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The use of ^{2}H NMR in the elucidation of the catalytic pathway of the hydroformylation reaction *

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Abstract

Differences in the behaviour of the metal-alkyl intermediates involved in the deuterioformylation of styrene in the presence of $Co_2(CO)_8$ or $Rh_4(CO)_{12}$ as catalytic precursors, have been readily revealed by ^{2}H NMR analysis of the crude mixtures present after partial conversion. The results clearly demonstrate the value of this simple method for mechanistic studies of catalytic reactions.

Introduction

New tools for investigation of the mechanistic aspects of catalytic processes [1] under actual catalytic conditions are of great interest for researchers working on important reactions, such as hydroformylation, hydrogenation, and polymerization [2–5]. In all the cases, the formation of metal-alkyl intermediates is regarded as an important step of the reaction [6–9]. Information about the behaviour of the metal alkyl intermediates involved in hydroformylation has been obtained by examining hydroformylation of labelled substrates [9,10,13] or deuterioformylation of unlabelled ones [11,12,14,15]. The deuterium distribution has been determined by ^{1}H NMR analysis of carefully purified reaction products (or derivatives), requiring synthesis of labelled compounds and tedious time consuming purification procedures.

In a recent paper [16] concerning the rhodium catalysed deuterioformylation of 1-hexene we reported the first use of ^{2}H NMR spectroscopy to determine the position of deuterium in the recovered substrate. The inherent simplicity of the ^{2}H NMR spectra suggested to us the possibility of using them to examine complex reaction mixtures, so avoiding the need for work-up of the mixtures.

We present below an account of the catalytic pathways in the cobalt and rhodium catalysed deuterioformylation of styrene (Scheme 1) deduced from ^{2}H

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* Dedicated to the memory of Professor Piero Pino.

NMR analysis of the crude reaction mixtures after partial substrate conversion (30%).

Results

The mixtures analysed by ^2H NMR spectroscopy were obtained by deuterioformylation of styrene, in benzene (at 20 and 110 °C with $Rh_4(CO)_{12}$ as catalyst and at 80 and 110 °C with $Co_2(CO)_8$) under 180 atm of CO and D_2 ($CO/D_2 = 1/1$), with $Rh_4(CO)_{12}$ as catalyst. The reactions were stopped when the drop of pressure corresponded to 30% conversion into aldehydes. Samples of the reaction mixtures, containing unconverted styrene and products, were directly analysed without any handling or treatment.

Inspection of the ^2H NMR spectra allowed rapid and complete identification of all the deuterated species present in solution. The deuterium content in each position of the different species was evaluated by integration of the respective signals, using the resonance of CDO as an internal reference [17*] (Table 1). In Table 2 the ^2H NMR chemical shifts for all deuterated species obtained in the deuterioformylation of styrene, with $Co_2(CO)_8$ as catalyst, are reported. Figure 1 shows the ^2H NMR spectrum of the crude mixture in benzene formed in the reaction at 110 °C. Three main groups of signals were distinguished (Table 2, Fig. 1): those arising from monodeuterio-styrenes (d_1-S), dideuterio-3-phenylpropanal (d_2-3PP) and dideuterio-2-phenylpropanal (d_2-2PP).

The three resonances at 6.47, 5.49 and 4.96 ppm are due to deuterium nuclei on the vinyl moiety of styrene. The signal at 6.47 ppm comes from the isotopic species $Ph-CD=CH_2$ having the deuterium in position 2 (2-d_1-S), and the two absorptions at 5.49 and 4.96 ppm from the two geometrical isomers (*E*)-1-deuterio-vinylbenzene (*E*-1-d_1-S) and (*Z*)-1-deuterio-vinylbenzene (*Z*-1-d_1-S) arising from the presence of deuterium in the position 1 ($Ph-CH=CHD$ species).

In the case of the branched aldehyde, three signals were easily recognized: that at 9.24 ppm from the CDO group, that at 1.02 ppm from the CH_2C group, and that at 2.87 ppm from a methine CD group (Fig. 2). Analogously, for the linear aldehyde (d_2-3PP), in addition to the CDO resonance at 9.13 ppm, other two absorptions were found, at 2.42 and 1.92 ppm; the first was due to a CHD group β to the carbonyl and the latter to a CHD α to it.

Two minor signals at 0.96 ppm and 2.29 ppm were present, due to the CH_2D and CHD groups of deuterated ethylbenzene arising from deuterium addition to the styrene.

Other features revealed by the spectrum were (Table 1): (i) the alkyl carbon atoms contained less deuterium than the CDO groups; (ii) in the branched aldehyde the deuterium was predominantly incorporated in the CH_2D group and, to a minor extent, in the CD group; (iii) in the linear aldehyde there is an almost equal distribution of deuterium between the two CHD groups. A similar feature was observed in the run at 110 °C.

The unconverted styrene had incorporated deuterium at both 80 and 110 ° C, the amount of deuterium being greater at the 1- than at the 2-vinyl carbon: the total deuterium incorporation increased with increasing temperature (Table 1).

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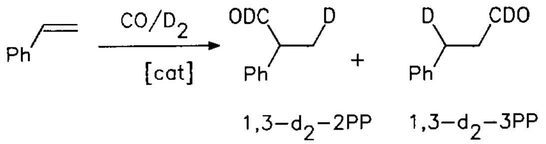
* Reference number with an asterisk indicates a note in the list of references.



Scheme 1

The deuterium distribution and content were both substantially different in the mixtures obtained by deuterioformylation of the olefin with $Rh_4(CO)_{12}$ as catalyst (Table 1). As shown in Fig. 2, at 20 °C the branched aldehyde contained equal amounts of deuterium on the CDO and CH_2D groups and no deuterium is present on the carbon atom adjacent to the carbonyl function. The linear aldehyde was formed in a very small amount (2%) and only CDO and CHD β to CDO were detected, and were present in equal amounts. Interestingly, there was no signal in the olefin region, indicating that no deuterated unconverted styrene was present in the mixture. The spectrum from the reaction at 110 °C (Fig. 3) contained only the expected CDO and CH_2D absorptions for the branched aldehyde, whereas for the linear isomer the CHD resonance α to the CDO group was also observed, in addition to the resonances due to the CDO and CHD β to CDO. In the case of the styrene, deuterium was detected on the vinyl region, but only on the terminal

Table 1

Deuterium content and distribution in the reaction products of the cobalt- and rhodium-catalyzed deuterioformylation of styrene after partial conversion (30%), determined by ^2H NMR analysis of the crude reaction mixtures

Component	Catalyst	Reaction temperature (°C)	Deuterium content [a]	Deuterium distribution		
				CDO	Ph-C(D)-C	Ph-C-C(D)
2-Phenyl-propanal	$Co_2(CO)_8$	80	1.83 [b]	1.00	0.13	0.70
		110	1.73 [b]	1.00	0.09	0.64
	$Rh_4(CO)_{12}$	20	2.00 [b]	1.00	–	1.00
		110	1.94 [b]	1.00	< 0.01	0.94
3-Phenyl-propanal	$Co_2(CO)_8$	80	1.74 [b]	1.00	0.36	0.38
		110	1.81 [b]	1.00	0.45	0.36
	$Rh_4(CO)_{12}$	20 [c]				
		110	1.68 [b]	1.00	0.45	0.23
Styrene	$Co_2(CO)_8$	80	0.21 [d]		0.03	0.18
		110	0.51 [d]		0.05	0.46
	$Rh_4(CO)_{12}$	20	< 0.01 [d]		–	–
		110	0.50 [d]		< 0.01	0.49
Ethylbenzene [e]	$Co_2(CO)_8$	80	< 0.05 [d]		–	–
		110	0.15 [d]		0.05	0.10

[a] Estimated accuracy ±2%. [b] Deuterium atoms per mole of α or β aldehyde evaluated by using the CDO resonance of α or β aldehyde as an internal reference. [c] Because at 20 °C the linear aldehyde (β) is formed in a very little amount (< 2%), the deuterium content of the β isomer cannot be determined in the presence of the α one. [d] Deuterium atoms incorporated in the styrene or ethylbenzene per mole of aldehydes formed, evaluated by using the CDO resonances of the aldehydes ($\alpha + \beta$) as an internal reference. [e] No deuterated ethylbenzene has been observed in the reaction mixtures obtained with $Rh_4(CO)_{12}$ as catalytic precursor.

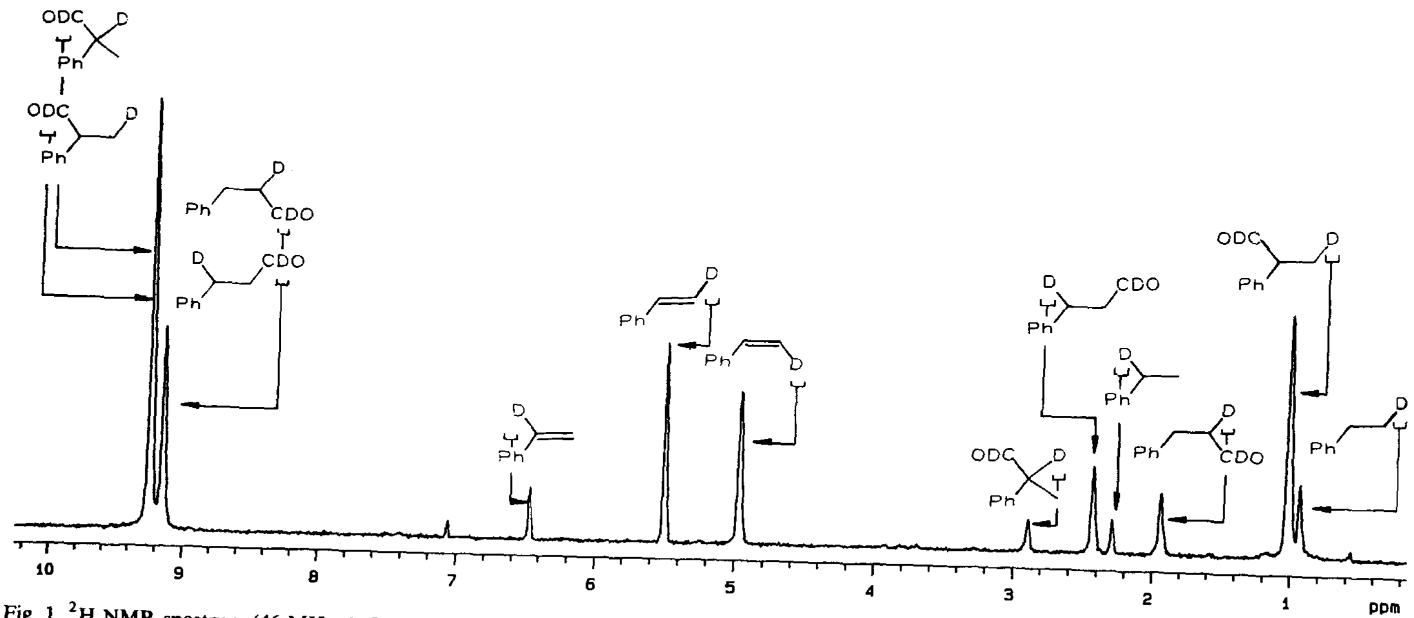


Fig. 1. ^{2}H NMR *spectrum (46 MHz, 25 °C) of the crude reaction mixture in benzene obtained by deuterioformylation of styrene at 110 °C and 30% conversion with* $Co_2(CO)_8$ as catalyst.

carbon atom. These results confirm those obtained in our previous investigations involving a different procedure [14].

Discussion

The analysis of the ^2H NMR data led to important mechanistic conclusions, which can be summarized as follows.

In the absence of isomerization processes during the deuterioformylation of styrene, the formation of the two metal-alkyl intermediates, normal (n) and branched (b), would lead to the two dideuterated isomeric aldehydes, 1,3-d_2-2PP and 1,3-d_2-3PP, as indicated in Scheme 2.

In the case of the cobalt catalysed reaction, the analysis of the deuterium resonances clearly indicates the formation of the two expected isomers. However, the detection of deuterium on the carbon atoms adjacent to the carbonyl functions clearly demonstrates that, in addition to the two expected 1,3-isomers, 1,2-dideuterated branched and linear aldehydes (1,2-d_2-2PP and 1,2-d_2-3PP) are also present. Their formation can be easily accommodated in terms of the reaction pathways described in Scheme 2: the formation of the two cobalt-alkyl intermediates is reversible both at 80 and 110 °C; they undergo β-hydride elimination to give the two cobalt-hydride π-complexes **1** and **2**, in which 1- or 2-deuterostyrene are respectively coordinated. In the complex **1**, the insertion of the olefin into the Co–H bond could regenerate the starting branched cobalt-alkyl b or produce the isomeric linear cobalt-alkyl intermediate n′, from which the 1,2-dideuterated linear aldehyde can be formed. By the same process, complex **2** gives rise to the branched cobalt-alkyl intermediate b′, from which the isomeric 1,2-dideuterated branched aldehyde is formed. The overall process is the isomerization of the starting branched metal-alkyl intermediate b to the linear isomeric intermediate n′ and, conversely, the isomerization of n to b′.

However, deuterated styrenes were also found in the unconverted substrate. They can be formed by the same π-complexes **1** and **2**, undergoing an intermolecular exchange with unlabelled styrene (Scheme 2), this process competing with the alkyl formation. In this way, E-1-d_1-S, Z-1-d_1-S and 2-d_1-S are formed.

Table 2

^2H NMR chemical shifts (δ, ppm) [a] (46 MHz, C_6H_6, 25 °C) of monodeuterated and dideuterated substrates [b] originating from the cobalt catalyzed deuterioformylation of styrene

2-d_1-S	Ph-CD=CH_2	6.47
(E)-1-d_1-S	(E)Ph-CH=CHD	5.49
(Z)-1-d_1-S	(Z)-Ph-CH=CHD	4.96
1,3-d_2-2PP or 1,2-d_2-2PP	Ph-CH(CH_2D)-CDO or Ph-CD(CH_3)-CDO	9.24
1,3-d_2-2PP	Ph-CH(CH_2D)-CDO	1.02
1,2-d_2-2PP	Ph-CD(CH_3)-CDO	2.87
1,3-d_2-3PP or 1,2-d_2-3PP	Ph-CHD-CH_2-CDO or Ph-CH_2-CHD-CDO	9.13
1,3-d_2-3PP	Ph-CHD-CH_2-CDO	2.42
1,2-d_2-3PP	Ph-CH_2-CHD-CDO	1.92
	Ph-CH_2-CH_2D	0.96
	Ph-CHD-CH_3	2.29

[a] Referred to C_6D_6 as external standard. [b] S = Styrene, 2PP = 2-phenylpropanal, 3PP = 3-phenylpropanal, d_1 = monodeuterated species, d_2 = dideuterated species.

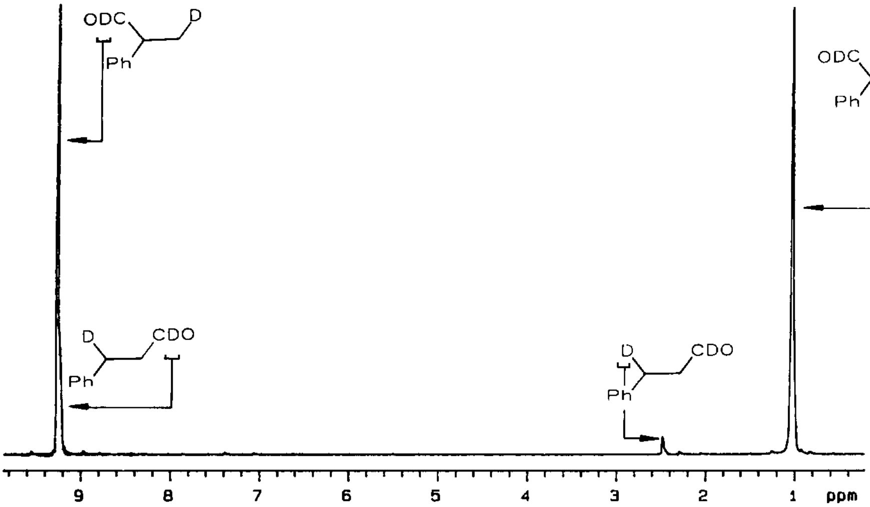


Fig. 2. ^2H NMR spectrum (46 MHz, 25 °C) of the crude reaction mixture in benzene obtained by deuterioformylation of styrene at 20 °C and 30% conversion with $Rh_4(CO)_{12}$ as catalyst.

The following important facts showed the differences between the behaviour of the linear and branched cobalt-alkyl intermediates:

(a) The branched aldehyde is predominantly labelled at 1 and 3 positions, while the linear aldehyde is labelled equally at the 1,3 and 1,2 positions.

(b) In the unconverted styrene the deuterium is incorporated mainly at the terminal carbon atom.

Thus the linear alkyl intermediate n mainly gives rise to the expected linear aldehyde and to a minor extent undergoes isomerization to the branched intermediate b′, producing the 1,2-dideuterated branched aldehyde. A small amount of

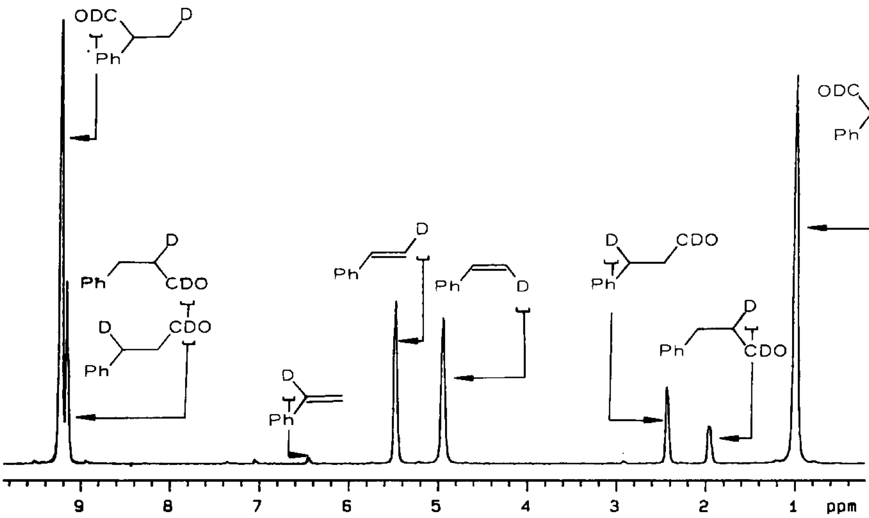
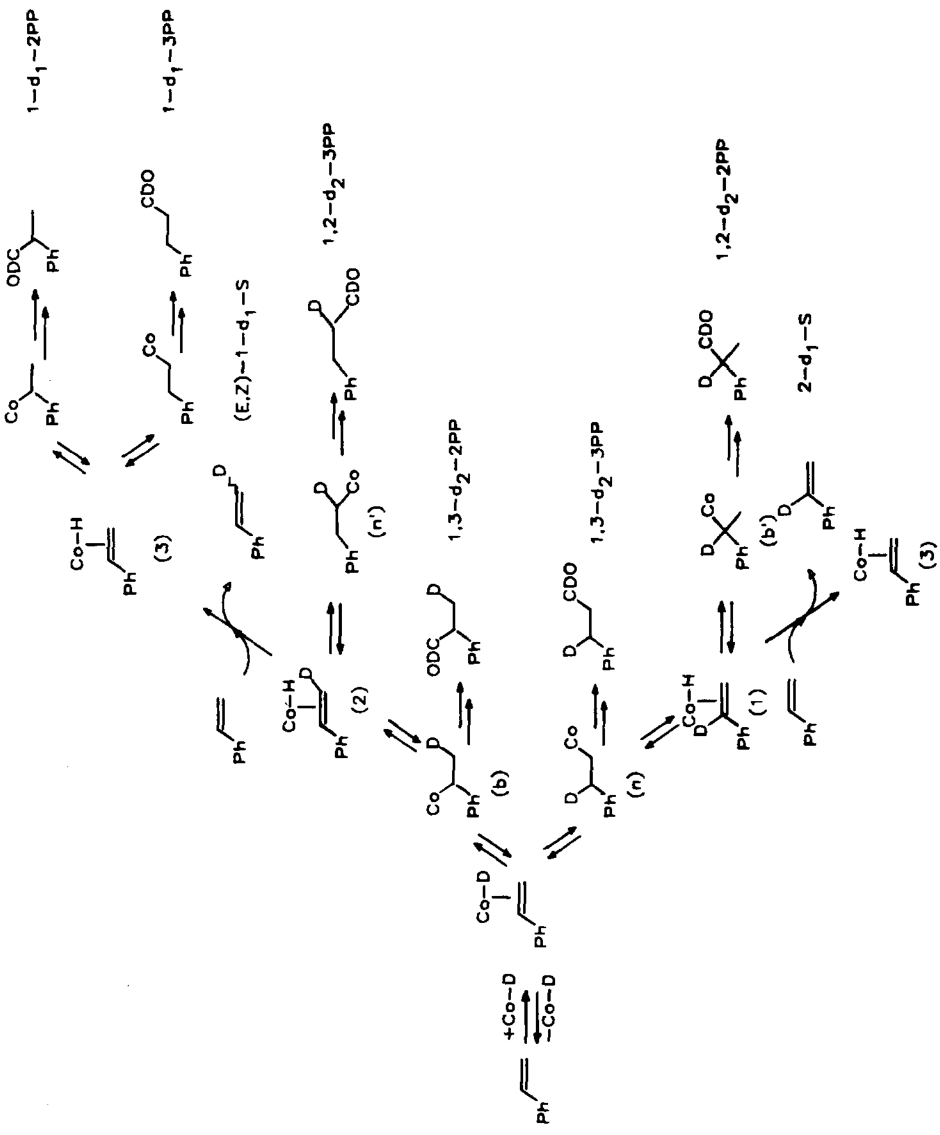


Fig. 3. ^2H NMR spectrum (46 MHz, 25 °C) of the crude reaction mixture in benzene obtained by deuterioformylation of styrene at 110 °C and 30% conversion with $Rh_4(CO)_{12}$ as catalyst.


+Co–D
−Co–D
Co–D
Co–H
(1)
(2)
(3)
(b)
(n)
(b')
(n')
1-d1-2PP
1-d1-3PP
1,2-d2-3PP
1,2-d2-2PP
(E,Z)-1-d1-S
1,3-d2-2PP
1,3-d2-3PP
2-d1-S

Scheme 2

exchange product is formed. By contrast, under the same conditions, the branched alkyl b mainly follows the isomerization process, leading to the linear 1,2-dideuterated aldehyde, and undergoes exchange or isomerization.

When the rhodium catalyst is used the fate of the metal-alkyl intermediates is very different. At low temperature only the expected 1,3-dideuterated species are found: the formation of the two rhodium alkyl intermediates is irreversible and no isomerization or exchange occurs. At high temperature, only the linear aldehyde is partially 1,2-dideuterated, showing that only the formation of the branched alkyl is reversible. In keeping with this the unconverted styrene contains deuterium only in the terminal vinyl carbon atom.

Conclusions

The account above reveals several advantages of the use of ^{2}H NMR spectroscopy in the analysis of the deuterioformylation products. First the identification of the deuterated species is easy, thanks to the similarity of the chemical shift ranges of ^{1}H and ^{2}H nuclei. The crude products can be directly identified, and so a separation procedure is avoided. Not only can the deuterium distribution in each species be evaluated, but furthermore the relative amounts of deuterium incorporation into the various species can be determined. Thus information on the behaviour of organometallic intermediates under catalytic conditions can be easily obtained. It is also noteworthy that such deuterioformylation studies do not require starting labelled materials.

Our approach has revealed some significant new features of hydroformylation involving cobalt and rhodium catalytic systems. For the cobalt-catalysed process, the reversibility of the formation of the branched alkyl intermediate, already indicated by stoichiometric [8] and catalytic [11,18] reactions, has been confirmed and, for the first time evidence has been obtained about the reversibility of the formation of the linear intermediate under hydroformylation conditions. It is noteworthy that this last possibility has not previously been taken into account in several mechanistic studies [8a,11,18]. By contrast, in the rhodium-catalysed deuterioformylation, the formation of the metal alkyl intermediates is not reversible at low temperature: under these conditions the regioselectivity of the reaction reflects the ratio between the two isomeric alkyl intermediates. Only at high temperatures does the formation of the isomeric rhodium-alkyl intermediates become reversible, mainly for the branched isomer.

The ready accessibility and precision of the results showed the great value of this extremely simple procedure for mechanistic studies of hydroformylation and, indeed, for catalytic reactions in general.

Experimental

Deuterioformylation of styrene

Deuterioformylation of styrene was performed by the general procedure previously described [10,12]. A solution of $Rh_4(CO)_{12}$ or $Co_2(CO)_8$ (6.7×10^{-4} mmol) and styrene (23.8 mmol) in benzene (10.0 g) was introduced by suction into a 50-mL evacuated stainless-steel autoclave. Carbon monoxide was introduced up to the desired pressure; the autoclave was then rocked and heated to the reaction temperature and deuterium was introduced up to the desired total pressure. When the reaction started the drop in pressure was compensated by injection of a carbon monoxide–deuterium mixture (1 : 1) from a high pressure container. The progress of the reaction was monitored by the pressure drop in the high-pressure gas reservoir. When the gas absorption had reached the value corresponding to desired conversion to aldehydes, the autoclave was rapidly cooled and the reaction mixture siphoned out. The composition of the reaction mixture was determined by GC analysis. In the rhodium-catalysed deuterioformylation the ratio between the isomeric branched and linear aldehydes was 98/2 at 20 ° C and 76/24 at 110 ° C. In the cobalt-catalysed reaction the ratio was 80/20 at 80 ° C and 65/35 at 110 ° C.

NMR measurements

^{2}H NMR spectra of the crude products in benzene were recorded on a Varian VXR 300 spectrometer, operating at 46 MHz for ^{2}H. Chemical shifts were determined by reference to C_6D_6 as external standard.

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