Cationic Rhodium(I) Complex-catalysed Asymmetric Isomerisation of Allylamines to Optically Active Enamines

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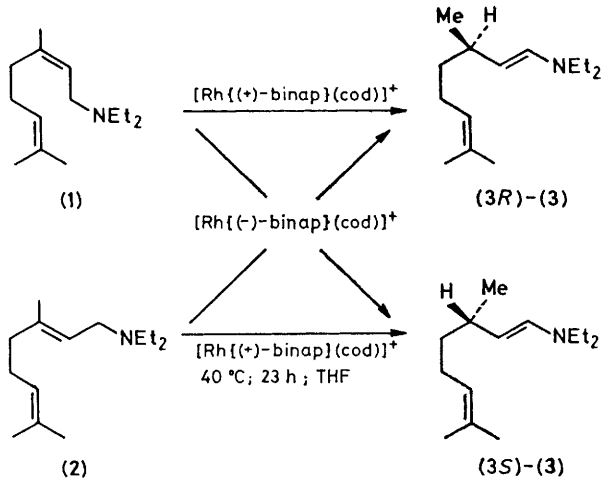
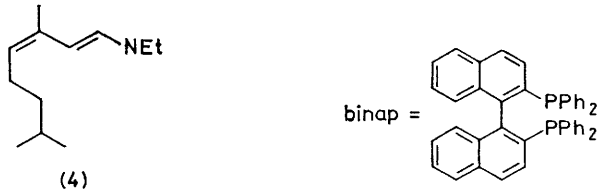
The cationic rhodium(I) complex (+)- or (−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl(cyclo-octa-1,5-diene)rhodium perchlorate, effectively catalyses the isomerisation of *N,N*-diethylnerylamine or *N,N*-diethylgeranylamine to produce optically active *N,N*-diethylcitronellal-(*E*)-enamine with excellent enantioselectivity (> *ca.* 95% enantiomeric excess) and chemoselectivity (> *ca.* 98%).

Despite numerous studies on catalytic olefin isomerisation, few reports describe enantioselective hydrogen migration.[1] The isomerisation of *N,N*-diethylnerylamine (**1**) and *N,N*-diethylgeranylamine (**2**) was effected with a chiral cobalt catalyst.[1a] The optical yield (<30% enantiomeric excess, e.e.) and chemoselectivity (<85%) for formation of *N,N*-diethylcitronellal-(*E*)-enamine (**3**) were too low to be of practical use. We report here a much better catalyst for the isomerisation.

Our preliminary experiments employing a cationic rhodium(I) diphosphine complex indicated a great improvement in the chemoselectivity. For example, the isomerisation of (**1**) with a catalytic amount (1 mol %) of $[Rh(dpe)(solv)_n]^+$ [dpe = 1,2-bis-(diphenylphosphino)ethane, solv = solvent] prepared *in situ* by treating $[Rh(dpe)(cod)]ClO_4$ (cod = cyclo-octa-1,5-diene) with H_2, showed a high conversion rate (92% after 23 h at 40 °C) with a high selectivity (>96%) for the formation of (**3**). The amine (**4**) with a conjugated diene unit, the main product of base-catalysed isomerisation of (**1**) or (**2**),[2] was practically absent. This effective catalysis for trisubstituted allylic systems contrasts with the very low activity of $HRuCl(PPh_3)_3$,[3] $H_2Ru(PPh_3)_4$,[4] or $[Ir(cod)(PMePh_2)_2]PF_6$.[5] The asymmetric hydrogen migration of the allylamines (**1**) and (**2**) was performed with cationic rhodium(I) complexes of chiral diphosphines. $[Rh\{(-)\text{-diop}\}(solv)_n]ClO_4$ [diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane],[6] prepared *in situ* by reducing $[Rh\{(-)\text{-diop}\}(cod)]ClO_4$ with H_2 in tetrahydrofuran (THF), isomerised (**1**) (40 °C; 23 h; in THF) into (3*S*)-(**3**) with 26 % e.e. (76 % conversion, 96 % selectivity). The isomerisation of (**2**) under the same conditions gave (3*R*)-(**3**) with 22 % e.e.





(100 % conversion, 93 % selectivity). The optical yields are comparable with those obtained with the Co–diop complexes.[1]

Extremely high enantioselectivity with a high catalytic rate was achieved with the atropisomeric chiral diphosphine, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap).[7] Thus, [Rh{(+)-binap}(cod)]ClO_4 isomerised (**1**) (40 °C; 23 h; in THF) into (3*R*)-(**3**) with 94 % e.e. (almost complete conversion and virtually 100 % selectivity). Similar isomerisation of (**2**) gave (3*S*)-(**3**) with 96 % e.e. The enantiomeric rhodium(I) complex, [Rh{(−)-binap}(cod)]ClO_4, under the same conditions produced (**3**) with the opposite stereochemistry at C-3 and with a comparable optical yield. These optical yields were based on the optical rotation of the citronellal-(*E*)-enamine (**3**), the optical purity of which was assessed by converting it into menthol *via* citronellal.[8] As is evident from the correlation between the starting olefin geometry, the stereochemistry of the product enamine, and the diphosphine chirality, the high optical yield can be obtained only when optically pure binap and one, pure, geometrical isomer of the olefin are employed. Because of the accessibility of both the starting allylamines and the chiral ligand, the present isomerisation is one of only a few examples of practical asymmetric catalytic processes and should be useful for the large-scale production of chiral aliphatic aldehydes and their derivatives.

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