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Preliminary communication

ASYMMETRIC HYDROGENATION USING READILY PREPARED CHIRAL SUGAR DIPHOSPHINITERHODIUM COMPLEXES

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Summary

Asymmetric hydrogenation of *N*-acetamidoacrylic acid derivatives has been achieved using a rhodium complex in the presence of a series of readily made chiral diphosphinites, small changes in the stereochemistry of which lead to significant difference in the optical yield of reduced product.

Asymmetric hydrogenations have been successfully performed using optically active phosphine-transition metal catalysts [1]. A wide variety of chiral ligands, which are often difficult to synthesise, have been studied but these bear little structural relationship to each other and no systematic search for new *C*-chiral ligands has been reported. We now wish to report the simple synthesis of a range of new chiral diphosphinites from readily available precursors and their application to asymmetric hydrogenation* [2].

The chiral backbone of these new ligands are the simple monosaccharides and their derivatives in which all but two of the free OH groups have been selectively protected by standard methods [3]. The resulting diol is then converted to the corresponding diphenylphosphinite by treatment with Ph_2PCl/pyridine or with Ph_2PNEt_2 and purified by chromatography on neutral alumina (Table 1). By this method the series of diphosphinites (I—V) were obtained in two steps from the corresponding commercially available glycosides as stable, colourless crystalline solids in good yields.

Hydrogenation was carried out with the rhodium complex $[Rh(1,4\text{-}COD)Cl]_2$ in the presence of two equivalents of the appropriate ligand. The results in Table 2 show that not only was good stereochemical control achieved but also that small variations in the stereochemistry of the sugar backbone greatly affected the optical yield. Thus the ligand based on β-D-glucose is good for the

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*During the preparation of this paper the use of ligand (I; R = Ph) in asymmetric hydrogenation has been described [2b].

TABLE 1

SUGAR DIPHOSPHINITES

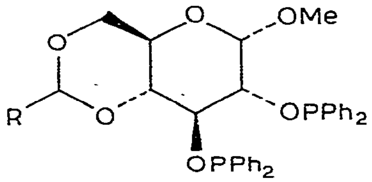
Compound	Melting point (°C)	$[\alpha]_D^{25}$ (c 0.1, toluene)	^{31}P NMR (ppm, H_3PO_4, as external standard)
I (R = Ph)	155—157	+25°	116.5, 113.0
I (R = Et)	138—139	+15°	116.3, 112.9
II	142—143°[a]	−60°	116.3, 114.7
III	70—72	+120°	111.5, 109.3
IV	165—168	+30°	117.1, 109.4

TABLE 2

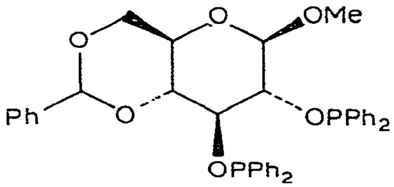
HYDROGENATION BY DIPHOSPHINITERHODIUM CATALYSTS[a]

Diphosphinite ligand derived from	Optical yield (%)[b] (configuration) in reduction of	
	PhCH=C·NHAc·CO_2H	PhCH=C·NHAc·CO_2Me
I (R = Ph) α-D-glucose	46 (L)	8 (L)
II (R = Et) α-D-glucose	36 (L)	10 (L)
III β-D-glucose	80 (L)	10 (L)
III β-D-galactose	0	46 (L)
IV β-D-galactose	0	20 (L)
V D-xylose	62 (D)	48 (D)

[a] 25°C, 50 atm; 1% catalyst; ligand/Rh 1/1. [b] Measured by GLC analysis of the methyl ester on a 9′ glass column packed with 3% *N*-phenyl-D-valyl-t-butylamide on Gas Chrom Q [5].



(I) R = Ph, Et



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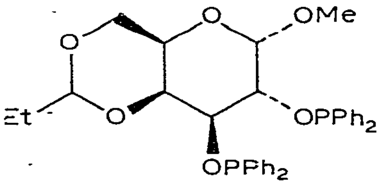
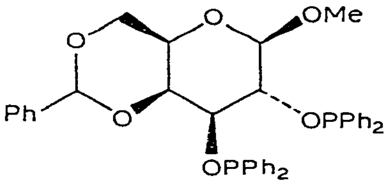


(III)



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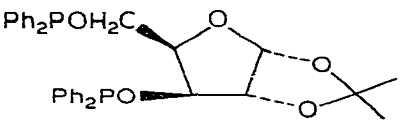

(V)

acid but not the ester substrate, whereas the ligand based on α-D-galactose has the opposite selectivity. It will be noted that the readily available D-sugars give the naturally-occurring L-amino acids in all cases.

Obviously a large number of chiral diphosphinites [illegible] synthesised by this approach and a further one of interest is based on D-xylose (V). This ligand when used with $[Rh(1,5\text{-}COD)Cl]_2$ is not only a more active catalyst than the other diphosphinite catalysts, complete reduction taking about 1 h compared with 8 h for the ligands I—IV, but also gives good optical yields for both the acid and methyl ester. In this case the more abundant D-xylose gives excess of the unnatural D-amino acid.

Further work is in progress on designing related catalysts and studying their reactivity and selectivity.

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PHOTOLYSIS OF DI-η^5-CYCLOPENTADIENYLDIMETHYLTITANIUM(IV): APPLICATION OF FREE-RADICAL POLYMERIZATION IN A STUDY OF THE MECHANISM

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Summary

Photolysis of di-η^5-cyclopentadienyldimethyltitanium(IV) (λ 435.8 nm) leads to the initiation of free-radical polymerization. Labelling studies reveal that no