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Preliminary communication

DIASTEREOSELECTIVITY IN THE RHODIUM-CATALYZED HYDROFORMYLATION OF (+)(*R*)-1-PHENYLETHYL VINYL ETHER

RAFFAELLO LAZZARONI, SERGIO PUCCI, SERGIO BERTOZZI and DARIO PINI
Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive c/o Istituto di Chimica Organica, Università di Pisa, Via Risorgimento, 35, 56100 Pisa (Italy)

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Summary

The degree of diastereoselectivity in the rhodium-catalyzed hydroformylation of (+)(*R*)-1-phenylethyl vinyl ether is much higher than that in the hydroformylation of the related olefin, 4-phenyl-1-pentene.

While the asymmetric hydroformylation of prochiral and racemic unsaturated substrates catalyzed by chiral complexes of Rh, Co, and Pt has been extensively investigated [1,2], the diastereoselectivity in the hydroformylation of chiral substrates in the presence of achiral catalysts has been studied only in a few cases [3—5].

The asymmetric induction arising from a chiral carbon atom directly bound to a vinylic group has been determined in the hydroformylation of (+)(*S*)-3-methyl-1-pentene [3] and of (*R*)(*S*)-3-phenyl-1-butene [4] in the presence of Rh and Co as catalysts; the observed diastereomeric excess (d.e.) is less than 32% in all the cases. In order to investigate the influence of the oxygen atom on the regio- and diastereo-selectivity of this reaction, we have studied the rhodium-catalyzed hydroformylation of (+)(*R*)-1-phenylethyl vinyl ether (I) and the related olefin (*R*)(*S*)-4-phenyl-1-pentene (II).

The runs were carried out at 90°C in benzene under a CO/H_2 pressure of 120 atm in the presence of $[RhCl(CO)_2]_2$ and triphenylphosphine (molar ratio 1/4) as catalytic precursor. The hydroformylation of I ($[\alpha]_D^{25}$ +14.1, o.p. 25% [6]) takes place in ca. 4 h with complete conversion of the vinyl ether, and gives a mixture of three isomeric aldehydes (yield 95%), (1′*R*,2*R*)-2-(1′-phenylethoxy)-propanal (IIIa) (46.3%), (1′*R*,2*S*)-2-(1′-phenylethoxy)propanal (IIIb) (10.9%), and (+)(*R*)-3-(1′-phenylethoxy)propanal (IV) (42.8%) (eq. 1).

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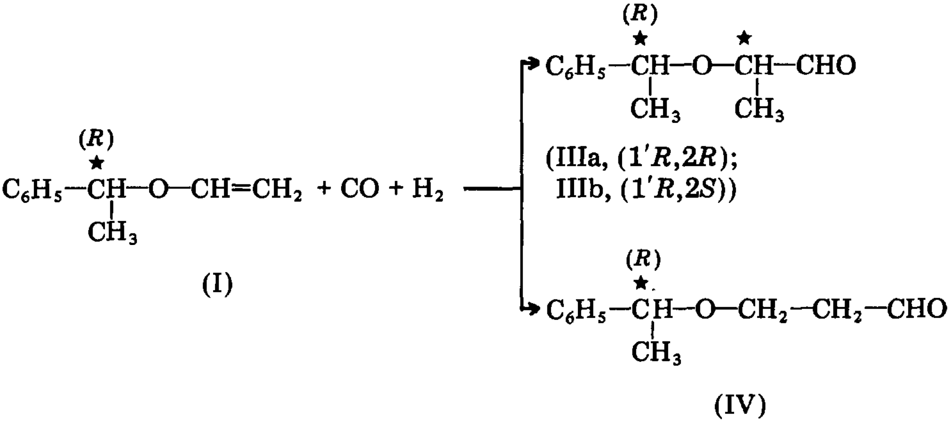
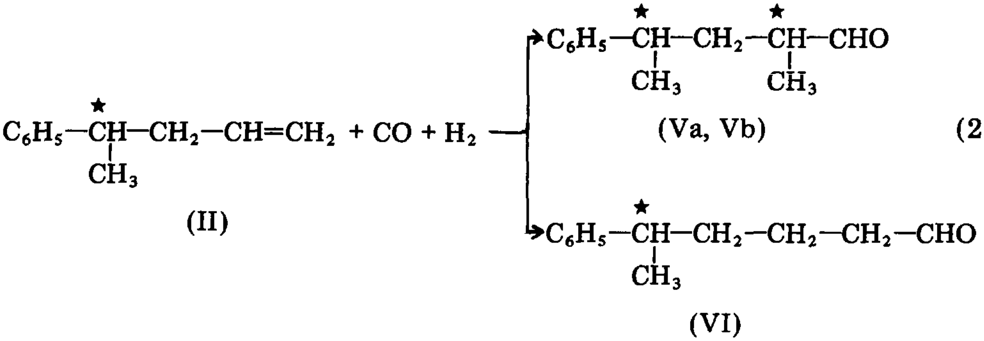


(1)

Compounds IIIa, IIIb, and IV, obtained as isomerically pure samples by fractional distillation with a spinning column, were identified by ^{1}H NMR and mass spectra, and their physical constants determinations.

The absolute configurations and optical purities of the diastereomeric aldehydes IIIa and IIIb were determined by comparing the optical rotatory power of the corresponding methyl esters, $[\alpha]_D^{18}$ +56.06 and $[\alpha]_D^{18}$ +3.63, respectively, with those of the methyl (–)(1'*S*,2*S*)-2-(1'-phenylethoxy)propanoate ($[\alpha]_D^{18}$ –224.0), and the methyl (+)(1'*R*,2*S*)-2-(1'-phenylethoxy)propanoate ($[\alpha]_D^{18}$ +14.5) obtained by reaction of the optically pure (–)(*S*)-methyllactate ($[\alpha]_D^{19}$ –8.2 [7]) with (*R*)(*S*)-1-chloro-1-phenylethane.

The hydroformylation of (*R*)(*S*)-4-phenyl-1-pentene (II) under the experimental conditions used for I gives the straight-chain aldehyde 5-phenylhexanal (VI) as the main product (66.5%), and the branched aldehyde 2-methyl-4-phenylpentanal (V) (33.5%) as a ca. 1/1 mixture of the two diastereomers Va (17.0%) and Vb (16.5%) (eq. 2).



(2)

The results show the following features: (1) As far as the regioselectivity is concerned, the formyl group is preferentially incorporated at the carbon atom bound to the oxygen atom of the vinyl ether I, while the terminal olefinic carbon atom is predominantly formylated in the case of olefin II.

(2) The extent of the diastereoselectivity exhibited by I (d.e. 62%) is higher by more than one order of magnitude than that for the related olefin II (d.e. 2%). It is also larger than that reported for the hydroformylation of chiral

olefins such as (+)(*S*)-3-methyl-1-pentene and (*R*)(*S*)-3-phenyl-1-butene in which the vinyl group is directly linked to the asymmetric carbon atom.

(3) The predominant diastereomer IIIa, with the absolute configuration 1′*R*,2*R* arises from the si—si face of I; this means that if the si—si and re—re faces are hydroformylated with the same regioselectivity, the si—si face reacts to a greater extent than the re—re face.

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