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Hydroaminomethylation of Styrene with Morpholine catalysed by a Rhodium Complex with a Phosphino Amino Alcohol Ligand†

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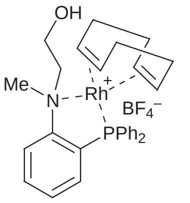
Hydroaminomethylation of styrene with morpholine catalysed by a cationic rhodium complex with a *P,N* ligand possessing a hydroxy group and the influence of the temperature on the chemo- and regio-selectivity are described.

Hydroaminomethylation of alkenes, originally discovered by Reppe and Vetter[1] was first applied to styrenes by Rische and Eilbracht[2] using [Rh(cod)Cl]$_2$ as catalyst and led with high yields predominantly to the corresponding *iso*-amines. The regioselectivity in the primary hydroformylation step appears to be influenced by the amine used for the reaction. Here a cationic rhodium complex **1** with a *P,N* ligand possessing a hydroxy group is applied to hydroaminomethylation of styrene with morpholine.



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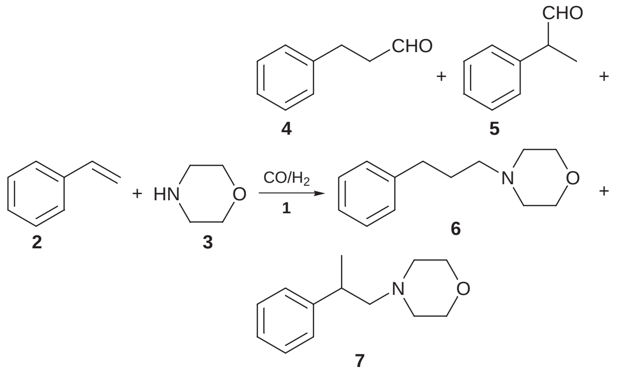

Scheme 1

The increased catalytic activity of some complexes by the use of *P,N*-bidentate ligands is well known.[3] Rhodium complex **1** for instance, the synthesis and characterization of which were reported in a previous paper, showed such activity in hydroformylation of styrene.[4] The presence of the uncoordinated hydroxy group lowers the rate of hydroformylation with no influence on the regioselectivity of the reaction.[4] The hydroaminomethylation of styrene with morpholine catalysed by complex **1** (Scheme 1, Table 1) proceeds to quantitative conversions of styrene and gives high yields of the *n*-amine **6** and *iso*-amine **7** with a good regioselectivity towards **7** and with no enamines as by-products, under a pressure of 100 bar ($CO:H_2 = 1:1$) and with a high styrene:**1** ratio of about 1500 : 1. On the other hand, it has been reported that, when [Rh(cod)Cl]$_2$ was used as catalyst for hydroaminomethylation of 1-alkenes under 110 bar total pressure of CO/H_2, a styrene : catalyst ratio of 100 : 1 was necessary in order to obtain up to quantitative conversions and yields of *n*- and *iso*-amines.[2] Thus, it is important to point out that the catalytic activity of the rhodium complex **1** in the hydroaminomethylation reaction is higher than that of [Rh(cod)Cl]$_2$, and it is reasonable to suppose that this is due to the presence of the *P,N* ligand having an additional alcohol function. The reaction is temperature dependent. As shown in Table 1, at 60 °C with a styrene : **1** ratio of 509 : 1, the chemoselectivity towards the amines **6** and **7** was poor. A significant amount of aldehydes **4** and **5**, obtained in the primary hydroformylation step, did not react further with morpholine. The regioselectivity towards the total of *iso*-products **5** and **7** (86.8%) is slightly lower than that obtained for the *iso*-aldehyde (89.4%), prepared by hydroformylation of styrene by complex **1**, at 60 °C.[4] Thus it appears that the presence of the amine affects the regioselectivity during the hydroformylation of styrene catalysed by complex **1**. At higher temperatures the chemoselectivity towards the amines **6** and **7** is high. Best results were obtained at 100 °C, yielding the corresponding amines, while only 1.1% of the aldehyde **4** was detected as

Table 1 Hydroaminomethylation of styrene with morpholine catalysed by complex **1**[a]

Entry	Styrene:**1** ratio	T/°C	t/h	Aldehydes(%) **4**	**5**	Amines(%) **6**	**7**	S_{am}[b] (%)	Total *iso*/*n* ratio[c]
1	509	60	39	2.0	38.1	11.2	48.7	59.9	6.6 : 1
2	1484	80	24	3.2	—	11.3	85.5	96.8	5.9 : 1
3	1500	100	24	1.1	—	13.3	85.6	98.9	5.9 : 1

[a]Reaction conditions: solvent, 1,4-dioxane–THF (1 : 1, entry 1; 5 : 1, entries 2 and 3); initial total pressure of CO/H_2 (1 : 1) = 100 bar. Conversion of styrene (in all experiments): 100%. [b]S_{am} = selectivity towards amines. [c]Represents the *iso* (aldehyde + amine) : *n* (aldehyde + amine) ratio.

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by-product. However, the regioselectivity towards the total *iso*-products **5** and **7**, which is the same for both 80 and 100 °C, is slightly lower than that obtained at 60 °C.

The influence of the solvent plays an important role on the course of the reaction. In 1,4-dioxane–dichloromethane (1 : 1), polymerization and side reactions are predominant and significant amounts of oligomers were detected, which were not investigated further. An analogous polymerization has also been reported during hydroaminomethylation of 1-octene in 1,2-dichloroethane as solvent.[5,6]

Experimental

Styrene (1.7 ml, 14.84 mmol), morpholine (1.3 ml, 14.92 mmol) and the rhodium complex **1** (0.01 mmol) in 1,4-dioxane–THF (30 ml, 5 : 1) were placed under argon in an oven-dried autoclave, which was then closed, pressurized with syngas ($CO : H_2 = 1 : 1$) to 100 bar and heated at the required temperature. After the required reaction time the autoclave was cooled to room temperature, the pressure carefully released and the solution passed through Celite and analysed by GC, GCMS and ^1H NMR. Conversions were determined by GC.

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