

Preliminary communication

# High $\alpha$ -regioselectivity in the rhodium-catalyzed hydroformylation of vinylpyrroles

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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  $\alpha$ -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  $\alpha$ -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  $\pi$ -excessive ring on the chemo- and regioselectivity of the reaction.

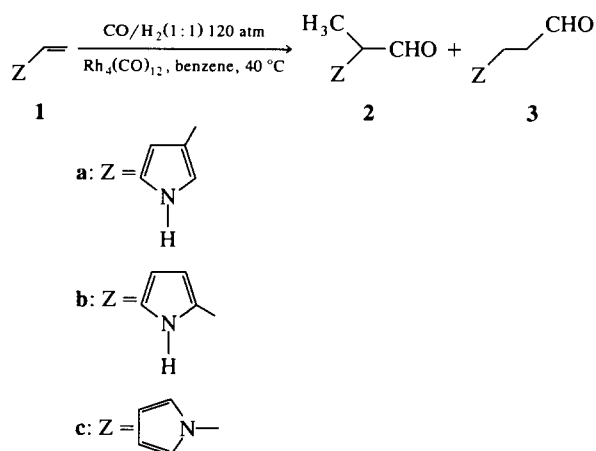
We found that at 40 °C, in the presence of  $\text{Rh}_4(\text{CO})_{12}$  as catalytic precursor, the hydroformylation of 3-vinylpyrrole (**1a**) [8], 2-vinylpyrrole (**1b**) [9] and 1-vinylpyrrole (**1c**) [10] gives the isomeric aldehydes **2** and **3** in moderate to good yield, the branched isomer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

A solution of **1** (5.4 mmol),  $\text{Rh}_4(\text{CO})_{12}$  ( $2.7 \times 10^{-2}$  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  $\alpha$ -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 <sup>1</sup>H 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  $\alpha$ -regioselectivity similar to that observed for styrene [13] in analogous experimental conditions (branched:linear aldehyde = 97:3 at 40 °C).



Scheme 1.

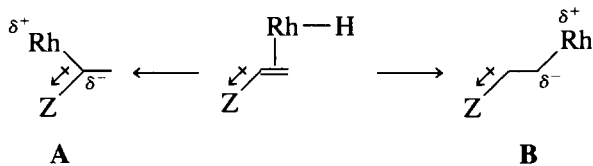
Table 1  
Characteristic proton chemical shifts<sup>a</sup> of the branched aldehydes 2

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

<sup>a</sup> In ppm from internal TMS; CDCl<sub>3</sub> as solvent.

As previously shown by studies on the rhodium-catalyzed deuteroformylation of styrene [14] and unsaturated ethers [15], the high  $\alpha$ -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  $\pi$ -excessive pyrrole could account for the higher  $\alpha$ -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)<sub>2</sub>Cl]<sub>2</sub>/PPhMe<sub>2</sub> and RhH(CO)(PPh)<sub>3</sub> on the regioselectivity in the hydroformylation of the vinylpyrroles isomers are now under investigation.

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### References and notes

- [1] (a) H.M. Colquhoun, J. Holton, D.J. Thompson and M.V. Twigg, *New Pathways for Organic Synthesis*, Plenum, New York (1984); (b) C. Botteghi, S. Paganelli, A. Schionato and M. Marchetti, *Chirality*, 3 (1991) 355.
- [2] (a) I. Ojima, *Chem. Rev.*, 68 (1988) 1011; (b) A. Polo, C. Claver, S. Castellón, A. Ruiz, J.C. Bayón, J. Real, C. Mealli and D. Masi, *Organometallics*, 11 (1992) 3525; (c) C.P. Casey and L.M. Petrovich, *J. Am. Chem. Soc.*, 117 (1995) 6007.
- [3] A. Alberola and M.F. Brana, *An. Real Soc. Espan. Fis. Quim., Ser. B*, 63 (1967) 683; *Chem. Abstr.*, 67 (1967) 63939.
- [4] A.F. Browning, A.D. Bacon and C. White, *J. Mol. Catal.*, 83 (1993) L11.
- [5] Y. Watanabe, T. Mitsudo, M. Tanaka, K. Yamamoto and Y. Takegami, *Yukagaku*, 23 (1974) 304; *Chem. Abstr.*, 81 (1974) 24995.
- [6] (a) A.L. Lapidus, A.P. Rodin, I.G. Pruidze and B.I. Ugrak, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 7 (1990) 1661, *Chem. Abstr.*, 113 (1990) 171816; (b) P. Kalck and F. Serein-Spiran, *New. J. Chem.*, 13 (1989) 515.
- [7] R. Settambolo, S. Pucci, S. Bertozzi and R. Lazzaroni, *J. Organomet. Chem.*, 489 (1995) C50.
- [8] R. Settambolo, R. Lazzaroni, T. Messeri, M. Mazzetti and P. Salvadori, *J. Org. Chem.*, 58 (1993) 7899.
- [9] (a) R.A. Jones and J.A. Lindner, *Austr. J. Chem.*, 18 (1965) 875; (b) C. Finzi, J.E. Fernandez, M. Randazzo and L. Toppare, *Macromolecules*, 25 (1992) 245.
- [10] (a) W. Reppe, *Ann.*, 601 (1956) 132; (b) O.A. Tarasova, A.G. Mal'Kina, A.I. Mikhaleva, L. Brandsma and B.A. Trofimov, *Synth. Commun.*, 24 (1994) 2035.
- [11] These ratios were determined by gas chromatography on the product obtained from at least three runs and are accurate to within 0.5%.
- [12] The tendency to give polymeric material accounts for the low yield obtained in the synthesis of **1b**.
- [13] R. Lazzaroni, A. Raffaelli, R. Settambolo, S. Bertozzi and G. Vitulli, *J. Mol. Catal.*, 50 (1989) 1.
- [14] (a) R. Lazzaroni, R. Settambolo, A. Raffaelli, S. Pucci and G. Vitulli, *J. Organomet. Chem.*, 339 (1988) 357; (b) G. Uccello-Barretta, R. Lazzaroni, R. Settambolo and P. Salvadori, *J. Organomet. Chem.*, 417 (1991) 111.
- [15] R. Lazzaroni, R. Settambolo and G. Uccello-Barretta, *Organometallics*, in press.