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Solvent-free cyanosilylation of ketones with $(CH_3)_3SiCN$ (TMSCN) catalyzed by NbF_5

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The addition of TMSCN to ketones catalyzed by dispersed NbF_5 gave corresponding cyanohydrin trimethylsilylethers with excellent yield (>90%). Cyano transfer occurs within 30 min at room temperature in the presence of 1 mol% of NbF_5 under solvent-free conditions. These conditions are extremely mild, simple, and tolerate various functional groups. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: cyanohydrins; catalysis; ketones; NbF_5; solvent-free

INTRODUCTION

The addition of TMSCN to carbonyl compounds is a popular strategy to afford cyanohydrins, which can be conveniently converted into various important building blocks such as α-hydroxy amines, α-hydroxy acids, α-hydroxy carbonyl compounds, α-amino alcohols and α-amino acid derivatives.[1–6] In the view of their synthetic potential, there has been considerable interest in recent years in the development of catalysts for the addition of cyanide source to carbonyl compounds leading to cyanohydrin derivatives.[7–9]

For the synthesis of cyanohydrins a plethora of procedures[10–16] has been reported employing ZnI_2, Ti(IV), $Cu(OTf)_2$, Ce(IV), $AlCl_3$, In(III), Sm(III), $Yb(OTf)_3$, $VO(OTf)_3$, $Gd(O\ ^iPr)_3$ and others as Lewis acid catalysts.[17–27] Lewis bases such as triethylamine, tributylphosphine, triphenylarsine, trisaminophosphines and triphenylantimony catalyze cyanosilylation of carbonyl compounds with TMSCN.[28–31] Very recently, *N*-heterocyclic carbenes (NHC) were reported for the activation of TMSCN.[32,33] Several chiral Lewis acids and Lewis bases have been used for the synthesis of non-racemic cyanohydrins.[34–40] There is still a need to develop a simple and efficient method for the cyanation of both aldehydes and ketones.

There have been several reports of the silylcyanation of carbonyl compounds under solvent-free conditions. K_2CO_3-catalyzed cyanosilylation of carbonyl compounds under solvent-free conditions has been reported.[41] Lithium chloride acts as an active and simple catalyst for cyanosilylation of aldehydes and ketones.[42] $LiClO_4$-catalyzed cyanosilylation of carbonyl compounds has been reported.[43] Tetramethylguanidine was successfully employed as an effective catalyst for cyanosilylation of ketones.[44] Al(salen)/N-oxide system, a catalytic double activation method without solvent, have been reported for the cyanosilylation of ketones.[45] The development of a facile synthetic method of the cyanation of ketones under mild reaction condition is still worthwhile due to the importance of these compounds in organic synthesis. Nb(V) is known to possess strong oxophilicity to promote Lewis acid-mediated reactions such as the Diels–Alder reaction, allylation of aldehydes, acetylation of alcohols and others.[46–51] Over recent years we have developed several chiral[52–56] and achiral[57–59] catalytic systems for the cyanosilylation of carbonyl compounds. As a follow-up of cyanosilylation studies, we report herein our results on the cyanosilylation of ketones catalyzed by dispersed NbF_5 as a catalyst under solvent free-conditions. The same reaction with various aldehydes required further reduced catalyst amount of 0.5 mol% NbF_5 within a 10 min reaction period. Thus the cyanosilylation of various aldehydes gives upto 96% isolated yield under the same reaction conditions.[60]

EXPERIMENTAL

Materials and instruments

All reagents were purchased from Aldrich Chemical Company and used as received. In all cases the ^1H NMR

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(200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded with a Varian Gemini 2000 spectrophotometer in $CDCl_3$ with tetramethylsilane as internal standard.

General procedure for cyanosilylation

Silylcyanation of acetophenone; 2-trimethylsilyloxy-2-phenylpropanenitrile (Table 2; entry 1)

A mixture of acetophenone (120 mg, 1 mmol), dispersed NbF_5 (1 mol%) and TMSCN (1.5 equiv.; TMSCN is very toxic by inhalation, in contact with skin and if swallowed; gloves and spectacles should be worn while working with TMSCN) was stirred for 20 min at room temperature in a 10 ml round bottom flask (Hydrofluoric Acid (HF) released due to the absorption of moisture is very toxic and mask and gloves should be worn to avoid contact). Then 0.5 ml of CH_2Cl_2 was added and the mixture was stirred for 10 min. Purification by silica gel flash chromatography (EtOAc–hexane; 1 : 9) gave the desired 2-trimethylsilyloxy-2-phenylpropanenitrile as a colourless oil (yield 90%). The other substrates (entries 2–12 in Table 2) were also silylcyanated using the same procedure. ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.16$ (s, 9H), 1.84 (s, 3H), 7.36–7.55 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 0.89$, 33.41, 71.46, 121.45, 124.46, 128.48, 141.87.

2-Trimethylsilyloxy-2-(4′-methylphenyl)propanenitrile (entry 2)

($CDCl_3$, 200 MHz): $\delta = 0.16$ (s, 9H), 1.84 (s, 3H), 2.36 (s, 3H), 7.21 (m, 2H), 7.43 (m, 2H). ^{13}CNMR ($CDCl_3$, 100 MHz): $\delta = -0.28$, 55.78, 63.87, 114.66, 119.47, 127.58, 128.78, 160.23

2-Trimethylsilyloxy-2-(4′-methoxyphenyl)propanenitrile (entry 3)

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.16$ (s, 9H), 1.85 (s, 3H), 3.83 (s, 3H), 6.95 (d, 2H, $J = 8.8$ Hz), 7.50 (d, 2H, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 0.98$, 33.31, 55.21, 71.18, 113.80, 121.70, 125.96, 133.95, 159.72. HRMS (EI): m/z calcd for $C_{13}H_{19}NO_2Si$ (M^+): 249.1185; found: 249.118

2-Trimethylsilyloxy-2-(4′-cholorophenyl)propanenitrile (entry 4)

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.22$ (s, 9H), 1.86 (s, 3H), 7.41–7.47 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 1.00$, 33.44, 71.02, 121.17, 126.05, 128.78, 134.56, 140.68.

2-Trimethylsilyloxy-2-(4′-fluorophenyl)propanenitrile (entry 5)

^1H NMR ($CDCl_3$, 200 MHz) $\delta = 0.18$ (s, 9H), 1.84 (s, 3H), 7.08 (m, 2H), 7.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 1.0$, 33.5, 71.0, 115.6, 121.4, 126.5, 138.0, 162.2.

2-(1-Naphthalen-1-yl)-2-(trimethylsilyloxy)propanenitrile (entry 6)

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.13$ (s, 9H), 2.19 (s, 3H), 7.45–7.57 (m, 3H), 7.85–7.93 (m, 3H), 8.56 (dd, 1H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 1.05$, 31.66, 73.12, 121.75, 124.59, 125.49, 125.74, 125.99, 129.07, 129.32, 130.10.

2-Trimethylsilyloxy-2-methyl-4-phenyl-3-butenenitrile (entry 7)

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.24$ (s, 9H), 1.74 (s, 3H), 6.16(d, 1H, $J = 15.83$ Hz), 6.92 (d, 1H, $J = 15.8$ Hz), 7.31–7.41 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 1.30$, 30.79, 69.89, 120.60, 126.82, 128.53, 128.70, 129.47, 130.89, 135.06.

1-Trimethylsilyloxy-2-cyclohexenecarbonitrile (entry 8)

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.24$ (s, 9H), 1.77–1.87 (m, 2H), 1.94–2.11(m, 4H), 5.77 (m, 1H), 5.94–5.99 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 1.40$, 18.26, 24.20, 36.86, 66.71, 121.75, 127.53, 132.49. HRMS (EI): m/z calcd for $C_{10}H_{17}NOSi$ (M^+): 195.1079; found: 195.107.

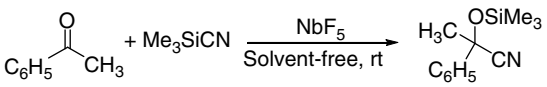
1-Trimethylsilyloxy-1, 2, 3, 4-tetrahydronaphthalene-1-carbonitrile (entry 9)

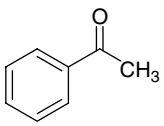
^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.23$ (s, 9H), 1.83–2.41 (m, 4H), 2.81 (t, 2H, 7.00 Hz), 7.09–7.29 (m, 3H), 7.61–7.66 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 1.33$, 18.69, 28.32, 37.73, 69.87, 122.11, 126.63, 128.02, 129.06, 129.26, 135.68, 136.11.

2-Trimethylsilyloxy-2-furan-2-yl-propanenitrile (entry 10)

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 0.09$ (s, 9H), 1.92 (s, 3H), 6.35–6.40 (m, 1H), 6.47–6.50(m, 1H), 7.41–7.43 (m, 1H). ^{13}C

Table 1. Cyanosilylation of acetophenone under various conditions



Entry	Substrate	Catalyst (mol%)	Time (min)	Yield (%)[a]
1		10	15	96
2		5	20	94
3		1	20	96
4		0.5	40	90
5[b]		1	20	90

[a] Isolated yield.
[b] In the presence of CH_2Cl_2.

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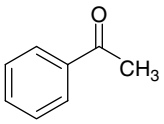
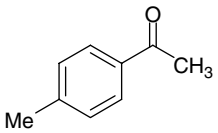
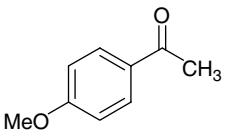
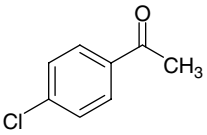
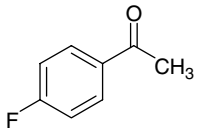
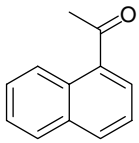
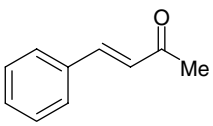
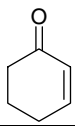
Table 2. Cyanosilylation of ketones with TMSCN catalyzed by NbF_5[a]

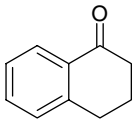
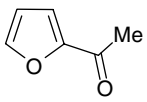
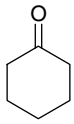
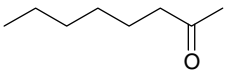
Entry	Substrate	Time (min)	Yield (%)[b]
1		20	96
		20h	85[c]
		12h	28[e]
		4h	92[f]
		3h	86[g]
		1h	90[h]
2		25	93
3		25	90
		2h	91[e]
4		20	94
5		30	90
6		25	96
7		25	90
		11.5	97[d]
		1h	99[h]
8		20	93
		3h	85[g]
		1h	99[h]
		20	92

NMR ($CDCl_3$, 100 MHz): $\delta = 0.49, 28.37, 65.89, 108.14, 110.68, 120.23, 143.09, 151.63$.

1-(Trimethylsilyloxy)cyclohexanecarbonitrile (entry 11)

^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.23$ (s, 9H), 1.51–1.68 (m, 8H), 2.02–2.08 (m, 2H). ^{13}C NMR($CDCl_3$, 100 MHz): $\delta = 1.37, 22.59, 24.48, 39.31, 70.59, 121.91$.

Table 2. (*Continued*)

Entry	Substrate	Time (min)	Yield (%)[b]
9		50h	80[c]
		5h	95[d]
		6h	89[f]
10		25	95
		1h	89[f]
11		20	92
		3h	84[c]
		2h	75[e]
		2h	98[g]
12		20	95

[a] 1 mol% NbF_5 used; [b] isolated yield; [c] 22 [d] 45 [e] 58 [f] 23 [g] 44 [h] 30.

2-Trimethylsilyloxy-2-methyloctanenitrile (entry 12)

^{1}H NMR (CDCl3, 200 MHz): δ 0 : 22 (s, 9H), 0.91(t, 3H, 6.60 Hz), 1.31–1.74 (m, 8H), 1.57 (s, 3H), 1.68–1.74 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 1 : 15, 13.88, 22.38, 24.09, 28.76, 28.84, 31.47, 43.25, 69.56, 121.91.

RESULTS AND DISCUSSION

We used acetophenone as a model substrate for the optimization of the reaction condition. NbF_5 exhibited excellent activity under solvent-free condition. When a mixture of acetophenone (1 mmol) and TMSCN (1.2 equiv.) was treated with dispersed NbF_5 at room temperature, the silylcyanation occurred so as to give the product cyanohydrin with 96% yield within 20 min. The results and reaction conditions are indicated in Table 1. We found that 1 mol% NbF_5 is the optimal condition to achieve excellent yield (96%) in short reaction time at room temperature under solvent-free conditions (entries 1–3). Further reduction in catalytic loading from 1 to 0.5 mol% doubled the reaction time (entry 4). The NbF_5-cataylzed system is an excellent method because only 1 mol% catalytic loading can produce 96% yield in 20 min that can be compared with the recently reported cyanosilylation method under solvent free-conditions (30 mol% catalyst, 24 h, 91% yield;[41] 100 mol% catalyst, 3 h, 86% yield).[43] Even 0.5 mol% of NbF_5 gives a better result (40 min, 90% yield) than the cyanosilylation of acetophenone with *N*-heterocycliccarbene (1 h, 80% yield)[32] because both systems employ 0.5 mol% catalytic loading. For the purpose of comparison we have also included one result

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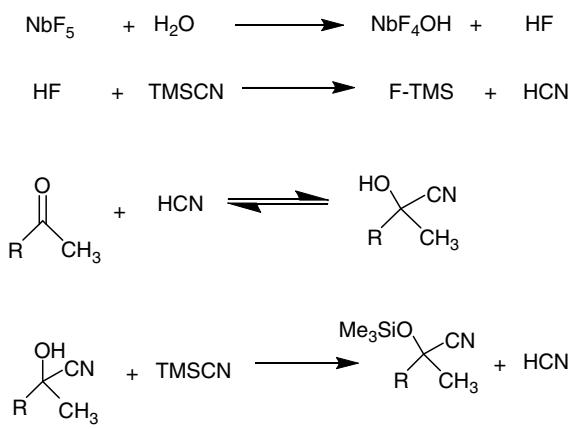
in dichloromethane as a solvent under comparable conditions (entry 5). These outcomes clearly indicate that the low catalyst loading and solvent-free conditions are good enough for the activation of TMSCN with dispersed NbF_5. In the presence of organic solvents 20 mol% of quaternary ammonium salt/N-oxide[61] or 5 mol% of $Cu(OTf)_2$[15] or 30 mol% of NMO[59] was required to promote complete conversion of acetophenone to the corresponding trimethylsilylated cyanohydrin.

Encouraged by the results obtained for acetophenone, we investigated a number of other ketones to probe their behaviour under the current catalytic conditions. The results are listed in Table 2. Unsubstituted and substituted aromatic ketones underwent very smooth silylcyanation with over 90% yield (entries 1–5). As a comparison, vanadyl triflate,[16] $LiClO_4$,[43] phenolic N-oxide[19] and K_2CO_3[62]-catalyzed cyanosilylation of aromatic acetophenones required longer reaction times (1–24 h), as well as higher catalyst loading (1–100 mol%). Although some systems were reported in organic solvents with low catalytic loading (0.1–2 mol%), the cyano transfer occurred in much longer reaction time (8.5–15 h).[44,45] The nature of the substituents on the aromatic ring seems to have minor effect on the reaction time. 1-Acetonapthone gave corresponding silylethers in excellent yield (entry 6). Both aromatic and aliphatic α,β-unsaturated ketones underwent cyanosilylation with good yield (entries 7 and 8). It should be noted that α-tetralone was cyanosilylated by NbF_5 in 20 min (entry 9) while the same reaction required 6 h in the presence of $VO(OTf)_2$.[16] Notably, 2-acetyl furan, a heterocyclic ketone, gave corresponding silylether in excellent yield (entry 10). Cyclic and open chain aliphatic ketones also underwent smooth silylcyanation (entries 11 and 12).

NbF_5 is superior in activity to TMSCN when compared with other recently reported achiral catalytic systems used for silylcyanation of ketones. The present system indicates greater yield with quite short reaction time. It is also worth noting that the addition reaction of TMSCN to ketones was done without any additive. As shown in Table 2, our catalytic system requires much less catalyst loading compared with previous studies.[15,16,30,43,44,63]

The mechanism of cyanosilylation reaction of ketones catalyzed by NbF_5 is proposed as follows. NbF_5 is hydrolyzed by moisture in the air to give HF. HF reacts with TMSCN, liberating HCN, which reacts reversibly with acetophenone to give cyanohydrins. TMSCN then reacts irreversibly with cyanohydrins, giving rise to the silylated product along with HCN. The liberated HCN may attack the ketone to continue the chain (Scheme 1). Spencer *et al*. have identified that protons are active catalysts in several Lewis acid-catalyzed reactions.[64]



Scheme 1. The mechanism of cyanosilylation of ketones catalyzed by NbF_5.

CONCLUSION

In summary, we have described a novel and efficient system for the synthesis of cyanohydrins using catalytic amount of NbF_5 (1 mol%) under solvent-free conditions at room temperature. The attractive features of this procedure are mild reaction conditions, high yields, solvent-free conditions, operational simplicity, and inexpensive and readily available catalyst. The wide substrate applicability represents the notable feature of this procedure. Efforts to extend NbF_5 catalysis to other organic transformations are on-going. Further investigations to clarify the reaction mechanism and recovery and reuse of catalyst are in progress.

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