

## Chelation Control by Phosphite Esters in Rhodium Catalysed Hydroformylation

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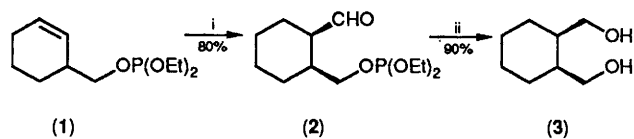
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Phosphite esters can be used to give excellent regiocontrol in rhodium catalysed hydroformylation reactions of alkenes and in addition excellent stereocontrol in the reactions of some cyclohexenyl phosphites.

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Remotely substituted groups, capable of chelating to a metal catalyst, can be used to control the regio-<sup>1-4</sup> and stereochemistry<sup>5,6</sup> of organic reactions. We have previously reported that the hydroformylation of several alkenyl phosphines can be achieved with good regiocontrol for the branch

chain aldehyde.<sup>2</sup> The resulting phosphino aldehydes have been manipulated by Horner-Wittig methodology<sup>7</sup> but it was of interest to develop other chelating groups which could be further manipulated under different reaction conditions. We now report that excellent regiocontrol can be obtained in the



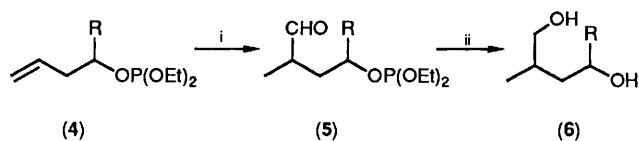
**Scheme 1.** Reagents and conditions: i,  $H_2/CO$  (1:1, 500 psi),  $[Rh(OAc)_2]_2$  (alkene: Rh, 50:1) in benzene, 100 °C, 44 h; ii,  $LiAlH_4$  in  $Et_2O$ .

hydroformylation of phosphite esters of homoallylic alcohols and that good stereocontrol can be achieved in some cases. Thus hydroformylation of the cyclohexenyl phosphite (1) and reduction of the intermediate aldehyde (2)<sup>†</sup> gave as a single product *cis*-1,2-bis(hydroxymethyl)cyclohexane (3) (Scheme 1). This compound was shown to be a single isomer by GLC,  $^{13}C$  NMR spectroscopy, and formation of a sharp melting di-*p*-nitrobenzoate derivative.<sup>8</sup>

Similar regiocontrol was shown in the reactions of open chain homoallylic phosphites (4) (Scheme 2) where reduction of the intermediate aldehydophosphites (5) gave only the 1,4-diols (6). Good yields of diols were obtained (84%, R = H; 70%, R = Me; and 85%, R = Ph) for the two steps. The two substituted diols [(6), R = Me and Ph] were formed as mixtures of diastereoisomers (ratios 60:40 for R = Me and 70:30 for R = Ph).

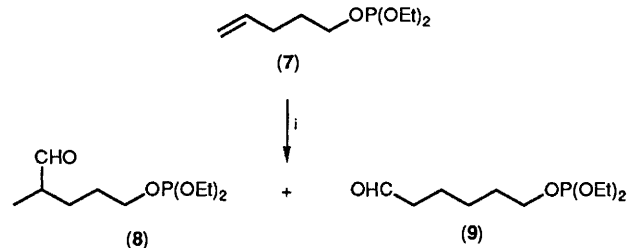
Reaction of the pentenyl phosphite (7) (Scheme 3) for 22 h at 90 °C gave the aldehydophosphites (8) and (9) in the ratio 87:13, showing that significant chelation control was operating even in this longer chain system.

In contrast, hydroformylation of both hex-1-ene and [but-3-en-1-yl] diethyl phosphate [the phosphate ester corre-



R = H, Me, Ph

**Scheme 2.** Reagents and conditions: i, as in Scheme 1 but reactions were carried out for 5–22 h at 50 °C; ii,  $LiAlH_4$  in  $Et_2O$ .



**Scheme 3.** Reagents and conditions: i, as in Scheme 1.

sponding to (4) (R = H)], under similar reaction conditions, gave approximately equimolar mixtures of branch-chain and terminal aldehydes.

Received, 26th February 1990; Com. 0/008721

## References

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<sup>†</sup> All new compounds gave satisfactory spectroscopic analyses. The intermediate aldehydophosphites (2), (5), (8), and (9) gave correct accurate masses and all other new compounds gave satisfactory elemental analyses.