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Rhodium catalyzed deuteroformylation of styrene: (*E*)- and (*Z*)-β-deuterostyrene and β,β-dideuterostyrene formation via selective β-hydride elimination from the branched alkylrhodium intermediate

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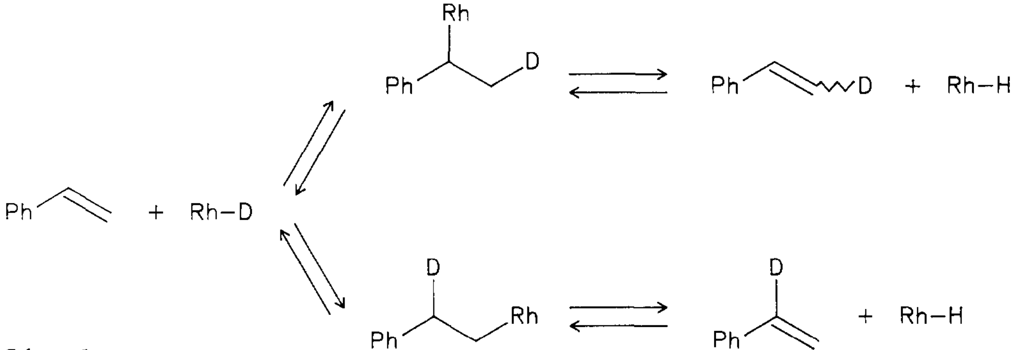
Abstract

Deuteroformylation of styrene in the presence of $Rh_4(CO)_{12}$ as a catalytic precursor was carried out at 160 atm of CO and D_2 1/1 at two temperatures (20 and 90 °C) and for times yielding partial or complete conversion. Compounds recovered from the mixture produced by reaction and partial conversion at 90 °C include unlabeled styrene, (*E*)- and (*Z*)-β-deuterostyrene, $C_6H_5CH{=}CHD$, and β,β-dideuterostyrene, $C_6H_5CH{=}CD_2$, whereas at room temperature the styrene does not take up deuterium. These results indicate that under hydroformylation conditions the branched alkylrhodium intermediate, which affords the branched aldehyde, in part dissociates into rhodium hydride and deuterated olefin. By contrast the linear alkyl intermediate does not dissociate under the same conditions, but instead yields almost completely the corresponding aldehyde.

According to the generally accepted mechanism for the rhodium-catalyzed hydroformylation of olefins, metal hydride addition to the double bond to give isomeric metal alkyl intermediates is a key step [1–3]. The reverse process, i.e. dissociation of alkyl metals via β-hydride elimination [4,5], has been reported to occur in the rhodium-catalyzed hydroformylation of unsaturated substrates having hydrogen atoms α to the double bond [6]. It accounts for the isomerization of substrate and hydrogen–deuterium exchange observed with deuterated alkyl olefins [7]. It is not clear from the literature [2,8] if dissociation of alkyl metals into Rh–H and olefin under catalytic hydroformylation conditions also occurs with substrates, such as styrene, vinyl ethers, and vinyl esters, which do not undergo isomerization.

To obtain more information, throwing light on the regioselectivity of the reaction, deuteroformylation of styrene at 20 and 90 °C at various degrees of substrate



Scheme 1

conversion has been investigated. If dissociation of the alkylrhodium intermediate takes place, deuterated styrene should be present in the unconverted substrate (Scheme 1). We found however that styrene incorporated deuterium only on the carbon atom β to the phenyl group, indicating that under rhodium-catalyzed hydroformylation conditions there is selective β-hydride elimination from the branched alkyl metal intermediate.

Results and discussion

Deuteroformylation of styrene

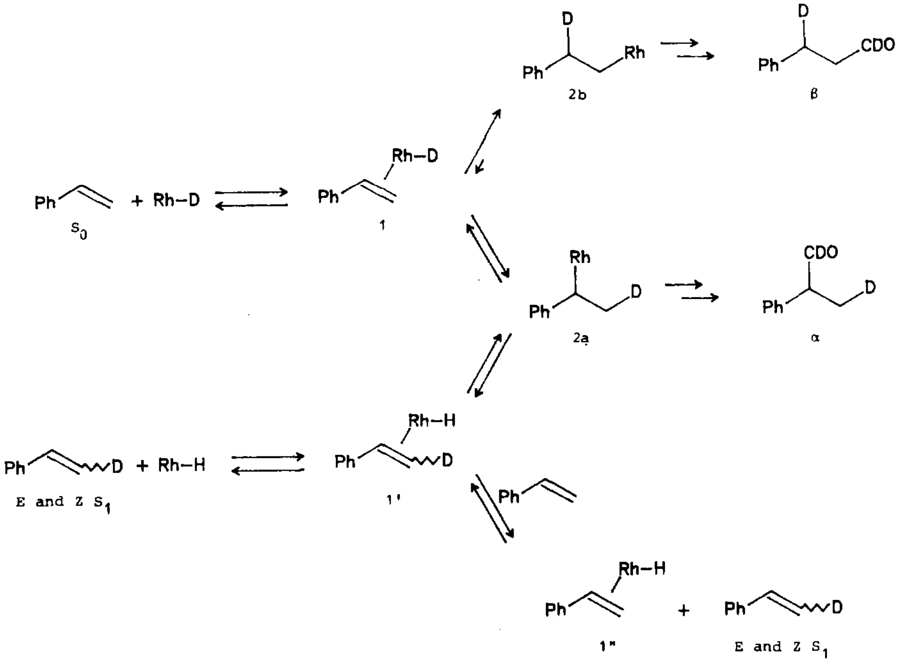
Deuteroformylation of styrene has been carried out at 20 and 90 °C under 160 atm of CO and H_2 (1/1) at constant pressure (± 2 atm) and for various degrees of substrate conversion with $Rh_4(CO)_{12}$ as catalytic precursor (Table 1). Less than 5% of polymerization of styrene occurs when the reaction is carried out at 20 °C but no high boiling point compounds are formed in reactions at 90 °C. The ratio between 2-phenylpropanal (α isomer) and 3-phenylpropanal (β isomer) (Scheme 2) obtained in each experiment was determined by GLC analysis. At 20 °C the α isomer strongly predominates over the β one (α/β 98/2); at 90 °C the ratio is somewhat

Table 1

Degree of regioselectivity in the rhodium-catalyzed deuteroformylation of styrene at various reaction temperatures and degrees of substrate conversion [a]

Reaction Temper. (°C)	$\frac{[\text{Subs.}]}{[\text{Rh}]}$ ratio	Reaction Time (min)	Convers to ald. [b] (%)	α% [c]	RE [d]
25	370	660	25	98	96
25	370	2500	85	98	96
90	37000	18	25	83	76
90	37000	30	42	83	76
90	37000	85	90	83	76
90	37000	120	100	83	76

[a] 5 ml benzene solution containing 0.02 mol of substrate and 0.1 mg of $Rh_4(CO)_{12}$; CO/D_2 (1/1), 160 atm (± 2 atm); volume of reaction vessel 60 ml. [b] Refers to styrene; determined by GLC with toluene as internal standard. [c] $\alpha\% = [\alpha/(\alpha+\beta)] \times 100$; estimated accuracy $\pm 1\%$. [d] $RE = [(\alpha-\beta)/(\alpha+\beta)] \times 100$.



Scheme 2

smaller (α/β 83/17) (Table 1). The isomer ratio does not depend to any appreciable extent on the degree of conversion either at 20 and 90 °C. Chemically pure samples of unconverted styrene and α and β isomeric aldehydes were obtained by fractional distillation at reduced pressure followed by preparative GLC.

Styrene recovered from the reaction mixture in the experiments at partial conversion was analysed by MS and ^{1}H NMR in order to determine the extent of incorporation of deuterium atoms in the vinyl group. The presence of deuterium in the isomeric aldehydes was shown by ^{1}H NMR spectroscopy.

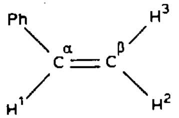
Deuterium content of unconverted styrene

MS analysis. It is known that the mass spectrum of styrene at 70 eV shows the molecular ion peak ($M^{+\cdot}$ 104) and a peak at m/z 103 ($M-1$), and this complicates the analysis of deuterated styrene [9]. We found that the latter peak is completely absent if the spectrum is obtained at lower energy ($\sim$ 10 eV). Thus the distribution of deuterated species in the unconverted styrene was very easily determined from the mass spectra at low energy either by direct introduction of pure samples into the source or by GLC-MS analysis of the reaction mixture. The results obtained are shown in Table 2.

When the reaction is carried out at 20 °C, less than 1% of mono-deuterated species is formed even at high substrate conversion. At 90 °C mono- and di-deuterated species are both present in the reaction mixture at partial conversion of the substrate; the tri-deuterated species is present only in a small amount (less than 1%). Mono-deuterated styrene predominates over the di-deuterated one in all experiments, with the predominance more marked at lower conversions. The amount of

Table 2

Deuterium content of the unconverted styrene determined by MS and ^{1}H NMR analyses in the rhodium-catalyzed deuteroformylation of styrene.



Temperature (°C)	Conversion (%)	Isotopic species distribution (%) [a]				Hydrogen content at each vinyl carbon [b]			NDM [c]	
		d_0	d_1	d_2	d_3	H(1)	H(2)	H(3)	via MS	via ^{1}H NMR
25	20	99.6	0.4	–	–	1.00	1.00	1.00	< 0.01	< 0.01
25	85	99.0	1.0	–	–	1.00	0.996	0.995	0.01	0.01
90	24	77.7	20.2	2.0	–	0.998	0.883	0.870	0.24	0.25
90	42	66.0	29.1	4.9	–	0.999	0.821	0.820	0.37	0.35
90	90	29.0	43.5	27.5	–	1.0	0.530	0.521	0.96	0.95

[a] Via MS analysis: estimated accuracy ±1%. [b] Via ^{1}H NMR: estimated accuracy: ±3%. [c] Average number of deuterium atoms per molecule.

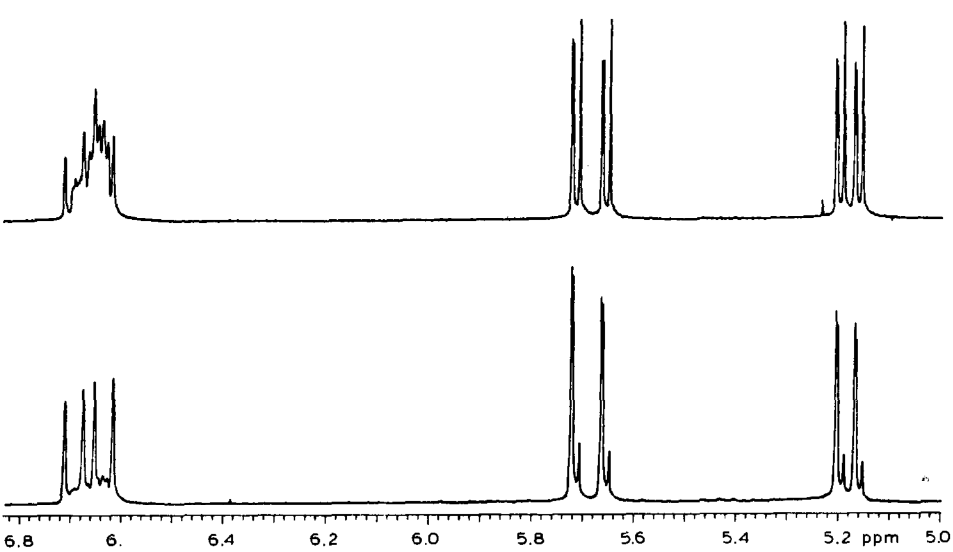


Fig. 1. The ^{1}H NMR spectrum in the vinyl protons region of the styrene recovered from deuteroformylation experiments at 90 ° C after 24% (lower spectrum) and 90% (upper spectrum) conversion.

deuterated species increases at higher conversions: the average numbers of deuterium atoms per molecule, NDM, are 0.24 and 0.96 at 24% and 90% conversion, respectively.

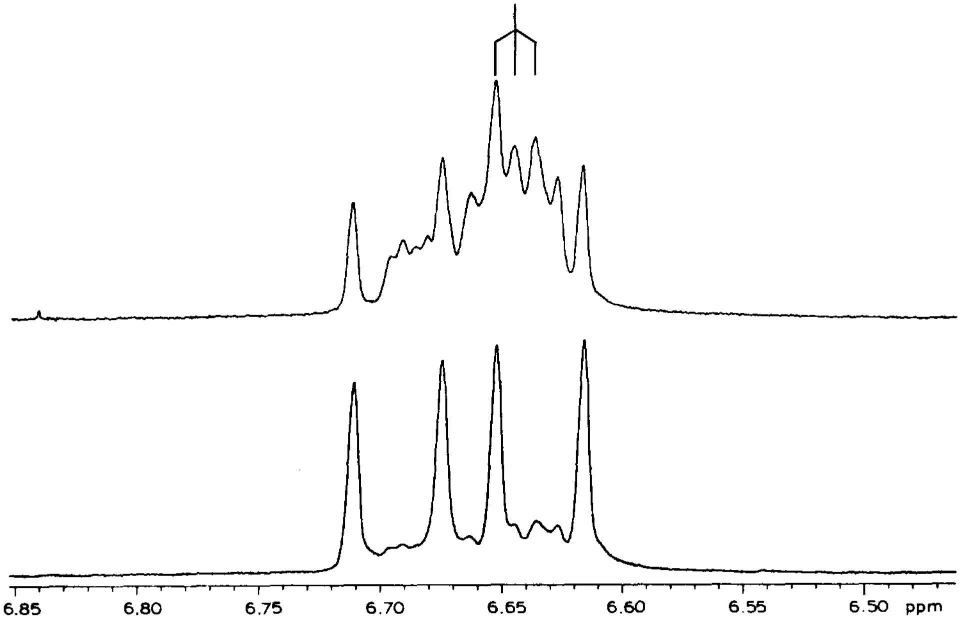
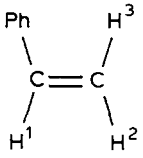


Fig. 2. The ^{1}H NMR signal from the α proton of the vinyl group of the styrene recovered from deuteroformylation experiments at 90 ° C after 24% (lower spectrum) and 90% (upper spectrum) conversion.

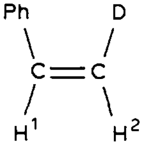
^1H NMR analysis. ^{1}H NMR analysis of chemically pure samples of unconverted styrene was carried out in CCl_4 at 300 MHz. Replacement of the protium atoms of the phenyl ring by deuterium atoms does not occur to any significant extent, as shown by the mass spectra of benzoic acid produced by permanganate oxidation of the recovered styrene as well as by ^{1}H NMR analysis of the corresponding methyl benzoate. Thus the five protons of the phenyl ring were used as the internal standard for determination of the number of protons at each position of the vinyl group. The results obtained at various degrees of conversion at 20 and 90 °C are shown in Table 2.

When the reaction was carried out at 20 °C the recovered substrate contained no deuterium within the experimental error. At 90 °C deuterium atoms to some extent replaced hydrogen atoms bound to the β carbon atom of the vinyl group, the amount of deuterium incorporation increasing with the conversion. In contrast no deuterium atoms are present on the α carbon of styrene, the number of protons in this position being 1 ± 0.02 H in all experiments (Table 2).

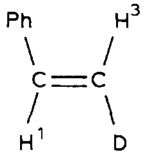
^{1}H NMR spectra of the substrate recovered at 90 °C, at 25% and 90% conversion in the vinyl proton region (Fig. 1 and 2) clearly indicate that four isotopic species are present in the unconverted substrate, namely (*E*)-β-deuterostyrene ((***E***)-$\mathbf{S_1}$), (*Z*)-β-deuterostyrene ((***Z***)-$\mathbf{S_1}$), β,β-dideuterostyrene ($\mathbf{S_2}$), and non deuterated styrene ($\mathbf{S_0}$).



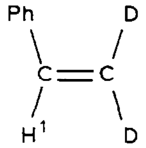
(S_0)



((Z)-S_1)



((E)-S_1)

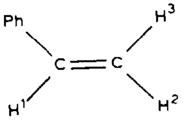


(S_2)

Monodeuterated species, (***E***)-$\mathbf{S_1}$ and (***Z***)-$\mathbf{S_1}$, are identified by the resonances of the H(3) proton (5.677 ppm) and the H(2) proton (5.163) ppm, respectively, which are shifted upfield with respect to the resonances of the undeuterated species $\mathbf{S_0}$ (Table 3). The H(1) proton give complicated sets of signals between 6.60 and 6.72 ppm (Fig. 2); double resonance experiments, however, allow the assignment of a

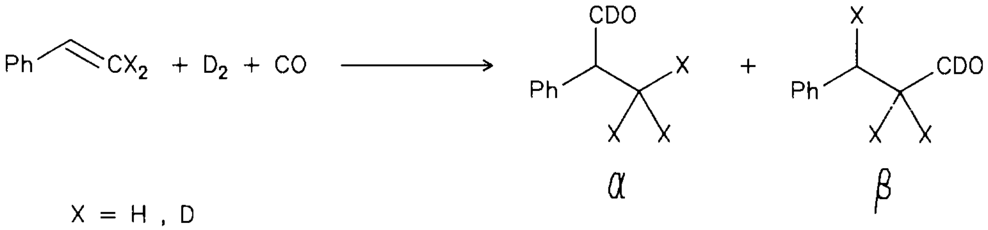
Table 3

Vinyl proton chemical shifts [a] of isotopic styrenes



Compound	Chemical shift (ppm)		
	H(1)	H(2)	H(3)
$\mathbf{S_0}$	6.663	5.180	5.695
(***E***)-$\mathbf{S_1}$	6.660	–	5.677
(***Z***)-$\mathbf{S_1}$	6.653	5.163	–
$\mathbf{S_2}$	6.645	–	–

[a] In ppm from internal TMS; $CDCl_3$ as solvent.



Scheme 3

triplet centered at 6.645 ppm to the H(1) proton of the dideuterated species S_2 (*trans*-^3J(H–D) 2.7 Hz; *cis*-^3J(H–D) 1.6 Hz), in accordance with literature data for the single isotopic species S_2 [10]. Comparison of the ^{1}H NMR spectra at various degrees of conversion shows that at high conversions the extent of deuteration increases. It is also noteworthy that the NDM values determined by MS and ^{1}H NMR analyses are in a very good agreement (Table 2).

^{1}H NMR analysis of chemically pure samples of aldehydes arising from the deuteroformylation was also carried out. At 20 ° C, in agreement with the stoichiometry of the reaction, only the di-deuterated species is formed for α and β isomers (Scheme 2).

At 90 ° C several species with different deuterium content are obtained for both α and β aldehydes because of the presence of mono- and di-deuterostyrene in the substrate in addition to the non deuterated species (Scheme 3). NMR data show that, in agreement with the result for the unreacted substrate, no deuterium atoms are present on the carbon atom bound to the phenyl ring in the α isomer. In addition, the formyl group is fully deuterated in both the α and β isomers (protium content less than 1%) [11*].

Concluding remarks

The most significant feature of the rhodium-catalyzed deuteroformylation of styrene is the formation of (*E*)- and (*Z*)-β-deuterostyrene as well as β,β-dideuterostyrene under typical hydroformylation conditions (90 ° C, high pressure of CO and H_2). The presence of deuterium atoms on the β carbon atom of the vinyl group can be rationalized on the basis of the reaction sequence shown in Scheme 2, in keeping with the generally accepted mechanism of the rhodium-catalyzed hydroformylation [1,2,7]. The π-complex **1** formed by coordination of styrene to a rhodium deuteride species gives rise to the isomeric alkylrhodium complexes, **2a** and **2b**. This step is reversible for the branched alkylrhodium intermediate, which yields the π complex **1′**, and then the deuterated substrate S_1 or the original π complex **1**, via Rh–H or Rh–D elimination, respectively. Dissociation of the π complex **1′** or exchange between labeled and unlabeled styrene (Scheme 2) in the π complex **1′** accounts for the presence of (*E*)-S_1 and (*Z*)-S_1 in the reaction mixture. In the presence of a large excess of substrate the last route is more likely. An analogous sequence starting from S_1 and Rh–D accounts for the formation of S_2. It is known that the β-hydride elimination is controlled by a kinetic deuterium isotope effect [4],

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* A reference number marked with an asterisk indicates a note in the list of references.

which means that elimination of Rh–H is faster than that of Rh–D; this effect could account for the observed accumulation of deuterated species in the unconverted substrate (Table 2). The absence in the reaction mixture of α-deuterostyrene, formally arising from the linear alkylrhodium complex **2b** via β-Rh–H elimination, suggests that under hydroformylation conditions the linear alkyl is rapidly transformed into the corresponding acyl complex and hence into the β-aldehyde. Thus formation of the linear alkyl intermediate can be the rate-determining step when the substrate yields the β-aldehyde. In contrast, the branched alkyl is partly transformed into the α-aldehyde and partly regenerates the complex **1** or **1′**, and hence the branched alkylmetal formation cannot be the rate-determining step for the reaction leading to the α-aldehyde, at least at high temperature (90 ° C). Under hydroformylation conditions, the branched alkyl can isomerize to the linear one, whereas there is no isomerization of the linear to the branched alkyl intermediate (Scheme 2).

The different behaviour of the isomeric alkylmetal intermediates towards the β-hydride elimination under rhodium-catalyzed hydroformylation conditions is of much relevance for the regioselectivity of the reaction, accounting for the increased yield of the β isomer at elevated temperature observed previously by several authors [1,12–14] and also found in our experiments. A similar explanation of the influence of the temperature on the regioselectivity was previously proposed for the hydroformylation of styrene using phosphine-modified rhodium catalysts [12], and was recently invoked in the case of cobalt-catalyzed hydroformylation of styrene and ethyl acrylate [15]. However, direct evidence for the isomerization of the branched to the linear alkylmetal intermediate under hydroformylation conditions had not previously been reported.

Experimental

Benzene and styrene were dried over molecular sieves and distilled under nitrogen. $Rh_4(CO)_{12}$ was prepared as previously described [16].

GLC analyses were performed on a Dani 6800 chromatograph fitted with 2 m × 0.4 cm columns of 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 fitted with 3 m × 0.95 cm columns of 5% FFAP on 60/80 mesh Chromosorb A-NAW.

^1H NMR spectra were recorded with $CDCl_3$ or CCl_4 solutions on a Varian VXR-300 spectrometer; chemical shifts are reported as δ (ppm) values relative to Me_4Si as internal reference.

Mass spectra were recorded with a VG 70/70E spectrometer at an electron energy such that the $M-1$ peak was undetectable (around 10 eV); the accelerating voltage was 6 kV and the emission current was 100 μA.

Deuteroformylation of styrene: general procedure

A solution of styrene (2.01 g; 20 mmol) and $Rh_4(CO)_{12}$ (0.1 mg; 5.4×10^{-4} mmol) in benzene (5 ml) was introduced by suction into an evacuated 50 ml stainless steel autoclave. Carbon monoxide was introduced up to 65 atm, the autoclave was heated at 90 ° C (P(CO) 80 atm) and deuterium was rapidly introduced up to 160 atm. When the gas absorption reached the value corresponding to the desired conversion the reaction vessel was rapidly cooled, and the reaction mixture was siphoned out and GLC was used to determine the isomeric composition. The degree of conversion was measured by GLC by use of toluene as internal standard.

The reaction mixture was distilled first at atmospheric pressure and later at reduced pressure (0.4 mmHg) and the isomeric aldehydes were separated from styrene and solvent. Pure samples of unconverted styrene and α- and β-aldehydes were isolated by preparative GLC.

Permanganate oxidation of a sample of styrene (500 mg, 4.8 mmol) recovered from the reaction at 90 °C and 42% conversion gave 320 mg (2.6 mmol) of benzoic acid giving the same mass spectrum as that of an authentic sample.

A sample of benzoic acid (200 mg, 1.6 mmol) arising from permanganate oxidation was treated with diazomethane to give a quantitative yield of the corresponding methyl benzoate, which was purified by preparative GLC. The ^1H NMR spectrum of this product in CCl_4 showed that the ratio of the intensities of the methyl (3.88 ppm) and phenyl (7.4–7.8 ppm) resonances was 3 to 4.98 (estimated accuracy $\pm 3\%$).

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