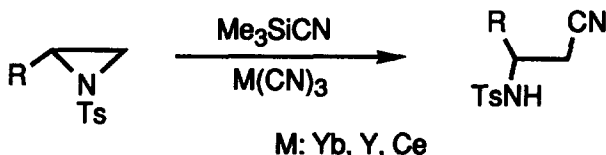


**Yb(CN)₃-CATALYZED REACTION OF AZIRIDINES WITH CYANOTRIMETHYLSILANE.
A FACILE SYNTHESIS OF OPTICALLY PURE β -AMINO NITRILES**

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Summary: Reaction of a N-tosylaziridine with cyanotrimethylsilane under lanthanoid tricyanide catalysis gives a N-tosyl β -amino nitrile by selective attack of cyanide at less substituted carbon of the ring; optically pure 2-substituted aziridine affords the corresponding amino nitrile with perfect retention of the stereochemistry of stereogenic center.


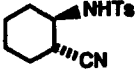

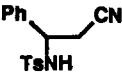

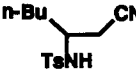
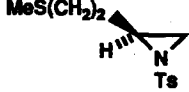
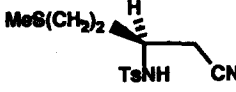
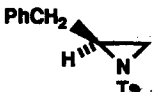
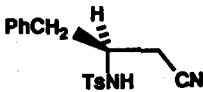
Optically pure β -amino acids are important chemical resources as chiral pool.¹ Since an optically pure aziridine derivative can be derived from an α -amino acid,² regio- and stereoselective nucleophilic ring opening reaction has been reported to give various important intermediates in organic synthesis.³ Recently reported highly selective nucleophilic opening of oxirane cyanotrimethylsilane under lanthanide catalysis⁴ prompted us the application to selective opening of aziridine ring. This paper describes that the reaction of an optically pure 2-substituted aziridine with cyanotrimethylsilane in the presence of Yb(CN)₃ occurs at the 3-position of the ring to give β -amino nitriles in an optically pure form.



A THF (7 mL) solution of N-tosylcyclohexeneimine (2.0 mmol) and cyanotrimethylsilane (4.0 mmol) in the presence of Yb(CN)₃ (25 mol%, 0.5 mmol)⁵ was stirred at 65°C for 2.5 h, and then cooled mixture was treated with water. The reaction mixture was extracted with ether and the ethereal solution was washed, dried over Na₂SO₄, and concentrated. Column chromatography (silica gel, hexane-ethyl acetate) gave trans-2-tosylaminocyclohexanecarbonitrile in 90% yield. Reaction using other lanthanoid tricyanide, Y(CN)₃ or Ce(CN)₃, gave the same product in similar yield.^{6,7} Optically pure (S)-3-tosylamino-4-phenylbutanenitrile was obtained from (S)-N-tosyl-2-benzylaziridine in 84% yield.⁸ Other N-tosylaziridines gave β -tosylamino nitrile in good yields. Results are shown in Table I.

As β -amino acid can be derived to the corresponding β -lactam with retention of configuration, the above described reaction opens a facile access to optically active β -lactams from easily accessible α -amino acids.

Table 1. $M(CN)_3$ Catalyzed Reaction of an Aziridine with Me_3SiCN (1)^a

Aziridine	$M(CN)_3$	Time (h)	Product	Yield ^b (%)
	$Yb(CN)_3$	2.5		90
	$Y(CN)_3$	2.5		98
	$Ce(CN)_3$	2.5		90
	$Yb(CN)_3$	3		85
	$Y(CN)_3$	3		80
	$Yb(CN)_3$	4		88
	$Yb(CN)_3$	2		93
	$Y(CN)_3$	2		87
	$Yb(CN)_3$	7		84

^a Substrate (2.0 mmol), $M(CN)_3$ (0.5 mmol), Me_3SiCN (4.0 mmol), THF (7 mL). All reaction were done at 65°C.^b Isolated yield.

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- Successive treatment of BuLi (3 eq) and Me_3SiCN (3 eq) with $YbCl_3$ (cf. ref. 4).
- Starting materials were recovered unchanged without lanthanoid catalyst.
- N-Benzylamine did not react with cynotrimethylsilane under $Yb(CN)_3$ catalysis.
- Perfect retention of optical purity was determined by the HPLC analysis using Chiralcel (Daicel Chemical Industry).