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Preliminary communication

Synthesis of a chiral phosphinite derivative of L-rhamnose, and its application to asymmetrical hydrogenation

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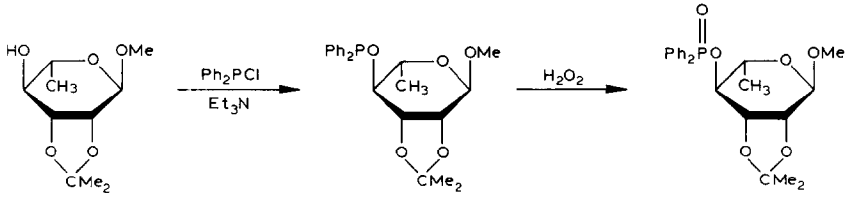
Carbohydrates have several chiral carbon atoms that may be used as chiral sources for asymmetric induction. Only a few studies have been published concerning homogeneous, asymmetrical hydrogenation reactions of prochiral materials in the presence of a rhodium(I) catalyst, using a sugar framework as an asymmetrical component[1–5]; however, the optical yields obtained were not always satisfactory. In preceding papers[6,7], we described a diphenylphosphinite derivative of D-galactose that was a more effective ligand of rhodium for asymmetrical hydrogenation than the diphenylphosphine derivative of D-glucose. In this communication, we report the synthesis of a diphenylphosphinite derivative of L-rhamnose, and its application to the homogeneous, asymmetrical hydrogenation of prochiral alkenes with rhodium(I) complex.

Methyl 4-*O*-(diphenylphosphino)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**2**) was prepared (in 95% yield) from methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[8] (**1**) by action of diphenylphosphinous chloride in the presence of triethylamine under a nitrogen atmosphere; **2** had $[\alpha]_D^{14}$ −8.1° (*c* 1.0, MeOH); n.m.r. ($CDCl_3$): δ 1.20, 1.30 (2 s, 6 H, CMe_2), 1.45 (d, 3 H, *J* 7.0 Hz, C-5-Me), 3.30 (s, 3 H, OMe), 3.9–4.3 (m, 4 H, H-2–5), 4.80 (s, 1 H, H-1), and 7.1–7.9 (m, 10 H, 2 Ph); *m/z* 402 (M^+, $C_{22}H_{27}O_5P$).

Oxidation of **2** with hydrogen peroxide gave oxide **3**.

Anal. Calc. for $C_{22}H_{28}O_6P$ (M + H): 419.1622. Found: 419.1661.



1 **2** **3**

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Homogeneous hydrogenation of prochiral alkenes with $Rh_2Cl_2(C_8H_{12})_2$ was conducted in the presence of chiral ligand 2 and triethylamine in 1:1 (v/v) benzene–ethanol under hydrogen at atmospheric pressure and room temperature. Removal of the catalyst by means of a cation-exchange resin [Dowex 50-W (H^+) or Amberlite IRC-50 (H^+)], and evaporation of the solution *in vacuo*, gave the corresponding products. The results, given in Table I, show that the catalyst afforded a high optical yield. The simple preparation of ligand 2 is an advantage of the present method.

TABLE I

ASYMMETRICAL HYDROGENATION OF PROCHIRAL ALKENES BY $Rh_2Cl_2(C_8H_{12})_2$ WITH CHIRAL PHOSPHINATE LIGAND 2[a]

Substrate	*Product*	*Time (h)*	*Chemical yield (%)*	$[\alpha]_D^{25}$ *(degrees)*	*Optical yield (%)* [b]	*Configuration*
α-Acetylaminocinnamic acid	*N*-acetylphenylalanine	24	100	−22.1	48	(*R*)
α-Benzoylamino-cinnamic acid	*N*-benzoylphenyl-alanine	24	100	+31.1	80	(*R*)
Itaconic acid	methylsuccinic acid	24	100	−11.6	68	(*S*)
Tiglic acid	2-methylbutanoic acid	24	100	−12.5	66	(*R*)

[a] The ratios of substrate to rhodium complex, and of compound 2 to rhodium complex, were 25:1 and 4:1, respectively. [b] Calculated on the basis of the value reported for the optically pure compound: *N*-acetyl-(*S*)-phenylalanine[9], $[\alpha]_D^{26}$ +46.0° (*c* 1.0, EtOH); *N*-benzoyl-(*R*)-phenylalanine[10], $[\alpha]_D^{25}$ +38.74° (*c* 1.6, 1,4-dioxane); methyl-(*R*)-succinic acid[1], $[\alpha]_D^{18}$ +17.01° (*c* 4.41, EtOH); and 2-methyl-(*R*)-butanoic acid[11], $[\alpha]_D^{18}$ −19.33°.

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