



Rhodium Catalysed Asymmetric Hydrosilylation of Ketones Using Phosphorus-Containing Oxazoline Ligands

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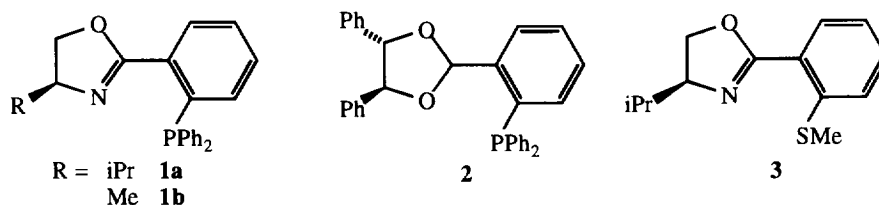
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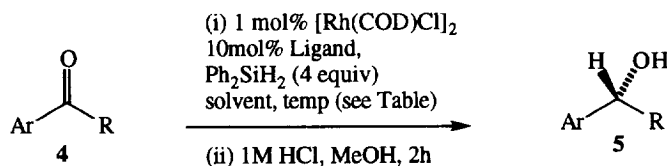
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Abstract: The rhodium catalysed hydrosilylation of ketones in the presence of the phosphorus-containing oxazoline ligand **1a** has afforded up to 86% ee in the conversion of acetophenone into phenethyl alcohol. Copyright © 1996 Elsevier Science Ltd

The rhodium catalysed asymmetric hydrosilylation of ketones in the presence of bis-oxazoline ligands and pyridyl oxazoline ligands has been reported by several groups.¹ Ligands **1**, **2**, and **3** have been reported by ourselves² and by others³ to afford excellent levels of enantioselectivity in palladium catalysed asymmetric allylic substitution reactions.



Herein we report our preliminary findings of the application of these ligands to the rhodium catalysed hydrosilylation of ketones.⁴ Thus the ketone was treated with catalytic amounts of ligand and rhodium complex and then with diphenylsilane under the conditions indicated in the Table. In the case of the hydrosilylation of acetophenone, we determined that the valinol derived ligand **1a** provided the highest enantioselectivity.⁵ The use of alternative rhodium complexes, including $\text{Rh}(\text{cod})_2\text{BF}_4$ or $\text{Rh}(\text{cod})\text{Cl}]_2 / \text{AgBF}_4$ were also effective catalysts, and the observed enantioselectivities were almost identical in the cases examined. Ligand **1b** was found to induce moderate levels of enantioselectivity, whereas the acetal ligand **2** and the sulfur-containing ligand **3** were ineffective.



The use of naphthylphenylsilane has been previously reported to afford enhanced enantioselectivities for other rhodium catalysed hydrosilylation reactions.⁶ We found that this reagent did enhance the enantioselectivity somewhat (to 86% ee). As well as acetophenone, several other ketones were reduced with good enantioselectivity, as indicated in the Table.

Table. Rhodium Catalysed Asymmetric Hydrosilylation of Ketone 4

Ketone	Ligand	Solvent	Temp (°C)	Yield of 5 (%)	E.e. of 5 (%) ^a
PhCOMe	1a	none	0	54	73
PhCOMe	1a	none	-40	79	73
PhCOMe	1a	THF	0	54	73
PhCOMe	1a	THF	-78	86	82
PhCOMe ^b	1a	THF	-78	85	86
PhCOC ₃ H ₇	1a	THF	-78	90	81
(1-Naph)COMe	1a	THF	-78	90	61
Tetralone	1a	THF	-78	70	59
PhCOMe	1b	THF	-78	77	51
PhCOMe	1b	CH ₂ Cl ₂	-78	70	48
PhCOMe	2	CCl ₄	0	58	14
PhCOMe	3	THF	-78	45	0

^aEnantioselectivities were determined by chiral hplc, and the (R)-configuration was determined by using commercially available standards and by specific rotation data.

^bIn this case, naphthylphenylsilane was used.

In conclusion, the phosphorus-containing oxazoline ligands **1a** and **1b** are effective for the rhodium catalysed asymmetric hydrosilylation of aromatic ketones. Further work is in progress to extend the scope of this reaction.

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References and Notes

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