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Solvent-free cyanosilylation of aldehydes catalyzed by SmI_2

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A novel method to obtain racemic cyanohydrin silylethers by reaction of trimethylsilyl cyanide with a variety of aldehydes promoted by catalysis of SmI_2 is reported. The corresponding cyanosilylethers were obtained in high yields (up to 99%) in solvent- free conditions at room temperature within a relatively short time using 0.01–0.5 mol% catalyst loadings. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: cyanohydrins; aldehydes; solvent-free; SmI_2

INTRODUCTION

Cyanohydrins are valuable organic synthons in the preparation of compounds such as α-hydroxy aldehydes, α-hydroxyacids, β-aminoalcohols, α-cyanoketones, 1,2 diols etc.[1–8] Different kinds of catalytic systems have been developed for the smooth conduct of cyanosilylation reactions worldwide.[9–20] Recently *N*-heterocyclic carbenes were found to be highly effective organocatalysts in activating trimethylsilyl cyanide (TMSCN) for facile cyanosilylation of carbonyl compounds.[21] Feng and co-workers observed that sodium-L-phenyl glycine is an effective catalyst for the cyanosilylation of ketones.[22] Very recently, proline-derived bifunctional organocatalysts have been developed for highly enantioselective cyanosilylation of α,α-dialkoxyketones.[23] In recent years, we have also identified several chiral[24–29] and achiral[30–36] catalysts for cyanosilylation of carbonyl compounds.

Since the pioneering studies of Kagan,[37] samarium diiodide has rapidly become an important reagent for performing carbon–carbon bond formation.[38–47] Recently, Concellon *et al.*[48] observed that 1.0 equivalent of SmI_2 in tetrahydrofuran (THF) promotes the synthesis of nitro aldol by the reaction of bromonitromethane with a variety of aldehydes in 2 h. Hwang *et al.*[49] have synthesized chiral phthalides by the reductive cyclization of 2-acylarylcarboxylates using 2 equiv. of SmI_2 in THF. Hamura *et al.*[50] conducted the ring expansion of alkenyl benzocyclobutenol derivatives into substituted naphthols by 0.07 mol of SmI_2 in CH_3CN. Very recently, Kimura and Nakata[51] have carried out the cyclization of alkoxyvinyl sulfones with aldehyde using 2.5 equiv. of SmI_2 in the presence of MeOH and THF. $SmI_2(THF)_2$ was used to catalyze the Mukaiyma–Micheal addition of a ketene silyl acetal on a cyclic α, β unsaturated ketone in CH_2Cl_2.[52] Reboule *et al.*[53] described the formation of β-amino acid derivatives by the addition of aromatic amines onto unsaturated *N*-acyloxazolidinones in the presence of 10 mol% $SmI_2(THF)_2$ in CH_2Cl_2. However, to the best of our knowledge, the synthesis of cyanohydrins using samarium diiodide has not yet been described.

In this paper we describe a novel synthesis of racemic cyanohydrin silylether by the reaction of trimethylsilyl cyanide with various aldehydes promoted by SmI_2 at as little as 0.01–0.5 mol% catalyst loadings at room temperature in solvent-free conditions.

EXPERIMENTAL

Materials and instruments

The ^{1}H NMR (200 MHz) spectra were recorded with a Varian Gemini 2000 spectrophotometer. Chemical shifts are reported in ppm in $CDCl_3$ with tetramethylsilane as internal standard. ^{13}C NMR data were collected on a Varian Gemini 2000 Spectrophotometer (100 MHz). HRMS analysis was carried out on a Hewlett-Packard 5890A gas chromatograph/Jeol JMS-DX303 mass spectrometer by chemical ionization with methane as the flow gas. SmI_2 powder was supplied by Sigma

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Aldrich with 99.9% purity. TMSCN, aldehydes and ketones were purchased from Aldrich.

General procedure

SmI_2 powder (0.5 mol%, 2.02 mg) was added to a stirred solution of TMSCN (1.5 equiv.) and the corresponding carbonyl compound (1 mmol, 1 equiv.) in a 10 ml round-bottomed flask under nitrogen atmosphere. After stirring the reaction at room temperature for the required time mentioned in Table 1, the reaction mixture was purified by silica gel flash chromatography using EtOAc–hexane (1 : 9) mixture as eluent. The cyanohydrin silylether obtained was characterized by ^{1}H NMR, ^{13}C NMR and HRMS analysis. The yield determined by ^{1}H NMR was 100%. *Caution*: TMSCN must be used in a well-ventilated hood due to its high toxicity and moisture-sensitive nature.

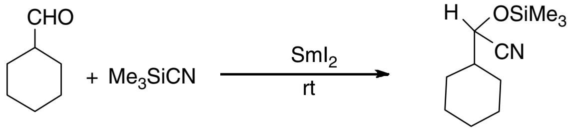
Cyclohexyl (trimethylsilyloxy)acetonitrile

Table 2, entry 1: colorless liquid; Rf = 0.83; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.20$ (s, 9H), 1.18–1.26 (m, 5H), 1.58–1.92 (m, 6H), 4.12–4.14 (d, 1H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.327$, 25.59, 26.10, 27.98, 28.22, 42.98, 66.53, 119.39. HRMS (EI):[54] m/z calcd. for $C_{11}H_{21}NOSi$ (M^+): 211.1392; found: 213.1387.

(Trimethylsilyloxy)octanenitrile

Table 2, entry 2: colorless liquid; Rf = 0.79; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.216$ (s, 9H), 0.88–0.90 (m, 3H), 1.2–1.6 (m, 8H), 1.79–1.81 (m, 2H), 4.4(d, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.267$, 14.106, 22.586, 24.597, 28.668, 31.63, 36.30, 61.51, 119.83. HRMS (EI): m/z calcd for $C_{11}H_{23}NOSi$ (M^+): 213.1549; found: 213.1566.

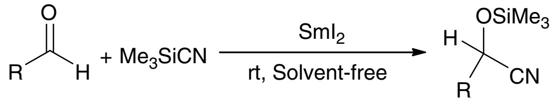
Table 1. Cyanosilylation of cyclohexane carboxaldehyde under various conditions[a]

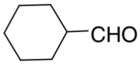
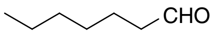
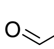
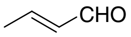
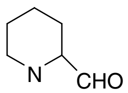
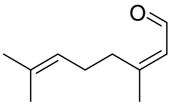
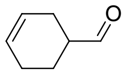
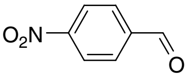
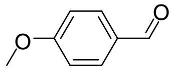
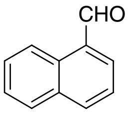
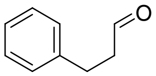
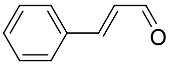
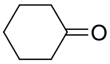


Entry	Catalyst (mol %)	Solvent (2 ml)	Time (min)	Yield[b] (%)
1	0.5	THF	5	93
2	3	THF	7	92
3	0.5	Neat	3	97
4	0.1	Neat	3	92
5	0.05	Neat	2.5 h	87
6	0.01	Neat	7 h	82
7[c]	0.5	Neat	5 min	70

[a] SmI_2 is added to a mixture of TMSCN (1.5 equiv.) and aldehydes (1 mmol, 1 equiv.) at room temperature.
[b] Isolated yield (100% conversion is observed with ^{1}H NMR).
[c] 1 equiv. of TMSCN was used.

Table 2. Cyanosilylation of various aldehydes under optimized conditions[a]



Entry	Substrate	Time (min)	Yield (%)[b]
1		3	97
2		5	88
3		5	87
4		5	83
5		4	97
6		30	99
7		5	85
8		15	80
9		60	87
10		40	91
11		8	90
12		30	93
13		6	94

[a] 0.5 mol% of SmI_2 is added to a mixture of TMSCN (1.5 equiv.) and aldehyde (1 mmol, 1 equiv.) at room temperature.
[b] Isolated yield (100% conversion is observed with ^{1}H NMR).

3-Methyl-2-trimethylsilyloxybutanenitrile

Table 2, entry 3: colorless liquid; Rf = 0.90; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.21$ (s, 9H), 1.00–1.06(m, 6H), 1.92–1.98 (m, 1H), 4.18 (d, 1H) ^{13}C NMR ($CDCl_3$ 100 MHz): $\delta = -0.335$, 17.36, 17.68, 33.921, 67.28, 118.4. HRMS (EI): m/z calcd for $C_8H_{17}NOSi$ (M^+): 171.1079; found: 171.1087.

2-(Trimethylsilyloxy)pent-3-enenitrile

Table 2, entry 4: yellow liquid; Rf = 0.83; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.36$ (s, 9H), 1.77–1.79 (d, 3H), 4.87–4.89 (d, 1H), 5.55-5.6 (m, 1H), 5.92–6.00 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.36, 17.17, 65.69, 118.45, 127.1, 128.46$. HRMS

(EI):[54] m/z calcd. for $C_8H_{15}NOSi$ (M^+): 169.0922; found: 169.0917

2-(Pyridine-2-yl)-2-(trimethylsilyloxy)acetonitrile

Table 2, entry 5: colorless liquid; Rf = 0.13; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.263$ (s, 9H), 5.6 (s, 1H), 7.28–7.32 (m, 1H), 7.58–7.60 (d, 1H), 7.76–7.81 (m, 1H), 8.59–8.60 (d, 1H), ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.271$, 65.163, 118.763, 120.606,124.104, 137.638, 149.420, 155.535

4,8-dimethyl-2-(trimethylsilyloxy)nona-3,7-dienenitrile

Table 2, entry 6: yellow liquid; Rf = 0.88; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.197$ (s, 9H), 1.60 (s, 3H), 1.68–1.81 (m, 6H), 2.09–2.16 (m, 4H), 5.07–5.14 (m, 2H), 5.38–5.41 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 2.02$, 17.78, 20.55, 25.72, 26.06, 39.27, 58.59, 119.40, 120.81, 123.29, 130.35, 141.63 HRMS (EI): m/z calcd for $C_{14}H_{25}NOSi$ (M^+): 251.1705; found: 251.1707.

Cyclohex-3-enyl(trimethylsilyloxy)acetonitrile

Table 2, entry 7: a pale yellow liquid; Rf = 0.79; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.21$ (s, 9H), 1.60–2.12 (m, 7H), 4.23–4.27(m, 1H), 5.70 (s, 2H), ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.305$, 23.93, 24.49, 26.80, 39.20, 65.84, 119.07, 124.885, 126.93, HRMS (EI): m/z calcd for $C_{110}H_{19}NOSi$ (M^+): 209.1236; found: 197.1236

2-(4-Nitrophenyl)-2-(trimethylsilyloxy)acetonitrile

Table 2, entry 8: a pale yellow liquid; Rf = 0.63; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.281$ (s, 9H), 5.59 (s, 1H), 7.65–7.69 (d, 2H), 8.26–8.30 (d, 2H), ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.26$, 62.74, 118.54, 124.25, 127.21, 143.03 148.5.

2-(4-Methoxyphenyl)-2-(trimethylsilyloxy)acetonitrile

Table 2, entry 9: yellow liquid; Rf = 0.69; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.204$ (s, 9H), 3.82 (s, 3H), 5.43 (s, 1H), 6.90–6.93 (d, 2H), 7.37–7.39 (d, 2H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.10$, 55.38, 63.38, 114.22, 119.32, 127.86, 128.46, 160.33. HRMS (EI): m/z calcd. for $C_{12}H_{17}NO_2Si$ (M^+): 235.1029; found: 235.1026

(Naphthalene-1-yl)-2-(trimethylsilyloxy) acetonitrile

Table 2, entry 10: yellow liquid; Rf = 0.72; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.226$ (s, 9H), 6.05 (s, 1H), 7.42–7.64 (m, 4H) 7.69–7.72 (d, 1H), 7.89–7.93 (d, 1H), 8.16–8.18 (d, 1H), ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.073$, 62.79, 119.17, 123.254, 125.18, 125.54, 126.40, 127.10, 129.06, 130.54, 131.08, 134.08, HRMS (EI): m/z calcd for $C_{15}H_{17}NOSi$ (M^+): 255.1079; found: 255.1077

4-Phenyl-2-(trimethylsilyloxy)butanenitrile

Table 2, entry 11: colorless liquid; Rf = 0.72; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.39$ (s, 9H), 2.09–2.14 (m, 2H), 2.76–2.72 (m, 2H), 4.34–4.38 (m, 1H), 7.18–7.35 (m, 5H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.26$, 30.74, 37.75, 60.76, 119.97, 126.50, 128.49, 128.71, 139.99 HRMS(M^+) cacld for $C_{13}H_{19}NOSi$: 233.1236; found: 233.1231

(E)-4-phenyl-2-(trimethylsilyloxy)but-3-enenitrile

Table 2, entry 12: colorless liquid; Rf = 0.56; ^{1}H NMR ($CDCl_3$, 200 MHz) $\delta = 0.25$ (s, 9H), 5.10–5.12 (d, 1H), 6.19–6.2 (d, 1H), 6.79–6.8 (d, 1H) 7.35–7.39 (m, 5H) ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -0.02$, 62.34, 118.48, 127.07, 128.45, 128.84, 128.89, 134.08, 135.16 HR HRMS (EI): m/z calcd for $C_{13}H_{17}NOSi$ (M^+): 231.1079; found: 231.1075.

1-(Trimethylsilyloxy)cyclohexane carbonitrile

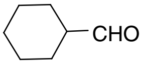
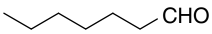
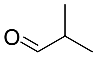
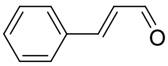
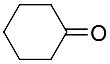
Table 2, entry 13): colorless liquid; Rf = 0.82; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.23$ (s, 9H), 1.53–1.72 (m, 8H), 2.02–2.08 (m, 2H), ^{13}C NMR ($CDCl_3$, 100 MHz): 1.54, 22.73, 24.59, 39.40, 70.59, 121.92, HRMS (EI): m/z calcd for $C_{10}H_{19}NOSi$ (M^+): 197.1236; found: 197.1249.

RESULTS AND DISCUSSION

The catalytic activity of SmI_2 was tested for the reaction of cyclohexane carboxaldehyde and TMSCN at room temperature. As many of the SmI_2-mediated reactions were carried out in THF, we also started the optimization studies in the presence of THF as solvent with 0.5 mol% of the catalyst and we found that silylethers are produced within 5 min with 93% yield (Table 1). On further increase of catalyst loading from 0.5 to 3 mol%, the reaction took 7 min to complete with a lower yield of 92%. We further carried out the reaction neat with 0.5 mol% SmI_2. To our surprise, the reaction worked well and gave the racemic product in 97% yield within 3 min (Table 2, entry 3). Encouraged by this result, we further investigated the catalytic reaction with 0.1 mol% SmI_2. The reaction completed within 3 min, although the yield was slightly reduced to 92%. We found that the reaction proceeds even with 0.05 mol% of SmI_2 produing 87% of the silyethers within 2.5 h. The catalyst loading was studied on a ~100 mmol scale, and we were pleased to see that only a minute amount of SmI_2 (0.01mol%) was required to catalyze the cyanosilylation of benzaldehyde at room temperature in solvent-free condition (100% conversion within 7 h; Table 2, entry 6). In order to understand the role of quantity of TMSCN, we carried out the cyanosilylation reaction with 1 equiv. TMSCN. It was observed that the reaction was completed within 5 min but the yield was reduced to 70% (entry 7).

A series of carbonyl compounds were evaluated (Table 2) using the conditions in entry 3 of Table 1. Most of the reactions afforded cyanohydrin trimethylsilylether in relatively good to excellent yields in less than 10 min in solvent-free conditions at room temperature. Aliphatic, heterocyclic and branched aldehydes are converted into the corresponding cyanohydrin trimethylsilylether in relatively short reaction time with good to excellent yield (Table 2,

Table 3. Comparative results of cyanosilylation reactions using SmI_2 with literature values

Entry	Substrate	Reaction time (min)	Yield (%)	Literature values Reaction time	 Yield (%)[a]
1		3	97	10 min	96[33]
				0.5 h	94[20]
				10 h	92[35]
2		5	88	0.5 h	77[55]
3		5	87	10 min	87[21]
				2 h	88[56]
4		30	93	1 h	81[56]
				0.5 h	75[55]
5		4	94	2.5 h	79[21]
				20 min	92[34]

[a] The respective reference values.

entries 1–7). Aromatic aldehydes took slightly longer reaction compared with aliphatic aldehydes (Table 2, entries 8–10). The silylcyanation of hydrocinnamaldehyde was found to be faster than that of cinnamaldehyde (Table 2, entries 11 and 12). Cyclohexane carboxaldehyde took 3 min (Table 2, entry 1) for the cyanosilylation, which is the best result of the present reactions in terms of reaction time and yield. We also examined the catalytic activity of cyclohexanone (Table 2, entry 13) with the same conditions as entry 3 of Table 1. Cyclohexanone underwent the cyanosilylation reaction within 6 min (Table 2, entry 13)

SmI_2 is superior in the activation of TMSCN when compared with other recently reported achiral catalytic systems used for silylcyanation of aldehydes, especially aliphatic aldehydes (Table 3).[33,34,20,21,55,56] This was the first practically feasible cyanosilylation reaction of various aldehydes with TMSCN in the presence of SmI_2. The reaction proceeded effectively at room temperature without any additives. The reaction went to completion within a relatively short time (<10 min in most cases).

SmI_2 was expected to react as a one-electron donor towards suitable acceptors. This was easily confirmed by the visual inspection of solutions in THF (dark-blue-green), which turned to yellow Sm (III) state after reduction of the substrate.[46] This happens in most SmI_2-catalyzed reactions as it is conducting in THF. In our case we conducted the reaction in solvent-free conditions. We also observed that the yellow coloration when SmI_2 was added to the carbonyl compound. This indicates that carbonyl compounds reduce with SmI_2 to form the corresponding ketyl radical as first step in the mechanism. The ketyl radical then recats with TMSCN smoothly to give the desired product cyanosilyl ether in good to excellent yield. The formation of ketyl radical was verified by the reaction between the carbonyl compound and SmI_2 without the addition of TMSCN and that led to the formation of pinacols. The formation of ketyl radical was due to the generation of Sm (III) rather than Sm (II). Several authors have reported the formation of ketyl radicals by the reaction of SmI_2 with carbonyl compound due to the generation of Sm (III).[46,57–60]

CONCLUSION

In summary, we have developed a novel method for the cyanosilylation of various aldehydes. The reported procedure clearly demonstrated that SmI_2 is an excellent catalyst for the preparation of racemic silylethers in relatively short reaction times with low catalyst loading under solvent-free conditions. The important features of our method are: mild reaction conditions, simple work-up, solvent-free conditions and inexpensive and readily available catalyst. Studies are in progress to confirm the mechanistic pathway as well as the reusability of the catalyst SmI_2

Acknowledgements

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