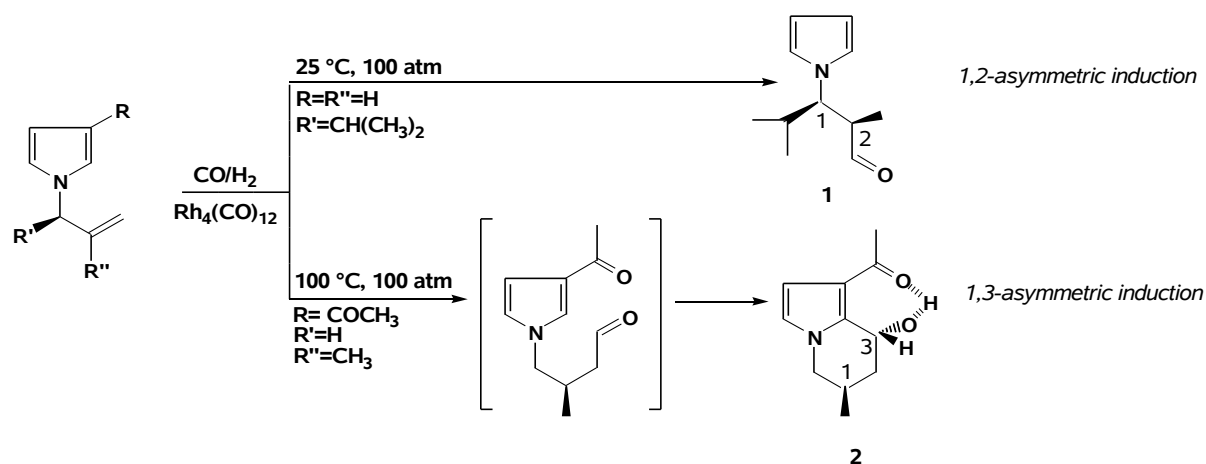


Rhodium-Catalyzed Hydroformylation of 3-(Pyrrol-1-yl)Alk-1-enes: Two Examples of High 1,2- and 1,3-Substrate-Induced Diastereoselectivity

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The generation of a new stereocenter, either with the aid of a chiral catalyst or by substrate-based asymmetric induction, is a topic of great interest in transition metal catalyzed reactions, especially if the involved processes are in accord with the criteria of atom economy. We observed, and report here, high values of both 1,2- and 1,3-asymmetric induction (d.e. up to 99%) under N-allylpyrroles¹ rhodium-catalyzed hydroformylation conditions (Scheme 1).

Scheme 1



The former example regards the formation of 4-methyl-3-(pyrrol-1-yl)pentanal (**1**) from the corresponding chiral N-allylpyrrole: due to a 1,2-asymmetric induction of the chiral center into the starting olefin, **1** was obtained with a d.e. value 80%.² In the latter a complete asymmetric induction was exerted by the new chiral center (1 carbon atom) of the formed pyrrolylbutanal intermediate on the carbon atom in position three during a one-pot intramolecular cyclization to tricycle **2** (d.e. 99/1). In both cases the diastereomer having the same configuration at both chiral centers was selectively formed. R,R Diastereomer is only depicted into Scheme 1.

Interestingly, regio-selectivity (> 85/15) and diastereo-selectivity as well as the absolute configuration of the prevailing diastereomer, evaluated from computational investigations on rhodium-alkyl transition states, perfectly correspond to those experimentally determined on diastereomeric products. The selectivity of the result together with the interest of these products on fine chemistry, make the oxo process of pyrrolylolefins a valid synthetic instrument.

1. R. Settambolo, G. Guazzelli, L. Mengali, A. Mandoli, R. Lazzaroni, *Tetrahedron: Asymmetry* **2003**, *14*, 2491.
2. R. Settambolo, S. Rocchiccioli, G. Uccello-Barretta, R. Lazzaroni, *Letters in Organic Chemistry* **2007**, *4*, 388.