The Asymmetric Cyclisation of Substituted Pent-4-enals by a Chiral Rhodium Phosphine Catalyst

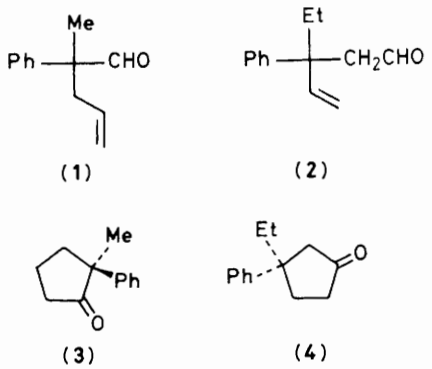
Brian R. James* and Charles G. Young

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6

Treatment of the racemic disubstituted pent-4-enals (**1**) and (**2**) at *ca.* 150 °C with the chiral complex [Rh(chiraphos)$_2$]Cl [chiraphos = 2*S*,3*S*-bis(diphenylphosphino)butane] results in a cyclisation reaction and catalytic asymmetric synthesis of the 2,2- and 3,3-disubstituted cyclopentanones (**3**) and (**4**), respectively.

While efficient asymmetric syntheses for a variety of processes have been reported using homogeneous catalysts,[1] those involving carbon–carbon bond formation have been generally less well developed.[2] We describe here such a process involving the synthesis of chiral disubstituted cyclopentanones from racemic pent-4-enals using a [Rh(chiraphos)$_2$]Cl catalyst.† Formation of cycloalkanones by non-chiral metal complex-catalysed cyclisation of carbonyl-containing substrates is known,[3,4] including the conversion of pent-4-enal itself to cyclopentanone using $RhCl(PPh_3)_3$.[3]

On heating about 1 ml of neat aldehyde (**1**)‡ with *ca.* 10 mg of [Rh(chiraphos)$_2$]Cl (substrate: Rh *ca.* 600) at 160 °C for 10 h under N_2, a mixture of products was obtained.§ An isomerisation product, the 2,2-disubstituted cyclopentanone (**3**), was formed in 40—50% yield [based on (**1**)] and, of significance, was formed with a maximum 52% e.e. of the (−)-(*S*) optical isomer; the optical purity was estimated using the reported specific rotation of pure (+)-(*R*)-(**3**) ($[\alpha]_D^{25}$ + 95.30°; *c* 3.87, EtOH) which has been prepared previously from resolved 2-methyl-2-phenylhexanedioic acid.[5] The other reaction products from (**1**) resulted from double bond migration (*E*- and *Z*-2-phenylpent-2-ene, *ca.* 35%) and from radical coupling (*e.g.*, diphenyl, <5%). In the absence of the rhodium complex, (**1**) was completely inert under corresponding conditions.



(**1**) (**2**) (**3**) (**4**)

It should be mentioned that the discovery of this asymmetric cyclisation was fortuitous, since the study was initiated with the aim of decarbonylating such racemic aldehydes to give chiral hydrocarbons. Cationic rhodium(I) bis(ditertiaryphosphine) complexes are known to be effective catalysts for decarbonylation of aldehydes.[6] The noted decarbonylation of (**1**), however, was accompanied by isomerisation to the non-chiral pent-2-ene product (see above).

In attempts to circumvent the problem of isomerisation, (**2**) was used as substrate since the anticipated decarbonyl-

† Chiraphos = 2*S*,3*S*-bis(diphenylphosphino)butane (Strem Chemicals); the [Rh(chiraphos)$_2$]Cl complex was synthesised *via* the cyclo-octene precursor $[RhCl(C_8H_{14})_2]_2$ and characterised as reported previously for other analogous bis(ditertiaryphosphine) complexes (B. R. James and D. Mahajan, *Can. J. Chem.*, 1979, **57**, 180).

‡ Details of the synthesis of (**1**) from *DL*-2-phenylpropionaldehyde, and of (**2**) from propiophenone *via* 1-bromo-3-phenylpent-2-ene, will be published elsewhere and are available on request from the authors.

§ The products may be analysed *in situ* (gas chromatography–mass spectroscopy), or isolated [230—400 mesh Kieselgel 60, 2% ethyl acetate–light petroleum (35—60 °C)] and characterised by usual spectroscopic methods.

ation product would have no migrateable hydrogen atom on the resulting tertiary carbon atom. Reaction with the rhodium complex again, however, resulted in the intramolecular addition of the aldehyde group to the alkene bond with formation of the previously unreported 3,3-disubstituted cyclopentanone (**4**) in about 50% yield; the product is optically active as judged by rotation, but common chiral shift reagents tested thus far have given insufficient resolution in the ^{1}H n.m.r. spectra to determine the enantiomeric excess. Small amounts of decarbonylation products have been detected, but their nature and optical purity have not been determined as yet.

In the earlier related work with the non-chiral system,[3] co-ordination catalysis involving a rhodium acyl–hydride intermediate was a preferred mechanism over a free-radical addition of aldehyde to the olefin bond, and seems likely in the present work in view of the induced asymmetry in the products.

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