

Preliminary communication

Remarkable α -regioselectivity in the rhodium-catalyzed hydroformylation of 2-vinylpyridine

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Abstract

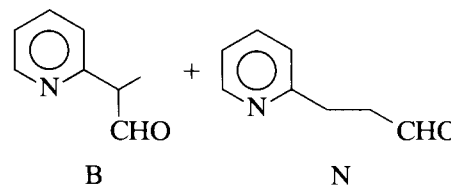
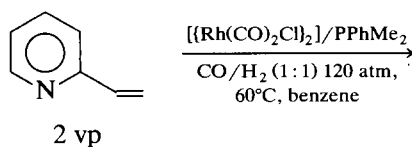
The $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]/\text{PPhMe}_2$ -catalyzed hydroformylation of 2-vinylpyridine gives the branched aldehyde 2-(2-pyridyl)propanal in good yield and 99% α -regioselectivity.

Keywords: Hydroformylation; Vinylpyridines; α -Regioselectivity; 2-(2-Pyridyl)propanal; Rhodium; Catalysis

Whereas the hydroformylation of styrene [1,2] and substituted styrenes [3,4] has been extensively investigated, the hydroformylation of vinyl heteroaromatics such as vinylpyridine [5], vinylpyrrole [6], and vinylfuran [7] has so far received little attention.

The $[\text{Co}_2(\text{CO})_8]$ -catalyzed hydroformylation of 2-vinylpyridine has been reported to give only the linear aldehyde 3-(2-pyridyl)propanal in good yield [5], but the rhodium-catalyzed hydroformylation of this substrate has not yet been described.

Because this is of interest from both synthetic [8] and mechanistic [9] points of view, we have studied the rhodium-catalyzed hydroformylation of 2-vinylpyridine (2vp). We find that when $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ and PPhMe_2 (Rh/P atom ratio 1 : 2) is used as catalyst precursor the reaction gives 2-(2-pyridyl)propanal (B) in good yield and very high α -regioselectivity (> 99%).

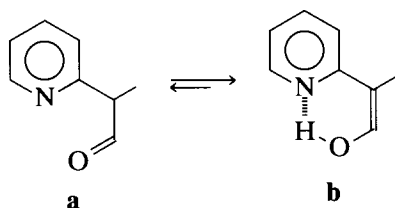


A solution of 2vp (44.3 mmol), $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ (0.31 mmol) and PPhMe_2 (1.24 mmol) in benzene (25 ml) was introduced into a 50-ml stainless steel autoclave and the mixture was stirred at 60°C for 7 h under dihydrogen and carbon monoxide (1 : 1, total 120 atm.). GC and GC-MS analysis of the reaction mixture showed that the conversion was complete and that the yield to aldehydes was 90%. A small amount (< 6%) of 2-ethylpyridine, the hydrogenation product of 2vp, was also formed, together with some polymeric material (4%). The ^1H NMR spectrum in C_6D_6 of the crude reaction mixture (after removal of the solvent) shows that the branched isomer, 2-(2-pyridyl)propanal (B), by far exceeds the linear one, 3-(2-pyridyl)propanal (N), the regioisomeric ratio being B/N = 99/1. The very weak resonances of the linear aldehyde were detected by comparing the ^1H NMR spectrum of the crude reaction product with that of an authentic sample of 3-(2-pyridyl)propanal [10] obtained by oxidation [11] of 3-(2-pyridyl)propanol.

The ^1H NMR spectrum in C_6D_6 of a pure sample of 2-(2-pyridyl)propanal recovered from the crude reac-

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tion mixture by fractional distillation at reduced pressure indicates that the keto-form **a** is in equilibrium with its enol tautomer **b**, the enol-form being prevalent (**a/b** = 25 : 75 at 25°C).



The keto-form is characterized by a doublet at δ 1.35 ppm (CH_3), a quartet at δ 3.43 ppm (CH) and a doublet at 9.76 ppm (CHO). The enol-form shows a singlet at δ 1.67 ppm (CH_3), a singlet (superimposed on aromatic protons signals) at δ 7.10 ppm (CH) and a broad signal at δ 14.60 ppm (OH).

When the hydroformylation of 2vp was carried out with $[\text{Rh}_4(\text{CO})_{12}]$ or $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ the reaction was much slower (15–20% conversion after 15 h), but the same high α -regioselectivity (B/N > 99/1) was obtained.

The hydroformylation of 4vp, carried out under similar experimental conditions ($[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]/\text{PPhMe}_2$, 60°C, benzene) occurs with a very high α -regioselectivity (> 99%) [12], similar to that shown by 2vp, showing that the relative positions of the pyridine nitrogen and the vinyl group do not influence the regioselectivity of the reaction.

Under similar conditions styrene hydroformylation takes place with a lower α -regioselectivity, the branched/linear isomeric ratio being 96/4.

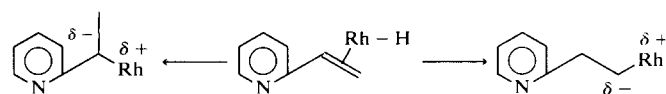
The above findings lead to the following conclusions.

(1) The strong coordination ability of dimethylphenylphosphine [13] makes $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]/\text{PPhMe}_2$ a very suitable catalytic system for the hydroformylation of vinyl pyridines and analogous substrates.

(2) The remarkable α -regioselectivity observed in the hydroformylation of both 2vp and 4vp, probably is connected with the electron-withdrawing character of the pyridine ring rather than with the coordination of the pyridine nitrogen to the rhodium, which is often supposed to occur in the hydroformylation of unsaturated amines [14–16].

Assuming, as with styrene, that at low temperatures the regioselectivity of the reaction reflects the regioselectivity of formation of the alkylrhodium intermediates [2,17], the more electron-withdrawing character of

pyridine compared with benzene could increase the stability of the branched isomer relative to the straight chain isomer, and account for the results obtained.



The hydroformylation of 3-vinylpyridine is now under investigation.

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References and notes

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