\ \quad\quad\quad CH_3 \\ \quad (\alpha\text{-isomer}) \end{cases} \quad (1a)$$

$$\rightarrow ROCH_2CH_2CHO \quad (\beta\text{-isomer}) \quad (1b)$$

The products were isolated as isomerically pure samples by fractional distillation at atmospheric or reduced pressure or by preparative GLC, and were characterized by ^1H NMR and mass spectra and by determination of other physical constants (see Table 1). Most of the isomeric aldehydes obtained are new. In the case of t-butyl vinyl ether, a non-volatile and viscous oil, identified as poly(t-butyl vinyl ether) was formed as a by-product in about 20% yield. No decomposition of the substrates or of the carbonyl derivatives was observed in the reaction or during recovery of the products provided that the temperature was kept below 150°C. Hydrogenation of the substrates to the corresponding saturated ethers occurs only to a very small extent.

The results obtained, shown in Tables 2 and 3, indicate that the isomeric distribution of the aldehydes arising from the hydroformylation of the vinyl ethers depends on the structure of the substrate, on the catalytic precursor employed, and on the temperature of the reaction. The isomer arising from the attack of the formyl group on the unsaturated carbon atom bound to the oxygen atom, i.e., the α-isomer, predominates in all cases. The isomer distribution is not influenced by the nature of the solvent used (benzene, n-hexane, THF, neat), and is independent of the degree of the conversion.

TABLE 1

PHYSICAL PROPERTIES OF THE ALKOXYALDEHYDES OBTAINED BY HYDROFORMYLATION OF VINYL ETHERS (eq. 1) [a]

R	B.p. (°C/mmHg)		n_D^{25}		^1H NMR [c]	
	α	β	α	β	α	β
Me	90/760	103/760	1.3908	1.3991	9.56	9.67
Et	93/760	118/760	1.3962	1.4044	9.50	9.66
i-Pr	114/760	130/760	1.4003	1.4068	9.63	9.70
t-Bu	34–35/20	53–54/20	1.4031	1.4101	9.60	9.73
n-Bu	48–49/20	67–68/20	1.4064	1.4116	9.63	9.73
$PhCH_2$	72–74/0.8	88–89/0.8	1.4925	1.5001	9.63	9.70
Ph	49–50/0.3	– [b]	1.4783	– [b]	9.55	9.60

[a] All products gave satisfactory elemental analyses. [b] The β isomer was not isolated. [c] Chemical shift of the aldehydic proton in ppm from TMS.

TABLE 2

DEGREE OF REGIOSELECTIVITY OF THE RHODIUM-CATALYSED HYDROFORMYLATION OF VINYL ETHERS [a]

$ROCH{=}CH_2$ R	$Rh_4(CO)_{12}$ [b]		$[Rh(CO)_2Cl]_2/PPh_3(1/6)$ [c]	
	α% [d]	RE [e]	α% [d]	RE [e]
Me	78	56	54	8
Et	76	52	54	8
n-Bu	76	52	53	6
i-Pr	72	44	52	4
t-Bu	63	26	53	6
$PhCH_2$	76	52	67	34
Ph	95	90	95	90

[a] 10 ml benzene solution containing 0.035 *M* of substrate; CO/H_2 (1/1) 100 atm (±5 atm); reaction temperature 100°C. [b] 0.020 g (2.7×10^{-2} mmol); [substrate]/[Rh] 330. [c] $[Rh(CO)_2Cl]_2$ 0.040 g (1.07×10^{-1} mmol) PPh_3 0.160 g (6.1×10^{-1} mmol); [substrate]/[Rh] 170. [d] $\alpha\% = \alpha/(\alpha+\beta)\times100$. [e] Regioselectivity (RE) = $[(\alpha-\beta)/(\alpha+\beta)]\times100$.

With the exception of the phenyl vinyl ether the regioselectivity is strongly affected by the nature of catalytic precursor. Thus, a greater dominance of the α-isomer was observed on using $Rh_4(CO)_{12}$ instead of the Rh/PPh_3 mixed system. As far as the nature of the substrate is concerned, the selectivity towards the α-isomer is higher for phenyl and benzyl vinyl ether than for alkyl vinyl ethers. The highest value of regioselectivity (90%) was observed in the case of phenyl vinyl ether. The structure of the alkyl group bound to the oxygen atom in the alkyl vinyl ethers weakly infuences the isomeric distribution of the aldehydes with both the catalytic systems (Table 2). In the hydroformylation of t-butyl vinyl ether in the presence of $Rh_4(CO)_{12}$, the regioselectivity was lower than with primary or secondary alkyl vinyl ethers.

The influence of the reaction temperature on the regioselectivity was studied over the range 20–100°C with $Rh_4(CO)_{12}$ as catalytic precursor, since this is active in the hydroformylation of vinyl ethers even at room temperature. As shown in Table 3 for

TABLE 3

INFLUENCE OF THE REACTION TEMPERATURE ON THE REGIOSELECTIVITY IN THE RHODIUM-CATALYSED HYDROFORMYLATION OF VINYL ETHERS [a]

Vinyl ether	Reaction temperature (°C)	Reaction time (h)	Conversion to aldehydes (%)	α (%)	RE (%)
$EtOCH{=}CH_2$	100	0.5	97	76	52
$EtOCH{=}CH_2$	80	0.8	96	77	54
$EtOCH{=}CH_2$	50	4.0	90	78	56
$EtOCH{=}CH_2$	20	15.0	50	82	64
$PhCH_2OCH{=}CH_2$	100	0.7	97	76	52
$PhCH_2OCH{=}CH_2$	80	1.0	97	79	58
$PhCH_2OCH{=}CH_2$	50	4.5	97	84	68
$PhCH_2OCH{=}CH_2$	20	15.0	50 [b]	88	76

[a] $Rh_4(CO)_{12}$; CO/H_2 (1/1) 100 atm (±5 atm). [b] 20% of poly(benzyl vinyl ether) was formed.

the ethyl and benzyl vinyl ether, the selectivity towards the α-isomer increases with decreasing temperature, the effect being larger in the case of benzyl vinyl ether.

The results show that in the rhodium-catalysed hydroformylation of vinyl ethers the formyl group is preferentially incorporated at the unsaturated carbon bound to the oxygen atom, and this preference is higher at low temperatures and when a phenyl substituent is present in β or γ with respect to the double bond in the substrate. A similar variation of regioselectivity was reported for the rhodium catalysed hydroformylation of unsaturated alkyl esters [5], vinyl esters [9], styrene [10], or substituted styrenes [11].

It is noteworthy that the regioselectivity shown by vinyl ethers is opposite to that observed with the α-olefins of comparable structure i.e. $RCH_2CH{=}CH_2$. In the latter the linear aldehyde predominates over the branched product with both the catalytic precursors ($Rh_4(CO)_{12}$ or Rh/PPh_3) [8].

Several and sometimes conflicting hypotheses have been advanced to explain the much discussed isomer ratio in the hydroformylation reaction, such as coordination of the carbonyl group to the catalytic system in the case of unsaturated esthers [5], the inductive effect of the groups linked to the double bond in the case of trifluoropropene [12] or substituted styrenes [11], and the kinetic lability of saturated and unsaturated acyl complexes in the case of styrenes [13] and vinyl esters [9].

We cannot offer a satisfactory explanation of the role played by the oxygen atom in determining the regioselectivity in the case of the rhodium-catalysed hydroformylation of vinyl ethers. The results indicate that electronic factors arising from the presence of the oxygen atom and of a phenyl group are more important than steric hindrance associated with the various alkyl groups bonded to the oxygen atom in determining the regioselectivity.

Hydroformylation of vinyl ethers represents another interesting application of a catalytic reaction to organic synthesis. The chemioselectivity, the regioselectivity favouring the α-isomer, and the possibility of modifying the isomeric composition, make hydroformylation of vinyl ethers a useful way of preparing the α- or β-OR derivatives of propionaldehyde.

Experimental

Benzene was dried and distilled under nitrogen. The catalytic precursors $Rh_4(CO)_{12}$ and $[Rh(CO)_2Cl]_2$ were prepared as previously described [14,15]. The starting vinyl ethers were either commercially available or were made by Reppe's procedure [16] and purified by distillation from Na.

GLC analyses were performed on a Dani 6800 chromatograph equipped with 2 m × 0.4 cm columns of 10% SE30 on 60/80 mesh Chromosorb WAW DCMS or 5% UCON LB 550X on 60/80 mesh Chromosorb WAW DCMS, and a flame-ionization detector, nitrogen was used as carrier gas. Preparative GLC was carried out on a Perkin–Elmer F21 instrument equipped with 3 or 5 m × 0.95 cm columns of 5% SE30 on 60/80 mesh Chromosorb A-NAW or 5% UCON LB 550X on 60/80 mesh Chromosorb A-NAW. ^1H NMR spectra were recorded with $CDCl_3$ or CCl_4 solutions on a Varian T60 or Varian Model XL-100 spectrometer; chemical shifts are reported as δ (ppm) values relative to Me_4Si as internal reference.

Hydroformylation reaction (General procedure)

A solution of vinyl ether (35 mmol) in benzene (10 ml) was introduced by suction into an evacuated 50 ml stainless steel autoclave containing $Rh_4(CO)_{12}$ (0.020 g) or $[Rh(CO)_2Cl]_2$ (0.050 g) and PPh_3 (0.200 g). Carbon monoxide was introduced up to the desired pressure, and the autoclave was locked and heated to the chosen temperature and hydrogen was rapidly introduced to give the appropriate gas composition. When gas adsorption ceased the autoclave was rapidly cooled and the gases were discharged, and the isomeric composition of the aldehydes was determined by GLC on the crude mixture. The mixture was distilled and pure samples of the various aldehydes were obtained either by fractional distillation with a spinning column or by preparative GLC. The structure of the products were established by ^1H NMR spectroscopy and by their physical constants (Table 1).

Hydroformylation of methyl vinyl ether. Hydroformylation of this ether gave 2-methoxypropionaldehyde and 3-methoxypropionaldehyde. The α-isomer was isolated as a pure sample by distillation: ^1H NMR (60 MHz, $CDCl_3$) δ 9.56 (d, 1H), 3.70 (dq, 1H), 1.23 (d, 3H), 3.43 (s, 3H); pure β-isomer was obtained by preparative GLC (SE30 5 m, 75°C): ^1H NMR (60 MHz, CCl_4) δ 9.67 (t, 1H), 2.60 (dt, 2H), 3.67 (t, 2H), 3.30 (s, 3H).

Hydroformylation of ethyl vinyl ether. The reaction gave a mixture of 2-ethoxypropionaldehyde and 3-ethoxypropionaldehyde; preparative GLC (UCON LB 550X, 3 m, 70°C) gave pure samples of the two products; 2-ethoxypropionaldehyde: ^1H NMR (60 MHz, CCl_4) δ 9.50 (d, 1H), 3.60 (dq, 1H), 1.18 (d, 3H), 3.53 (q, 2H), 1.20 (t, 3H); 3-ethoxypropionaldehyde: ^1H NMR (60 MHz, $CDCl_3$) δ 9.66 (t, 1H), 2.53 (dt, 2H), 3.70 (t, 2H), 3.46 (q, 2H), 1.13 (t, 3H).

Hydroformylation of isopropyl vinyl ether. The same experimental conditions were used. Preparative GLC (3 m UCON LB 550X 70°C) gave 2-isopropyloxypropionaldehyde: ^1H NMR (60 MHz, $CDCl_3$) δ 9.63 (d, 1H), 4.03–3.47 (m, 2H), 1.30 (d, 3H), 1.16 (d, 6H) and 3-isopropyloxypropionaldehyde: ^1H NMR (100 MHz, $CDCl_3$) δ 9.70 (t, 1H), 2.58 (dt, 2H), 3.73 (t, 2H), 3.90–3.30 (m, 1H), 1.16 (d, 6H).

Hydroformylation of n-butyl vinyl ether. The pure aldehydes were isolated by preparative GLC (3 m UCON LB 550X, 100°C) and they were identified as 2-n-butoxypropionaldehyde: ^1H NMR (60 MHz, $CDCl_3$) δ 9.63 (d, 1H), 3.70 (dq, 1H), 1.30 (d, 3H), 3.50 (t, 2H), 1.83–1.33 (m, 4H), 0.97 (t, 3H) and 3-n-butoxypropionaldehyde: ^1H NMR (60 MHz, $CDCl_3$) δ 9.73 (t, 1H), 2.63 (dt, 2H), 3.80 (t, 2H), 3.47 (t, 2H), 1.83–1.33 (m, 4H), 0.93 (t, 3H).

Hydroformylation of t-butyl vinyl ether. The hydroformylation products, were isolated as pure compounds by preparative GLC (3 m UCON LB 550X, 80°C): 2-t-butoxypropionaldehyde: ^1H NMR (100 MHz, CCl_4) δ 9.60 (d, 1H), 3.90 (dq, 1H), 1.18 (d, 3H), 1.20 (s, 1H); 3-t-butoxypropionaldehyde: ^1H NMR (100 MHz, CCl_4) δ 9.73 (t, 1H), 2.56 (dt, 2H), 3.70 (t, 3H), 1.18 (s, 9H).

Hydroformylation of benzyl vinyl ether. The aldehydes were isolated pure by fractional distillation: 3-benzyloxypropionaldehyde: ^1H NMR (60 MHz, CCl_4) δ 9.70 (t, 1H), 2.70 (dt, 2H), 3.90 (t, 2H), 4.80 (s, 2H), 7.42 (s, 5H); 2-benzyloxypropionaldehyde: ^1H NMR (60 MHz, CCl_4) δ 9.63 (d, 1H), 3.92 (dq, 1H), 1.39 (d, 3H), 4.70 (s, 2H), 7.42 (s, 5H).

Hydroformylation of phenyl vinyl ether. Pure 2-phenoxypropionaldehyde was isolated by distillation of the crude product mixture: ^1H NMR (60 MHz, $CDCl_3$) δ 9.55 (d, 1H), 4.55 (dq, 1H), 1.41 (d, 3H), 6.6–7.4 (m, 5H).

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