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Preliminary communication

ASYMMETRIC HYDROGENATION OF α-AMINO ACID PRECURSORS WITH A NEW CHIRAL DIPHOSPHINE (dioxop) DERIVED FROM 1,6-D-ANHYDROGLUCOSE

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Summary

High optical yields are obtained in the hydrogenation of α-amino acid precursors using [Rh(COD)dioxop]$^+ClO_4^-$ in presence of triethylamine as catalyst.

The efficiency of asymmetric hydrogenation for the synthesis of optically active α-amino acids has greatly improved since 1968 with the use of Wilkinson-type catalysts containing chiral phosphines [1—14]. Enantiomeric excesses of 95—98% are obtained with α-acylaminoacrylic acids in the case of chiral diphosphines [5, 11]. Acyclic, carbocyclic and heterocyclic diphosphines have been synthesized, and a more efficient functionalized chiral phosphine, derived from a natural product is (2*S*,4*S*)*N*-butoxycarbonyl-1-diphenylphosphino-2-diphenylphosphinomethyl pyrrolidine (BPPM) [13]. In the case of BPPM, triethylamine had a marked effect on the optical yields of amino acids obtained by asymmetric hydrogenation with BPPM—Rh complex. These results prompt us to report similar facts with another chiral complex.

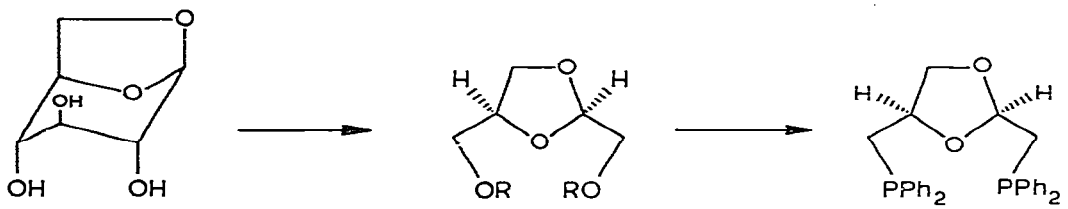
A new functionalized biphosphine was synthesized from D-glucosan (I) as shown in Scheme 1.

Periodate oxidation of I followed by reduction with sodium borohydride gave IIa. Tosylation of IIa yielded the bistosylate IIb. Further treatment of IIb with an excess of lithium diphenylphosphine afforded the biphosphine III (overall yield 24% from I, viscous oil, $[\alpha]_D^{20}$ 2.7 (*c* 2, acetone)), which will be referred to as "dioxop"*.

Hydrogenation of α-amino acid precursors (IV) were carried out with the complex [(1,5-cyclooctadiene)dioxoprhodium]$^+ClO_4^-$ according to the procedure

*Dioxop = (2R,4R)-2,4-bis(diphenylphosphinomethyl)-1,3-dioxolanne.

SCHEME 1



(I) (II) (III)

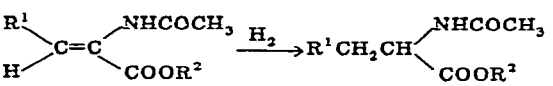
a, R = H

b, R = Ts

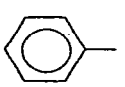
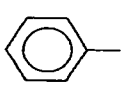
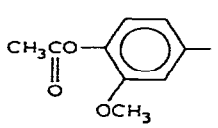
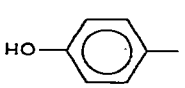
reported by Kagan et al. [10]. Table 1 shows the enantiomeric excesses (e.e.) of α-amino acids obtained by hydrogenation of IV in the presence or absence of base (triethylamine or potassium hydroxide) after removal of the base with a

TABLE 1

HYDROGENATION WITH $[Rh(COD)(dioxop)]^+ClO_4^-$ [a]



(IV) (V)

	R^1	R^2	Base	Conversion (%)	e.e. (%) [c]	Configuration
IVa	H	H	none	100	13	*R*
			$N(C_2H_5)_3$	100	38	*S*
			$N(C_2H_5)_3$ [b]	100	86	*S*
IVb		H	none	100	13	*S*
			$N(C_2H_5)_3$	100	78	*S*
			KOH	100	75	*S*
IVc		CH_3	none	100	0	—
			$N(C_2H_5)_3$	90	6	*S*
IVd		H	none	73	36	*S*
			$N(C_2H_5)_3$	100	79	*S*
IVe		H	$N(C_2H_5)_3$	100	85	*S*

[a] [Rh] 2 mmol l^{-1}; [substrate]/[Rh] 50; [substrate]/[base] 15; 1.1 atm. H_2 and 25°C.
[b] [Substrate]/$[N(C_2H_5)_3]$ 1. [c] % enantiomeric excess based upon: (*R*)-Va, $[\alpha]_D^{25}$ 66.5 (*c* 2, water) [15]; (*S*)-Vb $[\alpha]_D^{26}$ 46.0 (*c* 1.0, ethanol) [7]; (*S*)-Vc $[\alpha]_D^{25}$ 21.4 (*c* 1.9, methanol) [16]; (*R*)-Vd $[\alpha]_D^{22}$ −22.0 (*c* 1, acetone) [6]; (*S*)-Ve $[\alpha]_D^{25}$ 51.5 (*c* 1, methanol) [11].

cation exchange resin, and treatment and identification of V as previously described [6].

Table 1 shows clearly that: (a) The yields of hydrogenation and especially the enantiomeric excess of V are drastically increased by addition of triethylamine (as for BPPM complex) and reach values comparable with those obtained for other diphosphine complexes.

(b) This influence is only observed with acidic amino acid precursors. Thus with esters like IVc, no asymmetric hydrogenation occurred, suggesting a greater nucleophilicity of the carboxylate anion derived from the carboxyl group and triethylamine.

(c) Increasing the concentration of triethylamine raises the optical yield of Va, and also changes the configuration of Va.

(d) Replacement of the acetamido groups of IV by a methyl group ((*E*)-2-methyl-3-phenylpropenoic acid) does not cause any significant change in the results. Hydrogenation yielded (*S*)-2-methyl-3-phenylpropanoic acid (e.e. 58% with triethylamine and 22% without).

These facts suggest that novel and greater interactions are obtained with the dioxop-complex and the carboxylate anion. The structural similarity between "dioxop" and the well known "diop" favours the suggestion that one oxygen of the unsubstituted dioxolan ring participates in the formation of intermediate cyclic species. Additional work is in progress to determine the nature of these interactions.

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