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HIGHLY EFFECTIVE CATALYTIC ASYMMETRIC HYDROGENATION OF ITACONIC ACID WITH NEW CATIONIC CHIRAL PYRROLIDINEPHOSPHINE-RHODIUM COMPLEXES[1)]

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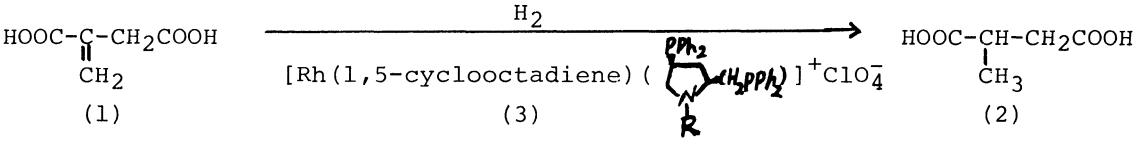
Syntheses of new cationic chiral pyrrolidinephosphine-rhodium complexes and their application to the asymmetric hydrogenation of itaconic acid were described. Thus, PPPM-, BZPPM-, FPPM- and BPPM-Rh^+ in the presence of triethylamine gave S-(-)-methylsuccinic acid in 87.1, 88.9, 94.2 and 93.6% optical yields respectively.

Recently, We have reported the effective catalytic asymmetric synthesis of S-(-)-methylsuccinic acid(2), a well-functionalized compound of tertiary asymmetric carbon atom, in 71.1-87.5% optical yields, by the asymmetric hydrogenation of itaconic acid (1) using neutral chiral pyrrolidinephosphine-rhodium complexes[2)].

We wish to describe here a systematic investigation of the catalytic asymmetric hydrogenation of itaconic acid(1) using new cationic chiral pyrrolidinephosphine-rhodium complexes; [Rh(1,5-cyclooctadiene)(PPPM)]$^+ClO_4^-$(3a), [Rh(1,5-cyclooctadiene)(BZPPM)]$^+ClO_4^-$(3b), [Rh(1,5-cyclooctadiene)(FPPM)]$^+ClO_4^-$(3c) and [Rh(1,5-cyclooctadiene)(BPPM)]$^+ClO_4^-$(3d), as chiral catalysts, which were synthesized similarly according to the procedure used for [Rh(1,5-cyclooctadiene)(DIOP)]$^+ClO_4^-$ [3,4,5)]. Neutral pyrrolidinephosphine-rhodium complexes have been also demonstrated to be quite effective catalysts for the syntheses of chiral α-amino acids[6)], β-amino acids[7)], isoquinoline alkaloid salsolidine[8)], α-hydroxy esters[9)] and pantolactone[10)].



3a: R= $(CH_3)_3CCO-$ (PPPM-Rh^+) 3c: R= HCO- (FPPM-Rh^+)
3b: R= C_6H_5CO- (BZPPM-Rh^+) 3d: R= $(CH_3)_3COCO-$ (BPPM-Rh^+)

In a typical experiment, the asymmetric hydrogenation of itaconic acid(5 mmole) was run in methanol under an initial hydrogen pressure of 50 atm at 20°C for 20h in the presence of 3d(0.05 mmole) and triethylamine(5 mmole). Purification of the reaction mixture was carried out by dissolving it in 10 ml of 1N-NaOH followed by filtration to remove the catalyst. The filtrate was then acidified with 6N-HCl and the product was extracted with ether (150ml×2). Thus, S-(-)-methylsuccinic acid, $[\alpha]_D^{20}$-15.8° (c 2.10, ethanol)(93.6% optical yield) was obtained in an almost quantitative yield.

Table I. Asymmetric hydrogenations of itaconic acid[a)]

Chiral reagent (R)		Solvent	$[\alpha]_D^{20}$(EtOH)	Optical y. (%)	(conf.)[b)]
$(CH_3)_3CCO-$	(PPPM-Rh)	methanol	-14.3	84.7	(s)
$(CH_3)_3CCO-$	(PPPM-Rh)	methanol[c)]	-14.2	84.1	(S)
$(CH_3)_3CCO-$	(PPPM-Rh$^+$)	methanol	-13.9[e)]	82.3	(S)
$(CH_3)_3CCO-$	(PPPM-Rh$^+$)	methanol[c)]	-14.7	87.1	(S)
C_6H_5CO-	(BZPPM-Rh)	methanol	-14.1[d)]	83.5	(S)
C_6H_5CO-	(BZPPM-Rh)	methanol[c)]	-13.6	80.6	(S)
C_6H_5CO-	(BZPPM-Rh$^+$)	methanol	-13.9[e)]	82.3	(S)
C_6H_5CO-	(BZPPM-Rh$^+$)	methanol[c)]	-15.0	88.9	(S)
HCO-	(FPPM-Rh)	methanol	-13.2	78.2	(S)
HCO-	(FPPM-Rh)	methanol[c)]	-15.5	91.8	(S)
HCO-	(FPPM-Rh$^+$)	methanol	-12.7[e)]	75.2	(S)
HCO-	(FPPM-Rh$^+$)	methanol[c)]	-15.9	94.2	(S)
$(CH_3)_3COCO-$	(BPPM-Rh)	methanol	-12.0[d)]	71.1	(S)
$(CH_3)_3COCO-$	(BPPM-Rh)	methanol[c)]	-15.4	91.2	(S)
$(CH_3)_3COCO-$	(BPPM-Rh$^+$)	methanol	-12.1[e)]	71.7	(S)
$(CH_3)_3COCO-$	(BPPM-Rh$^+$)	methanol[c)]	-15.8	93.6	(S)

a) All hydrogenations of 1(5 mmole) were carried out with 0.05 mmole of $[Rh(1,5\text{-cyclooctadiene})(\text{bisphosphine})]^+ClO_4^-$(3) or 0.025 mmole of $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ and 0.06 mmole of bisphosphine in 10 ml of methanol at 20°C for 20 h under an initial hydrogen pressure of 50 atm unless otherwise noted. b) Calculated on the basis of the reported value for optically pure R-2; $[\alpha]_D^{20}$ +16.88 (c 2.16, EtOH)(E.Berner and R.Leonardsen, Ann. 538, 1 (1939). c) Triethylamine(5 mmole) d) Data from ref.2. e) Contaminated with impurities.

Table I shows clearly that the sterically smaller N-substituents of the cationic and neutral pyrrolidinephosphine-rhodium complexes gave the better optical yields of the product especially in the presence of triethylamine, and also cationic BPPM- and FPPM-rhodium complexes afforded respectively almost the same optical yields as those of the corresponding neutral complexes. These facts may suggest that at least in triethylamine-methanol solution the neutral rhodium complexes behave as the cationic complexes and also the direct interaction between the cationic rhodium atom and the carboxylate of the substrate increases the optical yields of the product[11)].

Further investigations along this line are actively under way.

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