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ASYMMETRIC HYDROGENATION BY AN ATROPISOMERIC DIPHOSPHINITE RHODIUM COMPLEX

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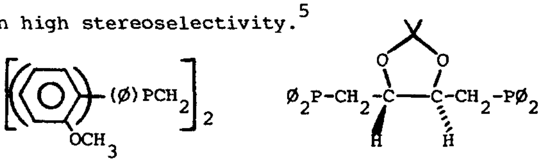
The direct production of optically active products from prochiral reactants can represent a substantial saving of time and materials. In the past few years chiral ligands, phosphines in most cases, have been developed which allow catalytic reactions to be carried out on prochiral substrates to produce chiral products of up to 96% optical purity.[1] Most of these studies, however, have focused upon P-chiral phosphines[1,2] such as I or C-chiral phosphines,[3,4] of which (-)diop II is best known, as chiral ligands. It has been recently shown that C-chiral phosphinites can also be used to obtain high stereoselectivity.[5]

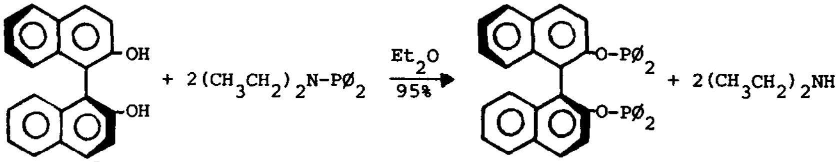
Figure 1.



I II

We now wish to report a new type of ligand whose chirality is the result of atropisomerism,[6] not due to an asymmetric center on phosphorous or carbon. (-)1,1'-Bi-2-naphthylbis(diphenylphosphinite) III was prepared from the easily resolved 1,1'-bi-2-naphthol IV.[7,8]

Figure 2.



(-) IV[8] 90% optically pure (-) III

Active IV was converted by diethylaminodiphenylphosphine into III in high yield; white needles from ethanol, mp 170-171° $[\alpha]_D^{20} = -38.7°$ (C=1.098 THF), slowly oxidized in air.

The complex formed by mixing two equivalents of III with one equivalent of $[Rh(cyclooctene)_2Cl]_2$(V) was an active hydrogenation catalyst, while other phosphinite to metal ratios gave poor results. Benzene, toluene, or a 1:1 mixture of toluene-acetone are good solvents for this catalyst system.

Prochiral unsaturated esters were reduced with this catalyst system under 95 atm. hydrogen. The resulting saturated acids and esters were from 6 to 76% optically pure, Table I. The carboxylic acids tended to give lower optical yields than the corresponding esters. Lowering the reaction temperature has a small effect on the rate, but resulted in improved optical yields.

Although the activity of this catalyst system is low, the optical purities of the products compare favorably with results obtained with the other two classes of chiral ligands.[9] For example, the optical yield in the case of N-acetyl-phenylalanine methyl ester was higher than that obtained using (-)diop.[4a]

It is becoming apparent that there must be a careful matching of ligand to substrate in order to obtain optimum optical purities. This new class of chiral ligands, therefore, provides a new tool in the arsenal of synthetic chemistry.

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R_1	R_2	R_3	R_4	Solvent	Temp. (C°)	Time (hrs)	Conv. [a](%)	O.Y. [b](%)	Average (atm) Abs. Pressure
H	NHAc	H	C_6H_5	toluene	25	24	50	9	102
CH_3	NHAc	H	C_6H_5	acetone toluene	0	24	41	76	97
H	NHAc	H	H	acetone toluene	0	24	100	6	95
CH_3	NHAc	H	H	acetone toluene	0	68.5	100	76	91
C_2H_5	H	C_6H_5	CH_3	toluene	0	53.5	60	44	99

Table I. Reduction of prochiral substrates R_1O_2C-CR_2=CR_3R_4 (R^3 cis to R^2) with $2x10^{-3}$ molar solution of 2:1-III:V. Substrate/catalyst=50. [a]± 5% analysis by NMR. [b]Determined on reaction mixture after isolation by distillation or simple chromatography and are corrected for the 90% O.P. of IV.

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