

An Improved Asymmetric Epoxidation of Allyl Alcohols using Titanium-pillared Montmorillonite as a Heterogeneous Catalyst

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A simple and convenient procedure for the catalytic asymmetric epoxidation of primary allyl alcohols with high enantiomeric purities and good yields using a heterogeneous titanium-pillared montmorillonite catalyst is demonstrated.

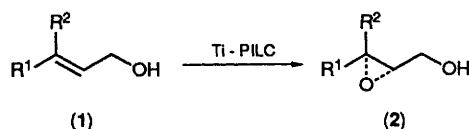
The Sharpless reaction, in its original¹ and modified² form, has provided a successful general solution to the problem of asymmetric epoxidation; asymmetric epoxides are good chiral intermediates in organic synthesis.³ Recently, we reported a novel heterogeneous vanadium-pillared montmorillonite catalyst for the regioselective epoxidation of allylic alcohols under straightforward conditions.⁴ However, the use of this catalyst in the asymmetric epoxidation of (*E*)-hex-2-enol using (+)-diethyl tartrate led to 20% enantiomeric excess (e.e.) only, and we used a titanium-pillared montmorillonite catalyst (Ti-PILC) in an attempt to obtain better enantiomeric purities. We now describe our preliminary results on the asymmetric epoxidation of various primary allyl alcohols (Table 1) using Ti-PILC as a heterogeneous catalyst.

Ti-PILC was synthesized by the procedure reported by Yamanaka *et al.*⁵ Ti(OPr)₄ was added dropwise to vigorously stirred 1 M HCl. The resulting slurry was stirred for 3 h to give a clear titania sol and then mixed with an aqueous suspension of 1 wt% Na⁺-montmorillonite. The suspension was then stirred for 3 h at 50 °C. The clay was washed with deionised

Table 1. Catalytic asymmetric epoxidation of allylic alcohols (1) using Ti-PILC (Scheme 1).^a

Entry	R ¹	R ²	Tartrate ^b	t/h	Product (2)	
					Isolated yield (%)	E.e. (%)
1	Pr ⁿ	H	(A)	3.5	86	94
2	Me[CH ₂] ₄	H	(A)	9	76	98
3	Me	H	(A)	7	68	90
4	Me	H	(A)	4.2	91	95
5	Ph	H	(B)	3.5	89	98
6	EtC≡CCH ₂	H	(A)	8	82	— ^c
7	Me ₂ C=CHCH ₂ CH ₂	Me	(A)	9	72	96 ^d
8	Me ₂ C=CHCH ₂ CH ₂	Me	(B)	7.5	79	98 ^d

^a All reactions were performed with the allylic alcohol (1) (4 mmol) in dry CH₂Cl₂ (6 ml) using Ti-PILC (20 mg) containing 0.12 mmol of titanium, (+)-di-isopropyl or (+)-diethyl tartrate (0.24 mmol) and azeotropically dried hydroperoxide (1.2 ml; ca. 4 M in toluene) at –15 to –20 °C under nitrogen. Products were purified by distillation or column chromatography, and characterised by IR and ¹H NMR spectroscopy. ^b (A) = (+)-di-isopropyl tartrate; (B) = (+)-diethyl tartrate. ^c Product had [α]_D²⁵ –17.8° (c 1.0, CHCl₃); the same reaction using the Sharpless method gave a product with [α]_D²⁵ –14.2° (c 1.0, CHCl₃). The [α]_D value for the optically pure compound has not been reported. ^d The acetoxy derivative was isolated by treatment of the product *in situ* with dimethylaminopyridine, triethylamine, and acetic anhydride.



Scheme 1

water, the mixture centrifuged, and the sample dried in air at room temperature. X-Ray diffraction of the resulting Ti-PILC gave a basal spacing of 24.6 Å with 50% by weight of titanium dioxide according to the elemental analysis of the calcined sample.

The epoxidation of allylic alcohols in Table 1 proceeded at rates and enantiomeric purities comparable with those achieved using homogeneous $\text{Ti}(\text{OPr}^i)_4$ with molecular sieves as water scavengers.² The present system is catalytic without the use of molecular sieves and does not require a low concentration of substrate as in the case of homogeneous conditions to avoid side reactions (see in particular entries 2, 4, and 5). The reaction of the trisubstituted dienol in entries 7 and 8 (Table 1) was slower and gave lower yields than obtained under the conditions used by Sharpless. The basal spacing of the recovered catalyst after the reaction was found to be unaltered, and so the catalyst can be recycled.

The possible pillaring species of Ti-PILC are long inorganic polymeric oxy-hydroxy cationic species with a large amount of zeolite-like pore space.⁶ Thus, during the addition of tartrate, the polymeric titanium oxy or hydroxy species may form a chiral complex which is responsible for the chiral induction. Ti-PILC plays a dual role, in replacing both the $\text{Ti}(\text{OPr}^i)_4$ and the molecular sieves used in the Sharpless reaction. Further, the separation of the catalyst after the reaction is difficult under homogeneous conditions whereas the use of Ti-PILC provides easy separation by simple filtration without tedious experimental work-up.²

Raney nickel modified by tartaric acid has been widely used as a catalyst for reduction of β -ketoesters and β -diketones, with e.e.'s of up to 90%,⁷ and our work provides the first example of the successful use of a different heterogeneous catalyst in this sort of reaction.

We thank Dr. A. V. Rama Rao, Director, Indian Institute of Chemical Technology, for his interest.

Received, 24th April 1990; Com. 0/01821J

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