## UNUSUAL DOUBLE HYDROFORMYLATION OF SUBSTITUTED ALLYLANILINES LEADING TO THE FORMATION OF N-ARYLPYRROLIDINE ALDEHYDES

Despina Anastasiou, Eva M. Campi, Hassan Chaouk, W. Roy Jackson\* and Quentin J. McCubbin.

Department of Chemistry, Monash University, Clayton, Vic., Australia 3168.

Abstract N-Arylpyrrolidine aldehydes are the unexpected products obtained from the rhodium-catalysed double hydroformylation of allylanilines.

Rhodium-catalysed reaction of N-2-methylprop-2-enylbenzenamine (1a) with CO/H<sub>2</sub> under relatively mild conditions (400 psi, 80°C, 20h) gave the isomeric pyrrolidine aldehydes (5a) and (6a) in 76% yield after chromatography and in ratio 2:1 (see Table). These products can be envisaged as resulting from the reaction sequence outlined in the Scheme.



Hydroformylation of the di-substituted alkene could be expected to give only the linear aldehyde (2) which could cyclise to the enamine (4). A second hydroformylation would then give the isomeric aldehydes (5) and (6). Double hydroformylation reactions are very unusual but Alper has reported some examples of double<sup>1</sup> and even a triple carbonylation in cobalt-catalysed reactions.<sup>2</sup> Reaction of the *ortho*-cyanoaniline (1b) gave an almost identical product mixture. In both cases the aldehydes were present as mixtures of diastereoisomers, (5) in ratio 60:40 and (6) in ratio 90:10. It can be assumed that the *trans*-isomer is the major product in each mixture. The isomers (5) and (6), but not their diastereoisomers were separated by preparative chromatography and their structure assigned by n.m.r. <sup>13</sup>C n.m.r. data for the diastereoisomers of (5b) are given,  $\delta$  (50 MHz) (trans): 17.77 (CH<sub>3</sub>); 31.27 (C4); 35.00 (C3): 58.03 (C5); 67.36 (C2); 94.97 (C2'); 114.50, 117.34 (C4', 6'); 121.12 (CN); 133.85, 135.87 (C3', 5'); 148.79 (C1'); 200.17 (CHO);

(cis): 17.14 (CH<sub>3</sub>); 33.41 (C4); 35.65 (C3); 59.87 (C5); 67.79 (C2); 97.21 (C2'); 114.56, 118.22 (C4', 6'); 133.73, 135.54 (C3', 5'); 150.03 (C1'); 200.77 (CHO).

Support for the proposed reaction sequence came from reaction of the N-allylaniline (1c). The monosubstituted alkene now gave some branched aldehyde (3c) in addition to the pyrrolidine aldehydes (5c) and (6c). Further support came from reaction of the corresponding *ortho*-nitroaniline (1d) which gave a mixture of the aldehydes (2d) and (3d) resulting from a single hydroformylation. Presumably the *ortho*-nitro group now reduces the nucleophilicity of the anilino nitrogen such that intramolecular cyclisation does not occur. Surprisingly the two aldehydes were formed in ratio (2d) 20 : (3d) 80 in contrast to that found for most terminal alkenes.<sup>3</sup>

We thank the Australian Research Council for support, the Australian Department of Education for a postgraduate award (to D.A.) and Johnson Matthey Ltd for a loan of rhodium.

Reactant (1) Ratio of Products <sup>‡</sup>							Yield	
	(2)	:	(3)	:	(5)	:	(6)	%
a					67		33	76
b	-		-		67		33	72
c	-		40		30		30	75
d	20		80		-		-	78

Table: Yields of aldehydes<sup>†</sup>

- <sup>†</sup> Reactions were carried out with alkene, [Rh(OAc)2]2, PPh3 in ratio 200:1:4 for 20 hours at temperatures in the range 70 to 100°C, typically using 3 mmole of alkene in ethyl acetate (10 ml) and a 1:1 molar mixture of CO/H2 (400 psi). Yields are of material isolated after chromatography.
- Estimated from <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra. No significant variation in product ratios was observed in the temperature range.

## References

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