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ASYMMETRIC HYDROFORMYLATION BY RHODIUM COMPLEX CATALYST IN THE PRESENCE OF (-)-2,3-*O*-ISOPROPYLIDENE-2,3-DIHYDROXY-1,4-BIS(5*H*-DIBENZOPHOSPHOLYL)BUTANE

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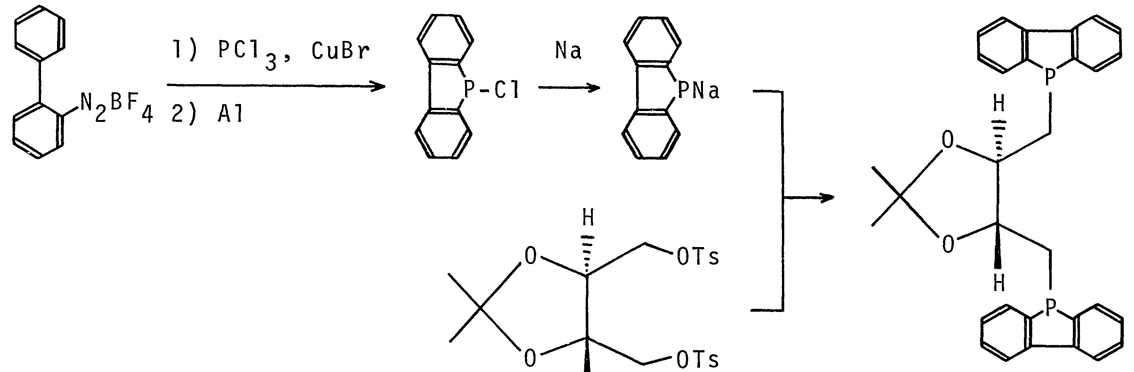
The highest stereoselectivity ever observed (16.9 ∿ 44.3% optical yield) was realized in the hydroformylation of styrene and butenes using a rhodium complex catalyst in the presence of (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(5*H*-dibenzophospholyl)butane.

Asymmetric hydroformylation has been studied for the last few years by several workers.1) However, the stereoselectivity still remains unsatisfactory compared with asymmetric hydrogenation.2) High reaction temperature required for hydroformylation as well as the presence of carbon monoxide of high partial pressure is the main reason for insufficient stereochemical control. In fact, improved optical yields have been noted in the hydroformylation at room temperature under atmospheric pressure of synthesis gas, the reaction being very sluggish.3) In the present communication, we wish to report the preparation of a new diphosphine and its use as a chiral ligand in rhodium catalyzed asymmetric hydroformylation.

The new diphosphine, (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(5*H*-dibenzophospholyl)butane (I),4) was easily obtained analogously to (-)-diop. Thus, 5-sodio-5*H*-dibenzophosphole prepared by the reaction of 5-chloro-5*H*-dibenzophosphole5) with metallic sodium in dioxane was treated with a tetrahydrofuran solution of 1,4-ditosyl-2,3-*O*-isopropylidene-*l*-threitol. A usual work-up followed by recrystallization from benzene-ethanol gave fine needles: mp 186.0 ∿ 187.5°C; $[\alpha]_D$ -60.8° (benzene, c 1.33).6) Its PMR spectroscopic data together with those of (-)-diop are listed in Table 1. As is shown in the table, the doublet



I

assigned to CH_2 adjacent to the phosphorus of the diphosphine I appears at markedly higher field than that of (-)-diop. Judging from this shielding of the methylene protons, the degree of the delocalization of the lone-pair electrons on the phosphorus over the fused hetero-aromatic ring system is rather low,$^{7)}$ and, therefore, it is presumed the σ-donor character may be stronger than that of (-)-diop. The branched/linear ratio of the products in the hydroformylation of styrene by $[Rh(CO)_2Cl]_2$ in the presence of I was 3.95, which was higher than that observed using (-)-diop (1.88) under the same conditions (135°C, $P_{H_2} = P_{CO} = 50$ atm). This suggests the stronger interaction of rhodium with the diphosphine I than that with (-)-diop, and is accordant to the expectation described above.$^{8)}$

The results of rhodium catalyzed asymmetric hydroformylation in the presence of I together with those obtained employing (-)-diop for comparison are summarized in Table 2. The results in the table show that the diphosphine I is far more effective than (-)-diop. The optical yields are higher than those obtained by the use of any other phosphines examined so far for asymmetric hydroformylation under

Table 1. PMR Spectroscopic Data*

Phosphine	Aromatic	CH	CH_2	CH_3
I	1.9 ~ 2.9	5.83 (m)	8.24 (d)	8.47 (s)
(-)-Diop	2.2 ~ 2.9	5.82 (m)	7.60 (d)	8.68 (s)

* Chemical shift in τ (ppm), 60 MHz, solvent; benzene-d_6.

Table 2. Asymmetric Hydroformylation[a]

Substrate	Temp. (°C)	P/Rh[b]	Reaction time (hr)	Conversion (%)	Branched / Linear	Branched isomer		
						$[\alpha]_D$[c]	O.Y.[d] (%)	Config.
Styrene	135	4	2.3	100	3.95 (1.88)	+37.2	25.0[e] (14.9)	S (R)
Styrene	80	4	28	80.9	8.43	+65.8	44.3[e]	S
1-Butene	90 (120)	8	10	66.7	0.46	+5.88	20.4[f] (∿0.8)	S (R)
cis-Butene	120	8	100	32.5	19.0	-4.88	16.9[f] (4.9)	R (S)

[a] Substrate; 3 ml, toluene or ethylbenzene; 6 ml, $[Rh(CO)_2Cl]_2$; 2.63 mg, $P_{CO} = P_{H_2} = 50$ atm. The results obtained using (-)-diop under the analogous conditions are shown in the round brackets. [b] 2 × the ratio of the diphosphine **I**/Rh. [c] Optical rotation was measured neat. [d] Optical yield was calibrated for the optical purity of the diphosphine **I** (92.9%). [e] Maximum rotation for (*S*)-hydratropaldehyde; $[\alpha]_D$+160° (ref. 1). [f] Maximum rotation for (*S*)-2-methylbutyraldehyde; $[\alpha]_D$+31.2° (ref. 9).

the analogous reaction conditions. The higher stereoselectivity of the diphosphine **I** may be attributed to the immutable chiral environment around the reaction site brought about by fixing the rotation of the phenyl groups of (-)-diop. Asymmetric hydrogenation of α-ethylstyrene (*S*, 1.2% optical yield) and α-acetamidocinnamic acid (*S*, 25.0%) as well as asymmetric addition of diphenylsilane to acetophenone (*S*, 7.4%) and pinacoline (*S*, 6.4%) was also examined in comparison with (-)-diop, but the extent of asymmetric synthesis was lower. It is interesting that the diphosphine **I**, which brings about higher stereoselectivity for hydroformylation than (-)-diop, gives much poorer optical yields for hydrogenation and hydrosilylation, though the reason cannot be clearly explained. More interestingly, the configuration of the products obtained in hydroformylation, hydrogenation, and hydrosilylation was opposite to that obtained with (-)-diop as the chiral ligand except the case of the hydrogenation of α-ethylstyrene, and this suggests that the mechanism of asymmetric induction is very complicated.

Further studies on the application of 5*H*-dibenzophospholes to the transition metal catalyzed reactions are now in progress.

References and Notes

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