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Rhodium-diphosphite catalysed hydroformylation of allylbenzene and propenylbenzene derivatives

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Dedicated to Brian James.

Abstract

The asymmetric hydroformylation of allylbenzenes and propenylbenzenes is an important tool for obtaining high value intermediates for the pharmaceutical and perfume industry. We have studied these reactions with rhodium-chiral diphosphite systems. The diphosphite ligands **6** and **7** with carbohydrate backbone have high regioselectivities in *trans*-anethole hydroformylation and moderate ones in estragole hydroformylation. Only low enantioselectivities have been observed in the *trans*-anethole hydroformylation with the diphosphite **6** based system.

Keywords: Hydroformylation; Rhodium; Allylbenzene; Propenylbenzene; Selectivity

1. Introduction

The asymmetric hydroformylation reaction is an important tool for synthesizing enantiomerically pure aldehydes. These are important precursors of biologically pure compounds, biodegradable polymers and liquid crystals [1–3]. On the other hand, the hydroformylation of terpenes makes it possible to produce aldehydes of interest to the perfume industry (Scheme 1) [4–8].

The hydroformylation of terpenes such as eugenol, safrole and estragol, which are allylbenzenes, and their isomers, isoeugenol, isosafrole and *trans*-anethole, which are propenylbenzenes (Fig. 1), is interesting for the formation of aldehyde derivatives for the flavour industry [8]. Although asymmetric hydroformylation of vinylaromatic compounds has been widely studied [1–3,9], there are very few studies on the hydroformylation of allylbenzenes and propenylbenzenes [10–13].

The hydroformylation of propenylbenzenes **1** (Scheme 2) makes it possible to synthesize two branched aldehydes **3** and **4**, but the isomerization of these olefins to the terminal alkenes **2**, allylbenzenes, leads to the formation of the branched and linear aldehydes **4** and **5**, respectively.

The hydroformylation of eugenol **2b** and isoeugenol **1b** with unmodified rhodium catalysts at very high pressures was studied 25 years ago [10]. A mixture of aldehydes **3**, **4** and **5** was obtained (Scheme 2). Temperature was observed to have a strong influence on the regioselectivity. At low temperature (70 °C), the ratio of aldehydes obtained from **1b** and from **2b** was very different, while at 130 °C the ratios were closer. This indicates that an isomerization process takes place when the temperature increases, so the process is less selective (Table 1).

Kalck et al. [11] reported high selectivities for linear aldehydes **5** when they used the catalytic system $[Rh_2(\mu\text{-}SR)_2(CO)_2L_2]$ (L: PPh_3, $P(OMe)_3$ and $P(OPh)_3$) in the hydroformylation of allylbenzenes (estragole **1c**, eugenol **2b**, eugenol methyl ether and safrole **3c**).

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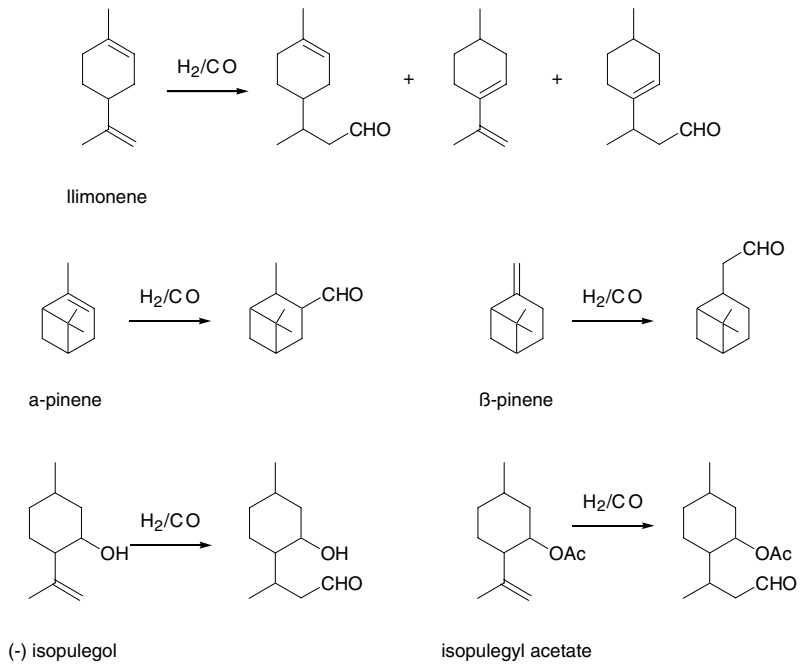

Scheme 1. Hydroformylation of some terpenes.

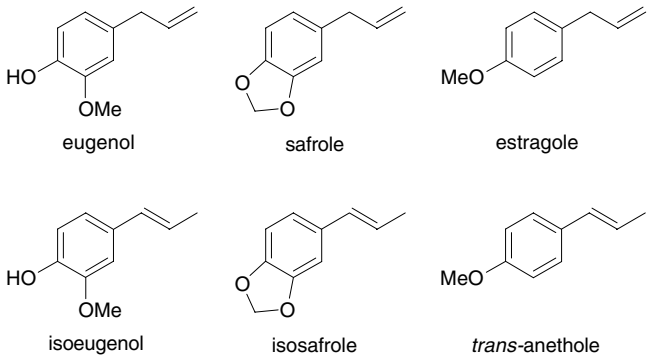

Fig. 1. Allylbenzenes and propenylbenzenes.

The asymmetric hydroformylation of *trans*-anethole **1a** and estragole **2a** was studied by Kollár [12] using $PtCl_2(bdpp) + SnCl_2$ and $[Rh(nbd)Cl]_2 + L$ (L: PPh_3 or DIOP) catalytic systems. The regioselectivities with the platinum system were low and were improved when rhodium systems were used. The enantioselectivity observed was low in the hydroformylation of *trans*-anethole **1a** and estragole **2a** with both systems. With $PtCl_2(bdpp) + SnCl_2$ and DIOP as the ligand, the regioselectivity to the branched aldehdyde **3a** was a 53% and with an enantioselectivity of 27.5%.

Dos Santos et al. [13] reported the hydroformylation of various allylbenzenes and propenylbenzenes with rhodium-based systems. They studied the electronic and steric effects of the ligands on the final distribution of aldehydes and they found that, when monodentate ligands were used, the regioselectivity depended on the basicity of the ligand. Thus, in the hydroformylation of eugenol **2b** with the Rh/$P(OPh)_3$ catalytic system, isomerization to the internal olefin was observed, but when the reaction was driven in the presence of PPh_3 it was not. However, the use of more basic phosphines, such as $P(Cy)_3$ and $P(n\text{-}Bu)_3$, decreased the activity and the regioselectivity in the linear aldehyde. The activity of the less basic ligands is higher because the electron-withdrawing ligands decreased the back-donation to carbon monoxide and thus weakened the binding of the carbonyls. This favours the dissociation of carbon monoxide because it increases the reaction rate [3]. The effect of the basicity of the monodentate ligand on the regioselectivity could be explained by the basicity of the hydride. A basic phosphine leads to an increase in the nucleophilicity of the hydride. Therefore, the interaction of the hydride with the terminal carbon (which bears a more positive fractional charge than the β-carbon) is favoured, leading to trace amounts of branched aldehyde **4a** [13].

When diphosphine-based systems (dppe, dppb, BISBI and NAPHOS) were used, the bite angle of the diphosphine and the regioselectivity were related (Table 2). Thus, it can be observed that ligands with big bite angles (BISBI and NAPHOS) afforded the linear aldehyde almost exclusively, while for ligands with small bite angles (dppe, dppp) the regioselectivity for the linear aldehyde decreased dramatically (<40%). This behaviour has been attributed to the coordination mode of these ligands.

In the trigonal-bipyramidal rhodium-hydride species, the ligands with small bite angles coordinate in apical-equatorial positions giving more basicity to the hydride (*trans* to a P ligand) than the diphosphines with major bite angle (around 120°) that coordinates in equatorial–equatorial mode. The greater basicity of the hydride makes it possible