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RHODIUM(I)-CATALYZED ASYMMETRIC HYDROBORATION OF ALKENES WITH 1,3,2-BENZODIOXABOROLE[1]

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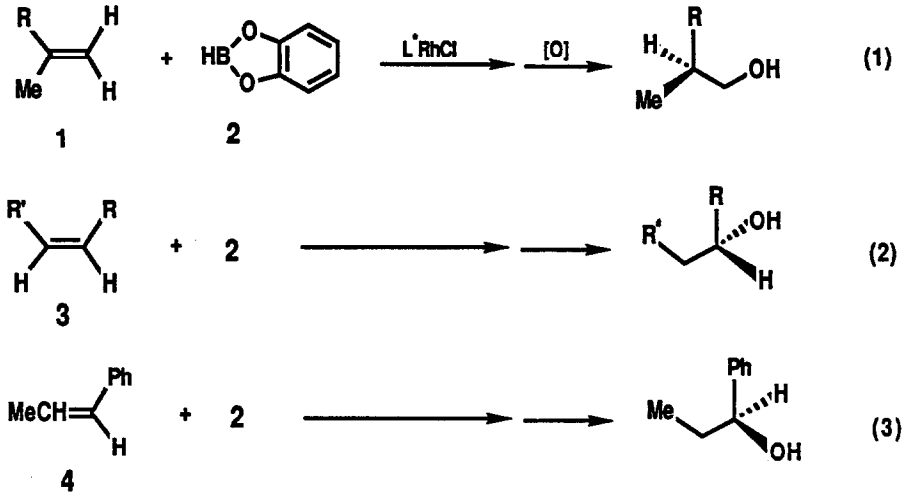
Summary: Several rhodium(I) complexes containing chiral phosphine, (+) DIOP, (+) BINAP, (S,S) CHIRAPHOS, and (S)(R) BPPFA, have been found to be effective as catalyst for the asymmetric hydroboration of prochiral alkenes with catecholborane (1,3,2-benzodioxaborole) to give optically active 2-alkyl-1,3,2-benzodioxaboroles. Among the ligands examined, DIOP has been recognized to be most effective to give high asymmetric induction.

Recently, Nöth and Mannig[2] reported that alkenes and alkynes can be hydroborated with catecholborane (2) in the presence of Rh-catalyst under extremely mild conditions. Although catalytic hydrometalations such as hydrosilylation[3] were widely examined, only a few reports were published on the catalytic hydroboration, because the reaction with most of hydroborating reagents proceeds readily without any catalysts. We wish to report here a catalytic hydroboration[4] for the synthesis of optically active alkylboronates by using homochiral Rh-complexes. Upon oxidation, these alkylboronates afford the corresponding alcohols with retention of configuration. Since halogenolysis, amination, and carbon homologation[5] are also known as useful synthetic methodologies, these optically active alkylboronate derivatives may provide corresponding asymmetric compounds.

Rhodium complexes with several chiral phosphine ligands such as (+) DIOP[6], (+) BINAP[6], (S,S) CHIRAPHOS[6], and (S)(R) BPPFA[6] have been examined with regard to the catalytic activity and enantioselectivity in the reaction of 1,1-disubstituted or internal alkenes with catecholborane (2). The results are summarized in Eqs 1-3 and Table 1.

Hydroboration of 2-phenylpropene with 2 in the presence of 1 mole% of [(+) DIOP]RhCl or [(+) BINAP]RhCl in toluene at -5 °C for 72 h, followed by oxidation with alkaline hydrogen peroxide gives (S)-2-phenyl-1-propanol in both 38% ee (entries 1 and 2). The same reaction with 2,3-dimethyl-1-butene in the presence of [(+) DIOP]RhCl provides (S)-2,3-dimethyl-1-butanol in 12% ee (entry 5). In both cases, catecohlborane preferentially attacks from the bottom enantiotopic face of the 1,1-disubstituted alkenes (1) to afford product alcohols with the same absolute configuration (eq. 1). Internal alkenes such as (Z)-3-hexene and norbornene are also hydroborated with 2 in the presence of [(+) DIOP]RhCl, and the resulting alkylborates, followed by oxidation are converted into the corresponding (S)-alcohols in yields of

71, and 81% with 10 and 59% ee respectively (entries 6 and 7). (Z)- and (E)-1-Phenyl-1-propene, 1,2-dihydronaphtalene, and indene also give the optically active alcohols in 47, 41, 14, and 73% ee (entries 10-15). It should be noted that the reaction with 1-phenyl-1-propenes gives the (S)-alcohol, whereas that with 1,2-dihydronaphthalene and indene affords the (R)-alcohols formed by the opposite stereoselection (eqs. 3 and 2).



The following observation and interpretation may be noteworthy. (a) In the presence of Rh-complexes with chiral phosphine ligands, catecholborane undergoes hydroboration with internal and 1,1-disubstituted alkenes to give, after oxidation, optical active alcohols. Although we have not optimized the conditions for the yields of alcohols, the rate of hydroboration is shown to be highly dependent on the substituents on alkenes and ligands employed. Rhodium complex with DIOP gives 58-93 % yields of alcohols from internal alkenes, while lower yields are given from 1,1-disubstituted alkenes. (b) All phosphine ligands examined have been found to be effective to asymmetric induction. Among them, DIOP has been recognized to be most effective and to give the optically active alcohols in high eantioselectivity. These inductions are greater than other results for hydrosilylation and hydroformylation of these alkenes, mediated by DIOP-rhodium catalysts[3a]. All of (+) DIOP, (+) BINAP, (S,S) CHIRAPHOS, and (S)(R) BPPFA complexes give alcohols having the same absolute configuration (S) in the reactions with 2-phenylpropene and norbornene, except the reaction in entry 4. (c) With regard to the mode of enantioface selection, the alcohols obtained by hydroboration/oxidation sequence have the same absolute configurations with those of products[3a] derived from asymmetric hydrosilylation, hydroformylation, and hydroesterification of these alkenes in the presence of DIOP-rhodium complexes. Thus, the asymmetric hydroboration proceeds virtually through the same mechanism of these chiral phosphine-rhodium catalyzed reactions which involves the cis-insertion of hydridorhodium species to the coordinated alkenes as a key step for asymmetric induction. (d) Both (E)- and (Z)-1-phenyl-1-propene give the same (S) alcohol with the comparable optical yield, whereas a significantly lower yield was reported[4b] for (E)-1,2-diphenylethene. Addition of borane takes place on the Re-face of 1-phenyl-1-propene which is opposite enantioface selection to other internal alkenes, and may be closely related to the results of asymmetric

Table 1. Asymmetric Hydroboration of Alkenes with Catecholborane[a]

Entry	Alkene	Ligand[b]	Product	Yield (%)[c]	%ee	Config.[d]
1	2-phenylpropene	(+) DIOP	(-)-2-phenyl-1-propanol	27	38[e]	S
2	2-phenylpropene	(+) BINAP	(-)-2-phenyl-1-propanol	73	38[e]	S
3	2-phenylpropene	(S,S)CHIRAPHOS	(-)-2-phenyl-1-propanol	31	16[e]	S
4	2-phenylpropene	(S)(R) BPPFA	(+)-2-phenyl-1-propanol	23	7[e]	R
5	2,3-dimethyl-1-butene	(+) DIOP	(-)-2,3-dimethyl-1-butanol	29	12[e]	S
6	(Z)-3-hexene	(+) DIOP	(+)-3-hexanol	71	10[f]	S
7	norbornene	(+) DIOP	(-)-exo-norborneol	81	59[f]	1S,2S,4R
8	norbornene	(+) BINAP	exo-norborneol	62	0[f]	
9	norbornene	(S,S)CHIRAPHOS	(-)-exo-norborneol	76	10[f]	1S,2S,4R
10	(Z)-1-phenyl-1-propene	(+) DIOP	(-)-1-phenyl-1-propanol	86	47[g]	S
11	(E)-1-phenyl-1-propene	(+) DIOP	(-)-1-phenyl-1-propanol	79	41[g]	S
12	(E)-1-phenyl-1-propene	(+) BINAP	(-)-1-phenyl-1-propanol	42	36[g]	S
13	1,2-dihydronaphtalene	(+) DIOP	(-)-1-tetralol	58	14[g]	R
14	indene	(+) DIOP	(-)-1-indanol	93	58[g]	R
15	indene	(+) DIOP	(-)-1-indanol	91	74[a,g]	R

[a]All reactions were carried out in toluene by using 1 mole% of Rh(I) complexes at -5 °C for 3 days (entries 1-14) or -30 °C for 5 days (entry 15).

[b]The catalysts were prepared in situ from $[ClRh(ethene)_2]_2$ and diphosphine ligands (2 equivs), see the text.

[c]Isolated yields by column chromatography.

[d]The absolute configuration of alcohols were determined by the reported rotations.

[e]Determined by ^1H NMR (400MHz) analysis of Mosher's ester derivatives.

[f]Determined by ^1H NMR (100MHz) analysis of the alcohol acetates with $Eu(hfc)_3$.

[g]Determined by capillary GC (fused silica, OV-101, 20 m) analysis of Mosher's ester derivatives.

hydroformylation[7] with DIOP ligand. (e) Since the alkyl group on boron of boronic esters is most efficiently utilized in transformations, much efforts have to be devoted to developing new methodologies[8] for preparing optically active boronic esters. Catalytic asymmetric hydroboration of prochiral alkenes presented here provides an alternative and straightforward method of forming chiral alkyl groups on boron.

The experimental procedure is as follows. A 25ml-flask equipped with a magnetic stirring bar, and a septum inlet was charged with chlorobis(ethylene)rhodium(I) dimer (3.9 mg, 0.01 mmol), DIOP (10 mg, 0.22 mmol) and flushed with nitrogen. Anhydrous toluene (2 ml) was added and the mixture was stirred for 20 min at room temperature. The solution was cooled to -78 °C, and indene (2 mmol), and catecholborane (2) (0.25 ml. 2 mmol) were added. After stirring for 5 days at -30 °C, the mixture was warmed up to 25 °C, and stirred for additional 2 h. The solution was diluted with ether (10 ml), and treated with an aqueous 3M-NaOH (1 ml) and 30% H_2O_2 (0.2 ml) for 1 h at room temperature. The organic layer was separated, washed three times with 1M-NaOH solution to remove catechol, and dried over magnesium sulfate. Column chromatography over silica gel with hexane/ether gave (-)-1-indanol; 0.244 g (91 %). The enantiomeric purity of 1-indanol was established by capillary GC (fused silica, SE-30, 25 m) analysis of its Mosher ester.[9] The ratio of diastereoisomer was 87 : 13 (73 %ee).

Reference and Notes

1. This work was presented at the 35th Symposium on Organometallic Chemistry, Osaka, Japan, November 1988.

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4. During the course of our study on the present reaction, three catalytic hydroboration reactions were appeared. (a) D. A. Evans, G. C. Fu, and A. H. Hoveyda, J. Am. Chem. Soc., **110**, 6917 (1988); (b) the asymmetric hydroboration; K. Burgress, and M. J. Ohlmeyer, J. Org. Chem., **53**, 5179 (1988); (c) T. Hayashi, Y. Matsumoto, and Y. Itoh, J. Am. Chem. Soc., **111**, 3426 (1989).

5. For example, see: A. Pelter, K. Smith, and H. C. Brown, "Borane Reagents", Academic Press, New York (1988).

6. Commercial reagents from Aldrich and Kanto Chemicals (Japan). DIOP is 2,3-O-isoproplidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane. BINAP is 2,2'-bis(diphenylposphino)-1,1'-binaphthyl. CHIRAPHOS is 2,3-bis(diphenylphosphino)butane. BPPFA is N,N-dimethyl-1-[1',2-bis(diphenylphosphino)ferocenyl]ethylamine.

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