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Ytterbium Tricyanide, a Highly Efficient Catalyst for the Addition of Cyanotrimethylsilane to Carbonyl Compounds

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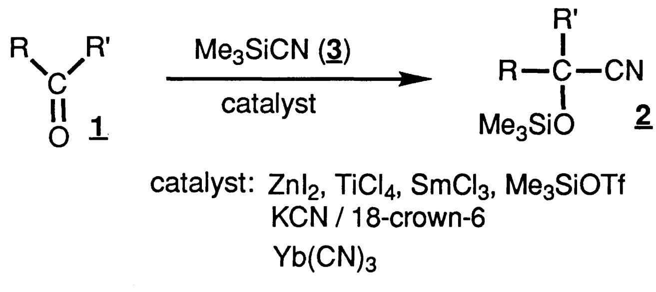
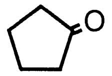
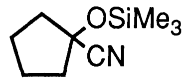
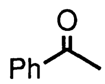
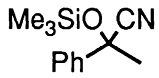
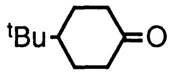
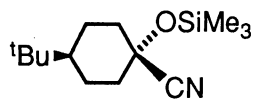
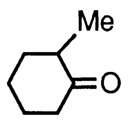
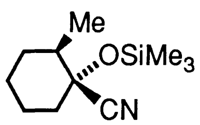
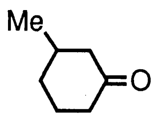
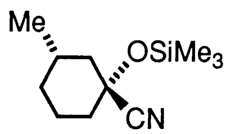
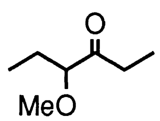
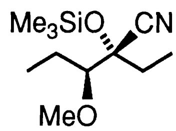
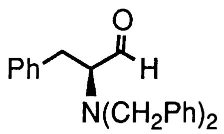
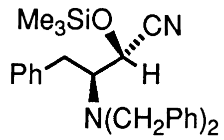
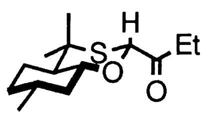
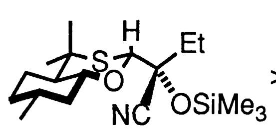
Reaction of cyanotrimethylsilane with various carbonyl compounds was effectively catalyzed by $Yb(CN)_3$ to give the adducts in excellent yields; reaction with substituted cyclohexanones proceeded in a highly stereoselective manner.

α-Trimethylsiloxy nitriles **2**, trimethylsilyl ether of cyanohydrins, are useful intermediates in organic synthesis and have been prepared by the reaction of a carbonyl compounds **1** with cyanotrimethylsilane (**3**).[1-8] Various types of catalysts have been employed: Lewis acids, such as ZnI_2 and $TiCl_4$, are generally used,[1,2,4] and lanthanoid salts have been applied.[5] Trimethylsilyl triflate also showed a high catalytic activity.[6] On the other hand, KCN-crown ether system generates highly reactive cyanating species and can be employed to the reaction with easily enolizable ketones.[7-9] We have reported that lanthanoid cyanides are highly effective catalysts for the reaction of **3** with oxiranes[10] or aziridines.[11] In these reactions, $Yb(CN)_3$ showed little Lewis acidity, although it worked as powerful cyanating reagent.[10] These observations prompted us to anticipate that $Yb(CN)_3$ might possess high catalytic activity for the above described cyanohydrin formation. This paper describes the successful application of $Yb(CN)_3$ as a catalyst for the reaction of **3** with various types of carbonyl compounds **1**.



Reaction of **3** with ketones proceeded smoothly under $Yb(CN)_3$ catalysis. To a mixture of $Yb(CN)_3$ (50 mg, 0.2 mmol) and **3** (2.4 mmol) in THF (5 mL), acetophenone (**1b**, 2.0 mmol) was added at room temperature and the reaction mixture was stirred for 1 h. Hydrolytic workup gives the adduct **2b** in 99% yield.[12] Various ketones reacted similarly with **3** to give the corresponding **2** in excellent yields and in high diastereoselectivity. The combinations of ketone **1**, reaction temperature, reaction time, yield of the product **2**, as well as the

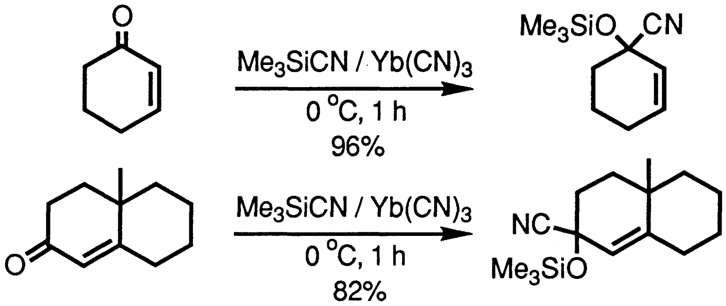
Table 1. $Yb(CN)_3$ Catalyzed Reaction of Ketones with Me_3SiCN[a)]

	Ketone (1)	Conditions Time / h	Conditions Temp / °C	Product (2)	Yield[b)] % (%de)	ZnI_2[c)]	Me_3SiOTf[d)]	KCN/ crown[e)]
a		1.5	0		93	94	>99	99
b		12	25		>99	91	88	>99
c		2	0		88 (88) [>99 (94)][f)]	97 (80)	99 (82)	99 (56)
d		3.5	0		87 (86) [92 (90)][f)]	94 (32)	>99 (31)	90 (46)
e		2	0		94 (54) [90 (94)][f)]	94 (2)	>99 (4)	90 (16)
f		5	0		81 (56)	82 (64)	85 (58)	80 (10)[g)]
g		1	0		91 (44)	89 (82)[h)]	99 (82)	92 (72)
h		1.5	0		>99 (70) [99 (74)][i)]	99 (44)	74 (44)	98 (26)[g)]

a) To a slurry of $Yb(CN)_3$ (0.1 mmol) in THF (4 mL), 3 (1.2 mmol) and a ketone (1.0 mmol) was added. The mixture was stirred at the indicated temperature. b) Isolated yields. c) ZnI_2, Ref.1 and 2. d) Me_3SiOTf, Ref.6. e) KCN/18-crown-6, Ref.8. f) Reaction at -89 °C. g) Major product is the diastereomer of the isomer shown in Table. h) See Ref.4. i) Reaction at -23 °C.

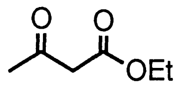
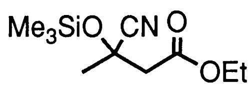
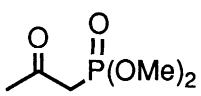
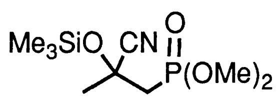
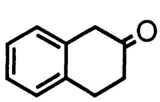
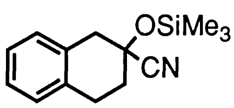
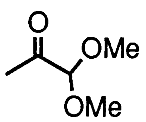
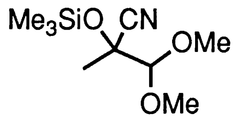
yield of the reported methods[13)] are summarized in Table 1. Reaction of **3** with 4-t-butylcyclohexanone (**1c**) completes at -89 °C within 6 min in highly diastereoselective manner to give **2c** in >99% (94% d.e.).

Reaction of α,β-unsaturated ketones with **3** afforded 1,2-adducts selectively at 0 °C; the reaction in refluxing THF gave the same 1,2-adducts.



Reaction with easily enolizable ketones (**1i** - **1k**) or a ketone (**1l**) containing acid-sensitive group afforded the corresponding adducts in good yields (Table 2). As can be seen from Table 2, $Yb(CN)_3$ catalyst gave the corresponding adducts in good yields as analogous to the KCN-crown ether catalyst system, whereas ZnI_2 could not be employed in these cases.

Table 2. $Yb(CN)_3$ Catalyzed Reaction of Enolizable Ketones with Me_3SiCN[a)]

	Ketone (1)	Condition Time / h	Condition Temp / °C	Product (2)	Yield[b)] / %	ZnI_2[c)]	Me_3SiOTf[d)]	KCN/ crown[e)]
i		4	25		90	45[f)]	42[f)]	73
j		5.5	25		84	0	0	96
k		2	0		88	68	94	84
l		1	0		91	0	30	83

a) To a slurry of $Yb(CN)_3$ (0.1 mmol) in THF (4 mL), **3** (1.2 mmol) and a ketone (1.0 mmol) was added. The mixture was stirred at the indicated temperature. b) Isolated yields. c) ZnI_2, Ref.1 and 2. d) Me_3SiOTf, Ref.6.
e) KCN/18-crown-6, Ref.8. f) Silyl enol ether was isolated in 50% yield (ZnI_2) and 48% yield (Me_3SiOTf).

The results shown in Table 1 and Table 2 indicates that $Yb(CN)_3$ can be widely employed as the catalyst for the addition of **3** with various carbonyl compounds.

Some remarks on $Yb(CN)_3$ are added lastly. Ytterbium tricyanide could be obtained by the following two methods: (1) $Yb(CN)_3$ was prepared by the reaction of **3** with $n\text{-}Bu_3Yb$ which was produced from $YbCl_3$ and 3 equiv. of n-BuLi. IR showed two prominent peaks at 2210 (medium) and 2110 (strong). $Yb(CN)_3$ thus obtained showed a high catalytic activity in the reaction of carbonyl compounds **1** with **3**. (2) $Yb(CN)_3$ was also obtained by the reaction of $Yb(O^iPr)_3$ with 3 equiv. of **3**. IR showed a strong peak at 2085. $Yb(CN)_3$ thus obtained showed a high activity in the reaction of **3** with **1** but much less active in the reaction of **3** with aziridines; the reactivity of $Yb(CN)_3$ was enhanced by the addition of LiCl or LiCN.[14,15] Structure of the individual sample as well as the relationships between the absorptions and reactivities are still open to be answered.[16]

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9) Structure of the reactive species of 18-crown-6/KCN-**3** is assigned as Si-N=C based on a theoretical calculation of IR absorption; M. B. Sassman, G. K. Prakash, and G. Olah, J. Org. Chem., **55**, 2016 (1990).
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11) S. Matsubara, T. Kodama, and K. Utimoto, Tetrahedron Lett., **31**, 6379 (1990).
12) Reaction of PhCOMe (**1b**) with **3** under $SmCl_3$ catalysis afforded the corresponding adduct **2b** in 50% yield, under $Eu(fod)_3$ catalysis gave a mixture of **2b** (25%) and the corresponding protodesilylated nitrile (29%); reaction of PhCHO with **3** afforded the adduct in 98% yield.[5]
13) Reactions were carried out under the conditions described in references: ZnI_2-catalyzed reaction;[1] Me_3SiOTf catalyzed reaction;[6] reactions catalyzed by KCN/18-crown-6.[7,8]
14) S. Matsubara, T. Kodama, and K. Utimoto, in preparation.
15) $Yb(CN)_3$ was prepared by the reaction of $YbBr_3$ with LiCN; K. Rossmanith, Monatsh. Chem., **97**, 1698 (1966); IR absorptions, 2185 (weak) and 2100 (medium).
16) The authors thank to the Japan Society for the Promotion of Science for a Grant-in-Aid for International Exchange Program.

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