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REACTION OF CYANOTRIMETHYLSILANE WITH OXIRANES UNDER $Yb(CN)_3$ CATALYSIS

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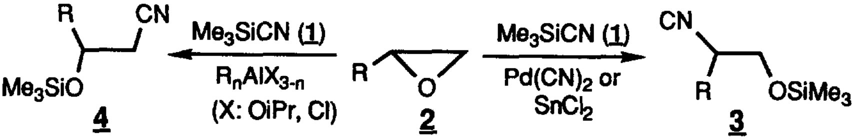
Summary: Reaction of R_3Yb, prepared from $YbCl_3$ and RLi, with Me_3SiCN gives $Yb(CN)_3$, which is a highly efficient catalyst for regio and stereoselective cleavage of an oxirane with Me_3SiCN under mild conditions to give a β-trimethylsiloxy nitrile in excellent yield.

Cyanotrimethylsilane (1) has been utilized as a versatile reagent for introduction of the cyano functionality to various electrophilic substrates.[1-10] Recently the ambident character of 1 has attracted considerable attention; reaction with an oxirane 2 under Lewis acid catalysis gives a β-trimethylsiloxy isonitrile 3 whereas aluminium-mediated reaction affords a β-trimethylsiloxy nitrile 4.[4,5] The selective formation of isonitrile can be explained by the attack of 1 on an oxirane activated by a Lewis acid. On the other hand, reactions with aluminium chlorides or alkoxides as mediators give trimethylsiloxy nitrile 4, by regioselective attack on the less substituted carbon of the oxirane by an aluminium cyanide, which is produced *in situ* by the reaction of 1 with Al-X species.[5]



Although an aluminium chloride (R_2AlCl) can be used as catalyst for the nitrile forming reaction,[5] aluminium chloride itself works as a Lewis acid and affords isonitrile 3 as a by-product. This paper describes a novel use of ytterbium species as a catalyst for selective nitrile synthesis.

A 1,2-dichloroethane solution of cyclohexene oxide (5) was treated with 1 in the presence of $YbCl_3 \cdot 6H_2O$.[11] Reaction at room temperature did not give any adduct. When the reaction mixture was heated under reflux for several hours, however, trans-2-trimethylsiloxycyclohexanecarbonitrile 6[5] was formed in 80% yield. Based on these results, the catalytic activities of several lanthanide salts[12] were examined, and the results are summarized in Table I.

These results indicate that lanthanide salts possess the desired catalytic activity with respect to both cyanotrimethylsilane (1) and an oxirane. Although $YbCl_3$ and $Yb(fod)_3$ gave the product in satisfactory yields, it is necessary to heat the reaction mixture to reflux even for highly reactive 5. Reaction of trans-2,3-diethyloxirane with 1 under $Yb(fod)_3$ catalysis gives the corresponding trimethylsiloxy nitrile in 54% yield after refluxing for 18 h. Improvement of the catalytic activity was needed, and we attempted to accomplish this by modification of the ligands.

A slurry of $YbCl_3$ (28 mg, 0.1 mmol)[13] in 7 mL of THF was treated with BuLi (0.33 mmol) at -78°C. After 15 min, **5** (2.0 mmol) and **1** (2.4 mmol) were added and the resultant mixture was stirred at room temperature for 3 h. Glc analysis of the reaction mixture indicated almost quantitative formation of **6** which was isolated in 99% yield. The catalytic activity of some other organolanthanide species obtained analogously was examined and the results are shown in Table I.[14] Although the species obtained from both $ScCl_3$ and $YbCl_3$ showed high reactivity, $YbCl_3$ was chosen for further studies.[15]

Table I. Lanthanide-Catalyzed Reaction of **1** with **5** affording **6**

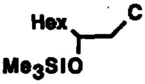
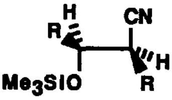
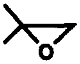
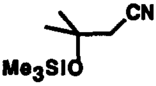
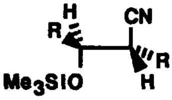
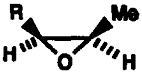
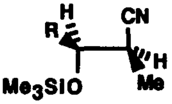
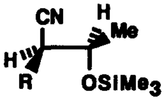
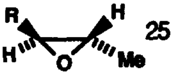
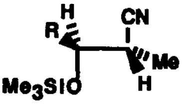
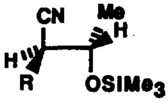
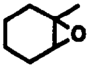
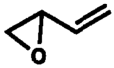
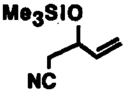
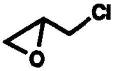
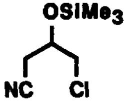
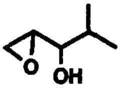
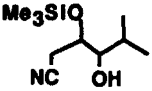
Lanthanide Salts Catalyzed Reaction		MCl_3-BuLi Catalyzed Reaction	
Catalyst[a]	Yield (%)[b]	Catalyst[c]	Yield (%)[b]
$ScCl_3 \cdot 6H_2O$	54	$ScCl_3$-BuLi	> 99
$Y(acac)_3$	92	YCl_3-BuLi	94
$CeCl_3$	11	$CeCl_3$-BuLi	75
$Pr(tfc)_3$	36		
$Eu(fod)_3$	66	$EuCl_3$-BuLi	84
$Eu(tfc)_3$	60		
$YbCl_3 \cdot 6H_2O$	80	$YbCl_3$-BuLi	99
$Yb(fod)_3$	85		

[a] A mixture of **5** (2.0 mmol), **1** (3.0 mmol), and catalyst (0.05-0.1 mol) in 5 mL of 1,2-dichloroethane was heated at reflux for 5 h. [b] Isolated yield of **6**. [c] To a slurry of MCl_3 (0.1 mmol) in THF (7 mL), BuLi (0.33 mmol, hexane solution) was added. **1** (2.4 mmol) and **5** (2.0 mmol) were added and the mixture was stirred at room temperature for 3 h.

The ytterbium species obtained by the above method is effective for the regio- and stereoselective cleavage of various types of oxiranes; the cyano group is introduced at the less substituted carbon with backside displacement of the C-O bond. Examples are shown in Table II.

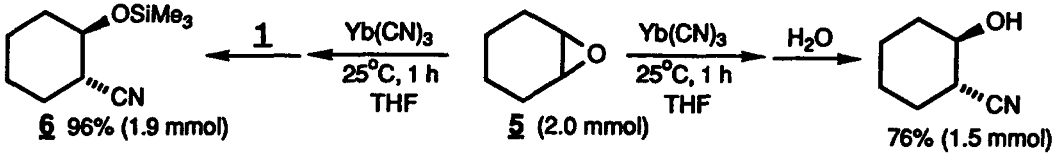
The reaction of the alkylytterbium species with **1** was examined in order to obtain any information about the action of Yb catalyst.[16] To a slurry of $YbCl_3$ (2.0 mmol) in THF maintained at -78°C, a hexane solution of BuLi (6.0 mmol) was added. The reaction mixture was stirred at -78°C for 15 min, and then 0°C for 30 min. Although the organometallic species present in the above reaction mixture has not been characterized, BuLi could not be detected in the reaction mixture by ^{13}C NMR. Therefore Bu_3Yb is assumed to be the main component.[17] To the above reaction mixture, **1** was added three times (2.0 mmol each; total 6.0 mmol) at the intervals of 20 min. Almost quantitative formation of butyltrimethylsilane was detected by glc analysis after each addition.[18] These results suggest that Bu_3Yb reacts smoothly with 3 eq of cyanotrimethylsilane to give $Yb(CN)_3$.[19] The above mixture containing

Table II. Yb(CN)$_3$ Catalyzed Reaction of an Oxirane with Me_3SiCN (1) [a]

Oxirane	temp (time) °C (h)	Product (%)	Oxirane (R: n-C_5H_{11})	temp (time) °C (h)	Product (%)
	25 (3)	 (> 99)		50 (12)	 (99)
	25 (3)	 (93)		65 (7)	 (63)
	25 (3)	 (90)		25 (6)	 (52)  (24)
	25 (6)	 (61)		25 (48)	 (30)  (12)
	25 (24)	 (92)			
	25 (6)	 (69)			
	25 (0.3)	 (91)			
	45 (2)	 (81)[d,e]			

[a] Substrate (2.0 mmol), [YbCl$_3$ (0.1 mmol)-BuLi (0.33 mmol)], 1 (2.4 mmol), THF (7 mL). [b] The ratio of the regio isomers was determined by ^{1}H-NMR. [c] Isolated yield. [d] Diastereomeric mixture (threo / erythro = 60 / 40) was used as the starting material. [e] 1 (6.0 mmol) was used.

$$\underset{(2.0\ mmol)}{Bu_3Yb} \xrightarrow[\downarrow\ BuSiMe_3\ (1.9\ mmol)]{Me_3SiCN\ (1,\ 2.0\ mmol)} [Bu_2YbCN] \xrightarrow[\downarrow\ BuSiMe_3\ (1.7\ mmol)]{1\ (2.0\ mmol)} [BuYb(CN)_2] \xrightarrow[\downarrow\ BuSiMe_3\ (1.9\ mmol)]{1\ (2.0\ mmol)} Yb(CN)_3$$



6 96% (1.9 mmol)

5 (2.0 mmol)

76% (1.5 mmol)

$Yb(CN)_3$ was treated with 5 to give trans-2-hydroxycyclohexanecarbonitrile in 76% yield after hydrolytic work up. Addition of excess cyanotrimethylsilane before hydrolytic work up afforded 6 in 96% yield.

The above described formation of 6 by both catalytic and stoichiometric reactions suggests that $Yb(CN)_3$ is the active species to produce a nitrile from an oxirane.

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18. Reaction of Bu-Yb species with 1 completes within 15 min at room temperature.
19. Although $Yb(CN)_3$ has beed prepared by the reaction of Yb with HCN in NH_3 (ref. 20), the reactivity has been little reported. Structure of $Yb(CN)_3$, obtained by the reaction of Bu_3Yb with 1 was determined by the comparison of IR with that of the reported $Yb(CN)_3$.
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