CHEMISTRY LETTERS, pp. 1691-1694, 1981.

NEW CHIRAL AMINOPHOSPHINES PREPARED FROM L-ORNITHINE AND CATALYTIC ASYMMETRIC HYDROGENATION USING THEIR RHODIUM(I) COMPLEXES

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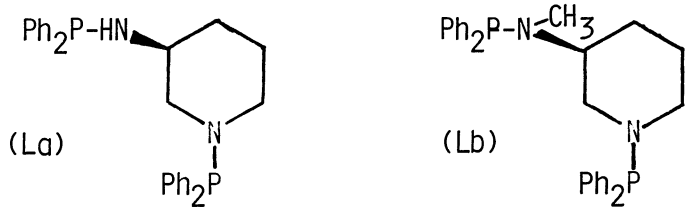
From readily preparable chiral diamines were obtained new aminophosphines, (3S)-[N,N'-bis(diphenylphosphino)]-3-aminopiperidine, and (3S)-[N,N'-bis(diphenylphosphino)]-3-(methylamino)piperidine. Asymmetric hydrogenation of α-acylaminoacrylic acids, employing Rh(I) complexes with these aminophosphines as catalyst, gave optically active N-acyl-α-amino acids.

In recent years asymmetric hydrogenation of α-acylaminocinnamic acids or α-acylaminoacrylic acids, using rhodium(I) complexes with chiral phosphine ligands as catalysts, has been extensively investigated for obtaining optically active α-amino acids[1]. Among various chiral phosphine ligands so far reported aminophosphines derived from chiral 1,2-diamines have been attracting much interest because these 1,2-diamines as chiral sources can be easily obtained in a variety of structures. However, most of chiral aminophosphines already known have two equal asymmetric centers with the same substituents and of the same chirality, and consequently have a C_2-symmetry axis in a molecule making two phosphorous atoms equivalent[2)3)4)]. There have been few reports about chiral aminophosphine ligands without C_2-symmetry and having two unequivalent phosphorous atoms[5)], while a number of chiral diphosphine ligands not only of the former type[6)7)8)] but of the latter type[9)10)] were reported to give good results in the asymmetric hydrogenation.

Here we wish to report the preparation of new chiral aminophosphines, (3S)-[N,N'-bis(diphenylphosphino)]-3-aminopiperidine(L_a) and (3S)-[N,N'-bis(diphenylphosphino)-3-(methylamino)piperidine(L_b), without a C_2-symmetry axis in a molecule, and the results of asymmetric hydrogenation of α-acylaminoacrylic acids using their rhodium(I) complexes as catalysts. It can be expected that (L_a) and (L_b), when coordinated to rhodium, form a seven-membered chelate ring with a rigid conformation and the number of its possible chelate conformer is very limited,

Fig. 1



(La) (Lb)

because three C, C, N atoms in the chelate are involved in a piperidine ring and bond angles of these atoms are quite restricted as is observed in the rhodium complex of BPPM[10], which also has two unequivalent phosphorous atoms and ring conjunct structure, and prefers exclusively one chelate conformation in its rhodium complex. From these structural features of (L_a) and (L_b) satisfactory results may be expected in the asymmetric hydrogenation using their rhodium complexes. Moreover detailed studies about asymmetric hydrogenation using these newly prepared aminophosphines, having unique structure, as ligands would provide some informations on the relationship between the asymmetric induction and the chelate ring strucutre.

The preparation of aminophosphines (L_a) and (L_b) were carried out as outlined in Fig. 2. (S)-3-Aminopiperidine[11], the parent diamine of (L_a), was obtained from L-ornithine monohydrochloride by the method designed by Saburi and Yoshikawa[12]. (S)-3-Methylaminopiperidine[13] was newly prepared by $LiAlH_4$ reduction of N-formyl-(S)-3-aminopiperidone obtained from the careful formylation of (S)-3-amino-piperidone hydroformate by formic acid in the presence of acetic anhydride[14]. These two diamines reacted with chlorodiphenylphosphine in the presence of triethylamine to give aminophosphines (L_a) and (L_b), respectively. (L_a) was obtained as a colorless viscous oily product, and (L_b) was crystallized from hexane to afford white microcrystals[15]. Cationic rhodium complexes with these aminophosphine ligands, [Rh(COD)(L_a)]ClO_4 and [Rh(COD)(L_b)]ClO_4 (COD stands for 1,5-cyclooctadiene)[16] were prepared according to the method in the literature[17]. After recrystallization from dichloromethane-ethanol mixture these complexes were used as catalyst for asymmetric hydrogenation of α-acylaminoacrylic acids.

The results of the hydrogenation in various conditions are shown in Table. Products were isolated according to the method in the literature[6], and the optical purities were determined by comparing the optical rotations of the products with those of optically pure N-acyl-α-amino acids[6]. The hydrogenation reaction proceeded almost quantitatively at initial hydrogen pressure of 8 kg/cm^2 and at room temperature when ethanol, methanol, or ethanol-benzene mixture was used as solvent

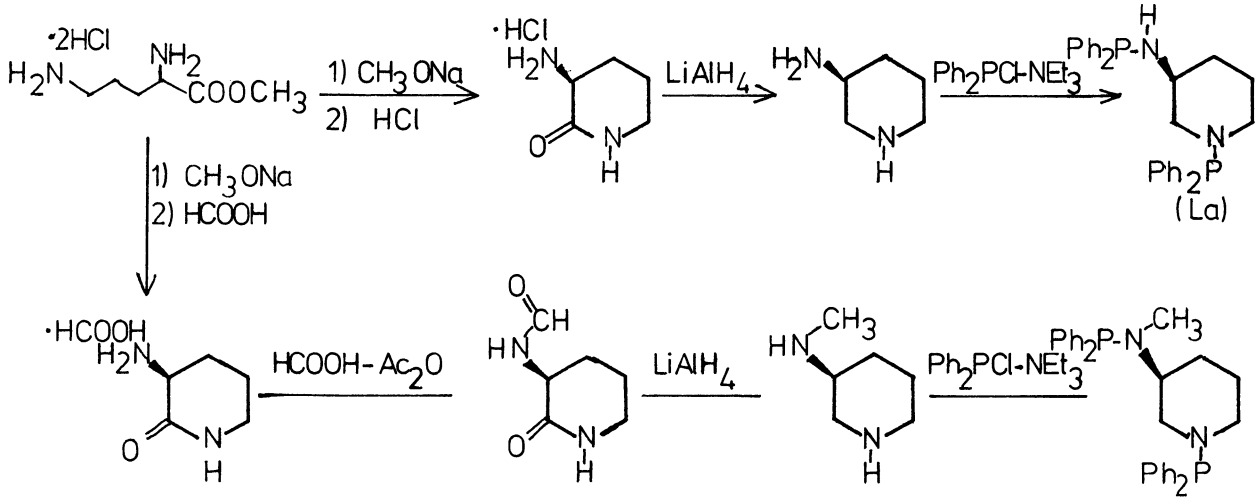
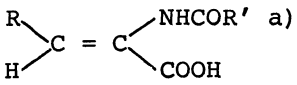


Fig. 2 Preparation of Aminophosphines

Table Asymmetric Hydrogenation of  a)

R	R'	Ligand	Solvent	Conv.	%e.e.	Confign.
H	CH_3	(L_a)	EtOH-PhH(7:3)	100	80	(S)
		(L_b)	EtOH-PhH(7:3)	100	84	(S)
Ph	CH_3	(L_a)	EtOH	100	45	(S)
		(L_a)	EtOH-PhH(1:1)	100	68	(S)
		(L_a)	EtOH-PhH(7:3)	100	73	(S)
		(L_a)	EtOH-PhH(7:3) b)	100	65	(S)
		(L_a)	MeOH	100	60	(S)
		(L_a)	PhH	5		
		(L_b)	EtOH-PhH(7:3)	100	79	(S)
Ph	Ph	(L_a)	EtOH-PhH(7:3)	100	59	(S)
		(L_b)	EtOH-PhH(7:3)	100	73	(S)

a) [Complex] = 5.0×10^{-2} mmol; [Substrate] = 5.0mmol; Solvent 50 ml; H_2 8 kg/cm^2

b) NEt_3(3.0eq. for Rh) was added.

while the reaction in some other solvents such as benzene and tetrahydrofuran did not smoothly proceed. Although the optical purities of the products vary significantly depending on the solvents, as is often observed in similar catalytic systems involving other aminophosphine rhodium complexes[4], the products with (S)-configuration were always obtained preferentially. It should be noted that N-methylation of the ligand does not affect the stereoselectivity of the reaction but causes slight increase in the optical yields.

Recently it has been reported that in the rhodium catalyzed hydrogenation using (R,R)-1,2-[bis-N-methyl(diphenylphosphino)aminocyclohexane] as a ligand, amino acids with (S)-configuration were preferentially formed in high selectivity, while (R)-amino acids were obtained as the major products in the hydrogenation by rhodium complex of (R,R)-[bis(diphenylphosphino)aminocyclohexane][3,4]. In the case of some other aminophosphine ligands similar drastic inversion of the stereoselectivity was brought about by N-methylation of aminophosphines[3]. This fact was explained in terms of the difference in the helical orientation of the phenyl rings in the ligands caused by steric repulsions between the phenyl and N-methyl groups in the aminophosphine coordinated to rhodium. In our results, contrary to them, rhodium complex of (L_b) containing N-methyl group exhibited the stereoselectivity similar to that of the complex of (L_a) with no N-methyl groups. This result indicates that N-methylation of the ligand does not cause any differences in the conformations of the ligand including the helical orientation of the phenyl rings.

The mechanism of asymmetric induction of hydrogenation using rhodium complexes having five-membered chelate ring has been gradually clarified[18,19]. However it is not necessarily applicable for seven-membered chelate diphosphine rhodium

complexes, especially for complexes of aminophosphines which may give unique stereoelectronic effects to the coordinated olefin or ligating alkyl group formed at the transition state of the reaction. So it is still ambiguous with regard to the mechanism of asymmetric induction of the hydrogenation using aminophosphines as ligands. Further studies on the structures of the complexes with (L_a) and (L_b) and its correlation to asymmetric induction are now in progress.

Acknowledgement: Authors express gratitude to Ajinomoto Co., Ltd., for kindly providing L-ornithine monohydrochloride.

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15) (L_a) ^{1}H NMR($CDCl_3$): δ(ppm)=1.1-3.2(m,9H,CH_2 and CH) 7.2(m,20H,C_6H_5) (L_b) ^{1}H NMR($CDCl_3$): δ(ppm)=1.2-3.4(m,CH_2 and CH), 2.45(d,N-CH_3,J_{P-H}=5.0Hz) 7.3(m,20H,C_6H_5)
16) [Rh(COD)(L_a)]ClO_4 Found: C,57.9; H,5.7; N,3.6; Cl,4.9. Calcd. for $C_{37}H_{42}N_2P_2ClO_4Rh$: C,57.2; H,5.4; N,3.6; Cl,4.6. ^{1}H NMR($CDCl_3$): δ(ppm)=1.6-3.8 (m,17H,CH_2 and CH), 4.7(m,4H,-CH=CH-), 7.2-8.1(m,20H,C_6H_5) [Rh(COD)(L_b)]ClO_4 ^{1}H NMR($CDCl_3$): δ(ppm)=1.5-3.4(m,CH_2 and CH),2.13(d,N-CH_3, J_{P-H}=8.0Hz), 4.9 and 5.3(m,4H,-CH=CH-), 7.2-8.0(m,20H,C_6H_5)
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(Received September 30, 1981)