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Catalytic Synthesis of (R) and (S) Citronellol by Homogeneous Hydrogenation over Amidophosphinephosphinite and Diaminodiphosphine Rhodium Complexes

M. Ait Ali, S. Allaoud, A. Karim*

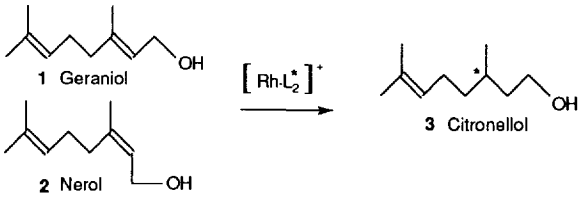
Departement de Chimie, Faculté des Sciences-Semlalia
Université Cadi Ayyad BP S15 Marrakech (Maroc)

A. Roucoux and A. Mortreux

Laboratoire de Chimie Organique Appliquée, URA CNRS 402, ENSC Lille,
BP 108, 59652 Villeneuve d'Ascq (France)

***Abstract** : The enantioselective production of citronellol (ee = 84 % R and 80 % S) is performed by hydrogenation of geraniol 1 and nerol 2 over cationic rhodium complexes modified by amidophosphinephosphinite and diaminodiphosphine chiral ligands.*

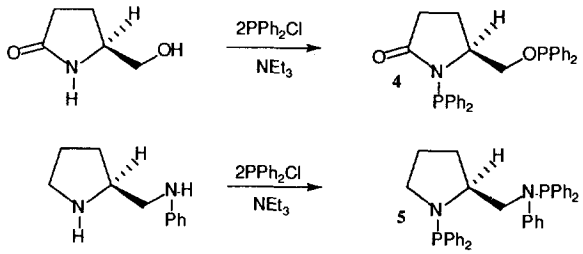
The asymmetric hydrogenation of allylic alcohols **1** and **2** has already been described using rhodium catalysts and chiral diphosphines[1] (eq. 1).



eq. 1

The optical yields observed so far with these systems are quite low, as compared with other ruthenium based systems, for which however catalyst and ligand synthesis still remain rather tedious processes[2,5].

We have found that ligands **4** and **5**, synthesized easily from pyroglutamic acid via the synthesis of (S)-5-oxoprolinol and (S)-2-anilinomethyl-pyrrolidine followed by a simple phosphinylation with PPh_2Cl (eq. 2)[6-10], are efficient chiral modifiers for the above reaction catalyzed by rhodium complexes.



eq. 2

The reactions were conducted with 0.1 mmol of catalyst and 5 mmol of substrate dissolved in 20 ml of solvent, in a 100 ml stainless steel autoclave under 10 atm of H_2 at room temperature for 8h. The catalysts used were the ionic $[Rh(COD)L_2^*]^+ ClO_4^-$ complexes synthesized according to literature methods[11-13]. Some typical results are reported in table 1.

Table 1. Asymmetric hydrogenation of allylic alcohols **1** and **2** catalysed by $[Rh(COD))L_2^*] ClO_4$ complexes.[a]

Ligand	Substrate	Solvent	yield (%)	Selectivity[b]	e.e. (%)	Configuration
4	1	THF	95.5	81.5	26	(S)
4	1	Ethanol	70.0	71.0	81	(R)
4	1	Benzene	86.5	81.5	84.5	(R)
4	2	THF	96.0	82	30	(R)
4	2	Ethanol	69.5	72.5	77	(S)
4	2	Benzene	91.5	84	80.5	(S)
5	1	THF	100	76.0	56	(R)
5	1	Benzene	98.0	97.0	60.5	(S)
5	2	THF	100	88	50	(S)
5	2	Benzene	95.5	94.5	68	(R)

[a] See text for conditions

[b] Defined as the monoolefin/monoolefin + saturated compound ratio

[c] (S) - citronellol specific rotation $\alpha_D^{25} = -3,2$ (c=5,CH_3OH)

The above results are interesting in several respects :

(i) The observed selectivities depend on the nature of the solvent, the coordinating ligand THF giving rise to the production of the enantiomer with the opposite configuration of that produced with ethanol or benzene.

(ii) According to the E or Z stereochemistry of the double bond in the substrate, the two different enantiomers of citronellol can be synthesized with good enantioselectivities (ee>80 %) : the stereochemical control of the enantioselectivity suggests an important role of the allylic hydroxyl group in the diastereoisomeric transition state responsible for the enantio differenciation[13].

(iii) Due to the large number of ligands available from aminoalcohols, and particularly to the now well established synthetic tool leading to modifications of the electronic and steric properties upon variation of the chlorodialkylphosphine used in eq.2, further studies are in progress with the aim to enhance both chemo and enantioselectivity of this reaction.

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