Journal of Organometallic Chemistry, 390 (1990) C81–C83
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 21010PC

Preliminary communication

Asymmetric catalysis

LVI *. Enantioselective hydrosilylation of acetophenone with a rhodium / picolineoxazoline catalyst 1:1

Henri Brunner * and Paul Brandl

Institut für Anorganische Chemie, Universität Regensburg, Universitätsstr. 31, D-8400 Regensburg (F.R.G.)

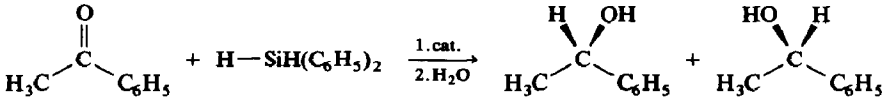
(Received April 9th, 1990)

Abstract

The direction of optical induction is inverted in going from pyridineoxazoline **1** to picolineoxazoline **2** as cocatalyst in the Rh-catalyzed asymmetric hydrosilylation of acetophenone with diphenylsilane. In the case of ligand **2**, a 1.2-fold excess of the ligand is sufficient to achieve the highest enantiomeric excess.

Optically active nitrogen ligands, such as pyridineimines [2,3], pyridinethiazolidines [4,5], and pyridineoxazolines [6,7] are good cocatalysts for the Rh-catalyzed enantioselective hydrosilylation of acetophenone with diphenylsilane, to give, after subsequent hydrolysis, 1-phenylethanol (Scheme 1). Common to all these catalyses is the fact that an excess of the nitrogen ligand is required for a high optical induction.

In the present study we have demonstrated that on going from the pyridineoxazoline cocatalyst **1** to its 6-Me analogue **2** that (i) the direction of the optical



Scheme 1

* For Part LV, see ref. 1.

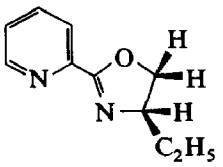
Table 1

Hydrosilylation of acetophenone (1 ml) with H_2SiPh_2 (1.6 ml); catalyst $[Rh(cod)Cl]_2$/ligand; 0 → 20 °C; 18 h; Rh/substrate 1/200

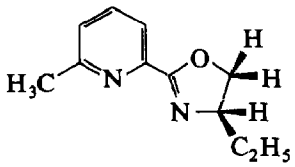
Entry	Ligand	Rh/ligand	% Hydrosilylation [a]	% Chemical yield [b]	% e.e.	Configuration	Number of runs
1	1	1/0.8	87	66	17.7, 19.7	*S*	2
2	1	1/0.9	90	65	17.3, 19.5	*S*	2
3	1	1/1.0	87	68	19.0, 21.2	*S*	2
4	1	1/1.1	85	67	21.0, 22.0	*S*	2
5	1	1/1.2	89	69	20.0, 21.8	*S*	2
6	1	1/2.0	91	70	32.6	*S*	1
7	1	1/5.0	89	70	37.8, 39.8	*S*	2
8	2	1/0.8	93	62	30.3, 32.7	*R*	2
9	2	1/0.9	94	68	34.1, 36.1	*R*	2
10	2	1/1.0	83	69	40.9, 42.1	*R*	2
11	2	1/1.1	91	75	44.4, 45.2	*R*	2
12	2	1/1.2	90	81	45.1, 47.3	*R*	2
13	2	1/2.0	93	82	47.4	*R*	1
14	2	1/5.0	92	83	46.9, 48.1	*R*	2

[a] Silyl ether $PhCH(Me)OSiHPh_2$ + silyl enol ether $PhC(OSiHPh_2)=CH_2$ [6]. [b] Silyl ether $PhCH(Me)OSiHPh_2$ which on hydrolysis gives 1-phenylethanol [6].

induction is inverted, and (ii) an excess of the ligand no longer is necessary to obtain high optical inductions.



(1)



(2)

In a procedure analogous to that used for **1** [6], oxazoline **2** was synthesized by condensation of (*R*)-(−)-2-amino-1-butanol with the corresponding carboximidate, obtained by methanolysis of 2-cyano-6-methyl-pyridine [8].

In the hydrosilylation reactions depicted in Scheme 1 the ratio of Rh/ligand was varied from 1/0.8 to 1/5 at a constant Rh/substrate ratio of 1/200 (Table 1). The features were as follows:

(i) Inversion of the product configuration. With pyridineoxazoline **1** as a cocatalyst we obtain an excess of (*S*)-(−)-1-phenylethanol (entries 1–7). However, when the corresponding picolineoxazoline **2** was used, the direction of the optical induction was changed to (*R*)-(+)-1-phenylethanol (entries 8–14). It is surprising that a small difference, involving only an additional methyl group in 6-position of the pyridine ring, should invert the enantioselectivity when all the other reaction conditions are kept constant.

(ii) Effects of excess of the ligand. For pyridineoxazoline cocatalysts it was previously found that the optical induction in the Rh-catalyzed hydrosilylation could be increased by use of a large excess of ligand [6]. This was confirmed in the present study. Variation of the Rh/**1** ratio in small steps from 1/0.8 to 1/1.2 caused a change in optical induction from 17.3% to 22.0% e.e. (entries 1–5). Use of a

two-fold ligand excess increased the e.e. to 32.6% (entry 6) and a five-fold excess to 37.8 or 39.8% e.e. (entry 7). With a Rh/**2** ratio of 1/0.8 an enantioselectivity of 30.3% and 32.7% e.e. was obtained (entry 8), although in this case and also in cases 1, 2, and 9, the hydrosilylation reaction is probably partially catalyzed by an achiral $[Rh(cod)Cl]_2$ species. When the concentration of the ligand is increased in small steps to a Rh/**2** ratio of 1/1.2, the optical induction increases up to 47.3% (entries 9–12). Interestingly, Rh/ligand ratios of 1/2 or 1/5 do not give higher e.e.s (entries 13, 14). Thus, as with to the Rh/phosphine ratios used in enantioselective hydrogenation reactions, a 1.2-fold ligand excess is sufficient for the $[Rh(cod)Cl]_2$/**2** system to achieve the highest enantiomeric excess in the hydrosilylation of acetophenone with diphenylsilane.

Experimental section

(*R*)-(+)-4-Ethyl-2-(2-pyridinyl)oxazoline (**1**) was made as described previously [6]. (*R*)-(+)-4-Ethyl-2-(2-picolinyl)oxazoline (**2**) was prepared in the same way as **1**, starting from 2-cyano-6-methylpyridine [8], which was converted into methyl 2-picoline carboximidate by use of a 10% excess of CH_3ONa. For purification, **2** was passed with ether through a 30 cm Al_2O_3-layer (medium activity). Yield 58–64%; colourless oil.

^1H NMR ($CDCl_3$, 250 MHz, i-TMS): δ 1.03 (t, $J = 7.5$ Hz, 3H), 1.55–1.88 (m, 2H), 2.64 (s, 3H), 4.13 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 1H), 4.29 (m, 1H), 4.56 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 1H), 7.25 (m, 1H), 7.66 (m, 1H), 7.88 (m, 1H). MS (EI): *m/z* (%) 190 (M^+, 8), 161 (100), 133 (37), 106 (73), 92 (38), 65 (37). Optical rotation (*c* 0.27, $CHCl_3$) $[\alpha]_{589}^{20}$ + 81.6, $[\alpha]_{578}^{20}$ + 85.7, $[\alpha]_{546}^{20}$ + 99.6, $[\alpha]_{436}^{20}$ + 200.6, $[\alpha]_{365}^{20}$ + 406.6.

Anal. Found: C, 69.09; H, 7.89; N, 14.26. $C_{11}H_{14}N_2O$ calcd.: C, 69.46; H, 7.41; N, 14.72%.

The enantioselective hydrosilylations were carried out as described in ref. 6, under the reaction conditions specified in Table 1.

Acknowledgement. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and BASF AG, Ludwigshafen, for support of this work.

References

1 H. Brunner, M. Muschiol and F. Prester, Angew. Chem., submitted for publication.
2 H. Brunner and G. Riepl, Angew. Chem., 94 (1982) 369; Angew. Chem. Int. Ed. Engl., 21 (1982) 377; Angew. Chem. Suppl., 769 (1982).
3 H. Brunner, B. Reiter and G. Riepl, Chem. Ber., 117 (1984) 1130.
4 H. Brunner, G. Riepl and H. Weitzer, Angew. Chem., 95 (1983) 326; Angew. Chem. Int. Ed. Engl., 22 (1982) 331; Angew. Chem. Suppl., (1983) 445.
5 H. Brunner, R. Becker and G. Riepl, Organometallics, 3 (1984) 1354.
6 H. Brunner and U. Obermann, Chem. Ber., 122 (1989) 499.
7 H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, M. Kondo and K. Itoh, Organometallics, 8 (1989) 846.
8 W.E. Feely, G. Evanega and E.M. Beavers, Org. Synth. Coll. Vol. V, (1973) 269.