

Preliminary communication

High α -regioselectivity in the rhodium-catalyzed hydroformylation of vinylpyrrolesRoberta Settambolo ^a, Aldo Caiazzo ^b, Raffaello Lazzaroni ^b^a *Istituto di Chimica Quantistica ed Energetica Molecolare del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy*^b *Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy*

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Abstract

The $\text{Rh}_4(\text{CO})_{12}$ -catalyzed hydroformylation at low temperature (40 °C) of the 1-, 2- and 3-vinylpyrrole gives the corresponding branched aldehydes 2-(1-pyrrolyl)propanal, 2-(2-pyrrolyl)propanal and 2-(3-pyrrolyl)propanal with high α -regioselectivity.

Keywords: Hydroformylation, 3-vinylpyrrole, 2-(3-pyrrolyl)propanal; Rhodium; Catalysis

The hydroformylation of functionalized unsaturated substrates is a very interesting topic in terms of synthetic utility [1] as well as mechanistic aspects [2]. To date, however, relatively few approaches to the oxo-reaction of vinyl heteroaromatic compounds have been documented [3–6]. Recently we reported [7] that the rhodium-catalyzed hydroformylation of 2-vinylpyridine and 4-vinylpyridine, in the presence of a suitable catalytic system, selectively gives the branched aldehydes, i.e. 2-(pyridyl)propanals, in good yield and with remarkable α -regioselectivity (99%). We report here the hydroformylation of another class of heteroaromatic substrates, i.e. the 1-, 2- and 3-vinylpyrroles, in order to investigate the influence of the π -excessive ring on the chemo- and regioselectivity of the reaction.

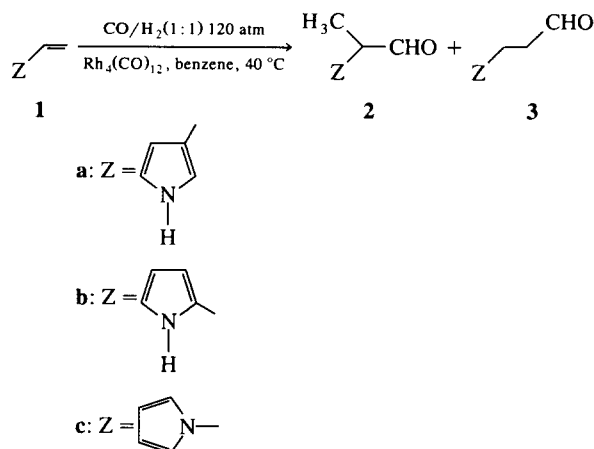
We found that at 40 °C, in the presence of $\text{Rh}_4(\text{CO})_{12}$ as catalytic precursor, the hydroformylation of 3-vinylpyrrole (**1a**) [8], 2-vinylpyrrole (**1b**) [9] and 1-vinylpyrrole (**1c**) [10] gives the isomeric aldehydes **2** and **3** in moderate to good yield, the branched isomer **2** predominating (Scheme 1).

A solution of **1** (5.4 mmol), $\text{Rh}_4(\text{CO})_{12}$ (2.7×10^{-2} mmol) in benzene (5 ml) was introduced by suction into a 25 ml evacuated stainless steel autoclave. Carbon monoxide and dihydrogen were introduced up to 120 atm total pressure ($\text{CO}/\text{H}_2 = 1:1$) and then the autoclave was rocked at 40 °C (24 h for **1a**; 44 h for **1b**; 36

h for **1c**). GC and GC-MS analysis of the reaction mixtures showed that the conversion was complete. In all three cases, high α -regioselectivity was observed; the regioisomeric ratios were 94:6 (**2a/3a** and **2b/3b**) for 3- and 2-vinylpyrrole and 97:3 (**2c/3c**) for 1-vinylpyrrole [11]. In the case of **1a**, the hydrogenation product 3-ethylpyrrole was also present (< 2%). A small amount of 2-(1-pyrrolyl)propanol, the reduction product of **2c**, was found in the case of the hydroformylation of **1c**. The formation of some polymeric material was observed in the hydroformylation of **1b** [12].

Chemically pure 2-(3-pyrrolyl)propanal and 2-(1-pyrrolyl)propanal were obtained by elution on column chromatography (silica gel, hexane/ethyl acetate (3:1)) (**2a**) and fractional distillation of the corresponding crude reaction mixtures (**2c**) respectively. In the case of 2-vinylpyrrole (**1b**) the branched aldehyde **2b** was recovered in the presence of the linear one **3b** by rapid elution of the hydroformylation product on a very short column of silica gel (pentane/ethyl acetate (3:1)). The characteristic ^1H NMR resonances of the above aldehydes are reported in Table 1.

The above findings clearly point out that the hydroformylation of the vinylpyrroles occurs with high α -regioselectivity similar to that observed for styrene [13] in analogous experimental conditions (branched:linear aldehyde = 97:3 at 40 °C).



Scheme 1.

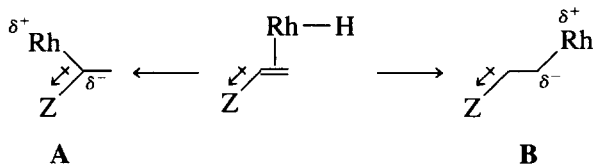
Table 1
Characteristic proton chemical shifts ^a of the branched aldehydes 2

compound	chemical shifts (ppm)		
	H(a)	H(b)	H(c)
2a	3.50	9.52	1.29
2b	3.62	9.54	1.43
2c	4.58	9.59	1.63

^a In ppm from internal TMS; CDCl₃ as solvent.

As previously shown by studies on the rhodium-catalyzed deuteroformylation of styrene [14] and unsaturated ethers [15], the high α -regioselectivity of the reaction must be related to the regioselectivity of formation of the rhodium-alkyl intermediates (Scheme 2).

The polarizable pyrrole ring directly bonded to the partially negative carbon atom favours the branched isomer A over the linear alkyl B, thus explaining the predominance of the branched aldehyde. In accord with the above scheme, the greater electron-attracting ability of the pyridyl ring compared with that of the π -excessive pyrrole could account for the higher α -regioselectivity observed in the hydroformylation of 2-vinylpyridine (99:1) [7] with respect to 2-vinylpyrrole (94:6).



Scheme 2.

The influence of temperature and of gas pressure and the effect of different catalytic precursors, e.g. [Rh(CO)₂Cl]₂/PPhMe₂ and RhH(CO)(PPh)₃ on the regioselectivity in the hydroformylation of the vinylpyrroles isomers are now under investigation.

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References and notes

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