CHEMISTRY LETTERS, pp. 1007-1008, 1985.

ASYMMETRIC HYDROGENATION OF GERANIOL AND NEROL CATALYZED BY BINAP—RHODIUM(I) COMPLEXES

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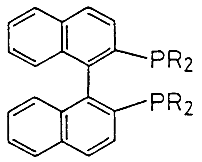
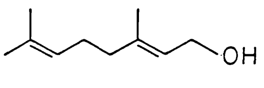
A novel direct synthesis of optically active citronellol has been investigated by asymmetric hydrogenation of geraniol and nerol catalyzed by various BINAP—Rh(I) complexes.

Homogeneous asymmetric hydrogenation of olefins using chiral phosphine—Rh(I) complex catalysts has been extensively investigated. Usually, however, high enantioselection has been achieved only with α-acylaminoacrylic acids or related substrates. In the course of exploring utility of our BINAP ligand 1,[1)] we found that geraniol (4) and nerol (5) can be hydrogenated in the presence of the Rh(I) complexes to citronellol (6) of up to 66% optical purity.[2)] Original BINAP (1) and newly synthesized TolBINAP (2) and CyBINAP (3)[3)] were used. Table 1 lists some representative results.

Although further efforts should be exerted to improve the conditions to be of practical value, the present reaction is important in that this is one of the limited number of examples of asymmetric olefin hydrogenation of non-enamide substrates accomplished in fair optical yields. The following observations are particularly noteworthy. (1) Neutral BINAP—Rh(I) catalysts gave higher optical yields than the corresponding cationic Rh catalysts. This is in contrast with the fact that the most effective catalysts for asymmetric hydrogenation of α-acylamino-acrylic acids are the cationic complexes of chiral diphosphines. (2) The cationic species exhibited higher catalytic activities, but they also catalyzed the hydrogenation of the C(6)—C(7) double bond. (3) A Rh(I) complex with CHIRAPHOS ligand[4)] which possesses a five-membered chelate ring was inactive as the hydrogenation catalyst, while a DIOP—Rh(I) complex[5)] promoted the reaction smoothly but in



1, R = C_6H_5
2, R = p-$CH_3C_6H_4$
3, R = cyclohexyl



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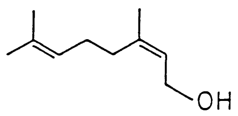

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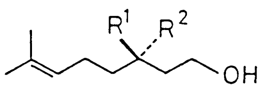

(R)-6, $R^1 = CH_3$, $R^2 = H$
(S)-6, $R^1 = H$, $R^2 = CH_3$

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Table 1. Asymmetric Hydrogenation of Geraniol (**4**) and Nerol (**5**)[a)]

Substrate	Catalyst precursor[b)]	Solvent	Initial H_2, atm	Product **6**	
				config.	% ee[c)]
4	[(+)-BINAP]-Rh^N	benzene	30	*R*	58
4	[(+)-BINAP]-Rh^+	benzene—CH_2Cl_2	2	*R*	18
5	[(+)-BINAP]-Rh^N	benzene	30	*S*	52
5	[(+)-BINAP]-Rh^N	CH_2Cl_2	20	*S*	52
5	[(+)-*p*-TolBINAP]-Rh^N	benzene	50	*S*	50
5	[(+)-CyBINAP]-Rh^N	benzene	20	*S*	66
5	[(+)-DIOP]-Rh^N	benzene	50	*S*	13
5	[(-)-CHIRAPHOS]-Rh^N	benzene	50	-	—[d)]

a) Substrate/catalyst = 50—190, room temperature, 24—80 h, 60—90% conversion. b) [(+)-BINAP]-Rh^N = Rh((*R*)-(+)-binap)(cod)Cl, [(+)-BINAP]-Rh^+ = [Rh((*R*)-(+)-binap)]ClO_4, [(+)-*p*-TolBINAP]-Rh^N = Rh((*R*)-(+)-tolbinap)(cod)Cl, [(+)-CyBINAP]-Rh^N = Rh((+)-cybinap)(cod)Cl, [(+)-DIOP]-Rh^N = Rh((2*S*, 3*S*)-(+)-diop)(cod)Cl, [(-)-CHIRAPHOS]-Rh^N = Rh((2*S*,3*S*)-(-)-chiraphos)(cod)Cl (cod = cyclooctadiene). These complexes were prepared by addition of the corresponding diphosphine to $[Rh(cod)Cl]_2$ in CH_2Cl_2 followed by removal of the solvent and analyzed by ^1H and ^{31}P NMR. c) Determined by HPLC according to Ref. 6. d) Conversion <4%.

poor optical yield under similar conditions. (4) Solvents such as benzene or dichloromethane afforded better results than methanol and THF. (5) Hydrogenation of stereoisomeric **4** and **5** with the same BINAP—Rh complex gave the enantiomeric **6** with comparable enantioselectivity, implying that difference of the C(3) methyl and 4-methylpent-3-enyl group is not important in the stereoselection. Rather the C(2) enantiofaces are differentiated at some stages of the catalysis. At this moment we know little about the reaction mechanism, but the allylic hydroxyl group seems to be playing an important role at the enantioselection stage.[7)]

References

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(Received April 30, 1985)