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Regio- and Stereo-Control in the Rhodium Catalysed Hydroformylation of Some Alkenylphosphines

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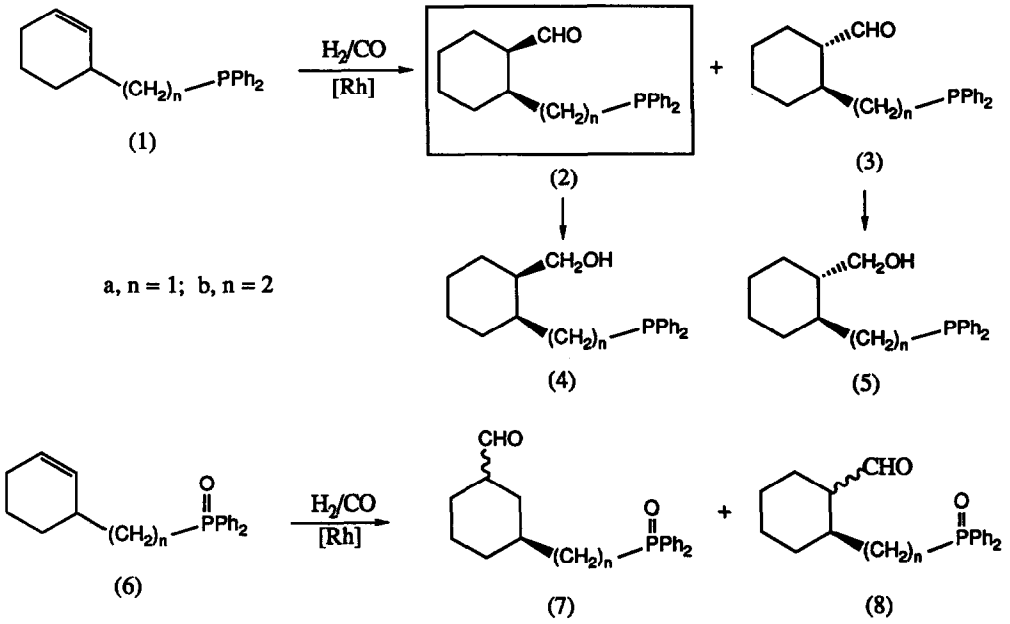
Excellent stereo as well as regio-control can be achieved in the rhodium catalysed hydroformylation of some substituted alkenylphosphines.

The use of remotely substituted groups, capable of chelation to a metal in the control of alkene reactivity, is becoming a useful tool in synthetic chemistry.[1,2,3,4] As an extension of our earlier work,[2] we now report that it is possible to achieve excellent stereo- as well as regio-control in the hydroformylation of some substituted alkenyl phosphines.

The cyclohexenyl phosphines (1a and 1b) were reacted with H_2/CO in the presence of rhodium acetate dimer and triphenylphosphine. Virtually complete control was achieved in the hydrofomylation of (1a) at 55° for 22 h in

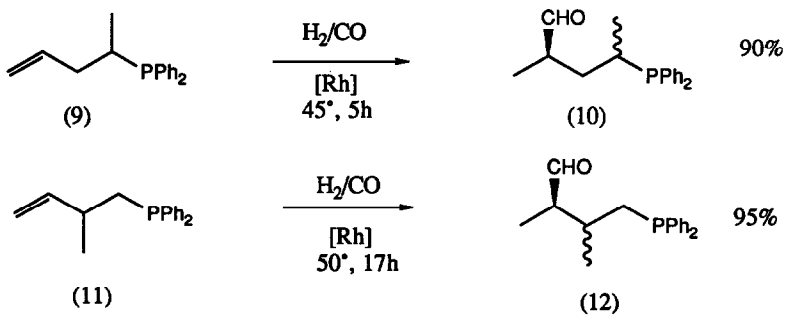


that the *cis*-aldehyde (2a) was formed (64%) with only trace amounts (≤ 4%) of the corresponding *trans*-isomer (3a) being detected. Increasing the temperature to 90° gave the alcohol (4a) in excellent yield (88%).

Reaction of the homologue (1b) at 90° gave a mixture of the alcohols (4b) and (5b) in ratio 80:20. No trace of other regioisomers was detected. Thus in this compound regiocontrol is complete but stereocontrol, though highly selective, shows some leakage to the *trans*-compound.

Reactions of the corresponding phosphine oxides (6a) and (6b) gave mixtures of four isomers in which the 1,3-disubstituted regioisomers (7a) and (7b) predominated over the 1,2-isomers (8a) and (8b) (*ca.* 70(7): 30(8)). The 1,2-isomers (8) showed a clear preference for the *trans*-isomer (*trans:cis*, 80:20). The diastereoisomeric 1,3-isomers (7) were formed in ratio 70:30 but the stereochemistry was not assigned.

The possibility of stereocontrol in the hydroformylation of some substituted 4-phosphinobut-1-enes (9) and (11) was also investigated. In each case complete regio-control was obtained, in agreement with the previously described reaction of the parent 4-phosphinobut-1-ene[2] but no appreciable stereoselectivity was observed. The aldehyde (10) was formed as a mixture of diastereoisomers in ratio 3:2 and the aldehyde (12) as an equimolar mixture of diastereoisomers. The product distributions (aldehyde *vs.* alcohol) in the hydroformylation reactions of these phosphinoalkenes are extremely sensitive to reaction temperature, in contrast to the large majority of hydroformylations where alcohols appear as significant products only under severe reaction conditions. The phosphino aldehydes appear to be genuine intermediates in the reactions where alcohols are formed. For example, when the aldehyde (10) was re-subjected to the hydroformylation conditions at 75° for 5 h, it was completely converted into the corresponding alcohol.



General conditions: H_2/CO (1:1), 400 psi in Parr autoclave (100 ml) using alkene, $[Rh(OAc)_2]_2$, PPh_3 in ratio 200:1:4 in ethyl acetate. Product ratios were determined from the 300 MHz ^1H n.m.r. and ^{31}P n.m.r. spectra of the crude products. All compounds were fully characterized as the corresponding phosphine oxides, giving satisfactory spectroscopic and elemental analyses.

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