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Organocatalytic synthesis of cyanohydrin trimethylsilyl ethers by potassium 4-benzylpiperidinedithiocarbamate under solvent-free conditions

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Potassium 4-benzylpiperidinedithiocarbamate was found to be an efficient organocatalyst for facile addition of trimethylsilyl cyanide to a wide variety of aldehydes and ketones to afford corresponding cyanohydrin trimethylsilyl ethers in high to quantitative yields. The reaction proceeded smoothly by employing 2.0 mol% PBPDC loading under mild conditions at room temperature within a very short reaction time.

Keywords: cyanosilylation; organocatalysis; potassium 4-benzylpiperidinedithiocarbamate; carbonyl compounds; solvent-free conditions

Introduction

The addition of cyanide to carbonyl compounds is one of the most powerful strategies for the synthesis of cyanohydrins as poly-functionalized organic molecules. Cyanohydrins are highly versatile synthetic blocks in organic synthesis as they may be easily converted into other functional groups such as α-hydroxy acids, α-hydroxy aldehydes or ketones, α-amino acids, β-amino alcohols, 1,2-diols, etc. Because of their importance in the pharmaceutical, agrochemical and other industrial applications, a large body of work has been devoted to the development of cyanohydrin synthesis.[1–5] Various cyanide sources, such as HCN, NaCN, KCN and different trialkylsilyl cyanides have been reported for the nucleophilic addition of cyanide to carbonyl compounds. In particular, the use of trimethylsilyl cyanide (TMSCN) in organic synthesis has proven valuable from the standpoints of improving of the reaction yield, safety and simplicity in the hydrolysis of the products under mild conditions. However, this compound is only effective in the transfer of the CN group to the carbonyl group of aldehydes or ketones under the action of activators.[6–12]

Many different catalytic systems including Lewis acids[8–22] and inorganic Lewis bases[23–26] have been developed for the addition of TMSCN to carbonyl compounds. Furthermore, double activating[3,27–35] or bifunctional[36–41] catalytic systems have been described for asymmetric synthesis of cyanohydrin trimethylsilyl ethers. However, many of these procedures suffer from many disadvantages, such as the requirement for relatively expensive heavy metal catalysts, anhydrous toxic solvents, inert atmosphere and drastic reaction conditions with tedious work-up procedures. On the other hand, organocatalytic protocols for organic synthesis have received considerable attention in recent years because they provide a platform for catalyzing reactions in the absence of precious or toxic transition metals. Many organocatalysts are simple molecules that show excellent selectivity and afford good yield. Organocatalysts have several advantages. They are usually robust, inexpensive, readily available and non-toxic. Many organocatalysts are inert towards moisture and oxygen. Because of these unique features, demanding reaction conditions like inert atmosphere, low temperature, absolute solvents, etc., are in many instances not required. Because of the absence of transition metals, organocatalytic methods seem to be especially attractive for the preparation of compounds that do not tolerate metal contamination, e.g. pharmaceuticals. Therefore, they have a high industrial and also ecological potential to be applied in many branches of chemical science and industry.[42–46] Although some organocatalytic protocols have been described for cyanosilylation of carbonyl compounds,[47–71] development of new methods which are catalytic in nature, cost-effective and simple to use is a very active research effort. The bidentate dithiocarbamate ligand has proved to be an extremely versatile and robust motif in coordination chemistry. Its ease of formation and wide ranging coordination chemistry have received a great deal of attention from both academia and industry. Examples are metal-directed self-assembly,[72,73] speciation of trace elements using non-chromatographic methods,[74–77] biological studies[78,79] and catalysis by transition metals.[80–83] However, there are very few reports available in the literature regarding the use of pure dithiocarbamate (DTC) anions as nucleophilic catalysts in organic transformations. We have previously reported sodium or potassium piperidinedithiocarbamate as effective catalysts for the efficient cyclotrimerization of aryl and alkyl isocyanates under

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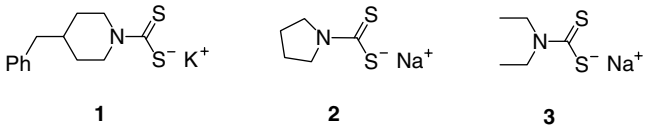
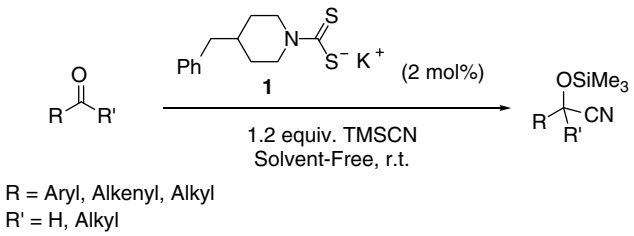


Figure 1. Different dithiocarbamate anions used for catalyst survey.

solvent-free conditions.[84] Furthermore, considerable advancement has been made during the past few years for the Lewis base-catalyzed reactions, using silylated reagents.[23,50] In continuation of our research for new efficient organocatalysts,[48–51,57] we decided to investigate the possibility of using different nucleophilic dithiocarbamate anions **1–3** (Fig. 1) to catalyze the cyanosilylation of carbonyl compounds with TMSCN. Herein, we wish to report potassium 4-benzylpiperidinedithiocarbamate (PBPDC, **1**) as an efficient catalyst for the rapid cyanosilylation of carbonyl compounds with TMSCN under solvent-free conditions (Scheme 1).



Scheme 1. Cyanosilylation of carbonyl compounds catalyzed by PBPDC.

Experimental

Materials and Instruments

Sodium diethyldithiocarbamate (SDEDC, **2**) and sodium pyrrolidinedithiocarbamate (SPIDC, **3**) were purchased from Merck. The catalysts were powdered and dried at 70 °C for 1 h under reduced pressure prior to use. Other chemicals were supplied by Merck, Aldrich or Fluka and used as received except for benzaldehyde, for which a fresh distilled sample was used. Analytical TLC was carried out using Merck 0.2 mm silica gel 60 F-254 Al-plates. FT IR spectra were recorded as KBr pellets on a Shimadzu FT IR-8400S spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were obtained using a Bruker DRX-500 Avance spectrometer. All NMR spectra were determined in $CDCl_3$ at ambient temperature. GC chromatograms were recorded on Shimadzu 2010 and Perkin-Elmer 8420 instruments. Melting points were determined using an Electrothermal 9100 apparatus and are uncorrected.

Preparation of Potassium 4-Benzylpiperidinedithiocarbamate (PBPDC, 1)

To a 50 ml round-bottom flask equipped with a magnetic stirrer and a condenser were added stoichiometric amounts of 4-benzylpiperidine (10 mmol in 10 ml of diethyl ether), KOH (10 mmol in 10 ml of distilled water) and CS_2 (10 mmol). The mixture was stirred for 1 h at room temperature. After separation of phases, the resulting yellow precipitate was collected by filtration. The water phase was also evaporated and the solid residue washed with diethyl ether. The combined solids were powdered and dried at 70 °C for 1 h under reduced pressure prior to use.[75–77]

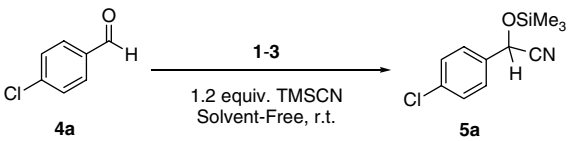
General Procedure for Cyanosilylation of Carbonyl Compounds

TMSCN (1.2 mmol, 0.15 ml) was added to a mixture of 1.0 mmol of carbonyl compound and PBPDC (**1**, 0.02 mmol, 5.8 mg). The resulting mixture was stirred at room temperature for time indicated in Table 2. The reaction was monitored by TLC. After completion, the reaction mixture was quenched with water (1.0 ml) and the organic materials were extracted with EtOAc (2 × 1.5 ml). The organic phase was washed with brine followed by water (1.5 ml) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to afford the desired products which in some cases were essentially pure cyanohydrin TMS ethers. Further purification of the products could be performed by silica gel column chromatography (EtOAc–hexane, 1 : 10). The isolated yields were in good agreement with those obtained by GC analysis.

Results and Discussion

To examine the catalytic activity of the dithiocarbamate anions **1–3** for cyanosilylation of carbonyl compounds, the reaction of 4-cholorobenzaldehyde **4a** and TMSCN was carried out in the presence of potassium 4-benzylpiperidinedithiocarbamate (PBPDC, **1**), sodium pyrrolidinedithiocarbamate (SPIDC, **2**) and sodium diethyldithiocarbamate (SDEDC, **3**) (2 mol %), respectively (Table 1, entries 1–3). As shown in Table 1, the catalytic ability of dithiocarbamate anions is tightly associated with lipophilicity and rigidity of the anion moiety as well as bulkiness of the counter cation (entries 1–3). As can be seen, PBPDC **1** was found to be the best catalyst for this reaction at room temperature. On further increase of catalyst loading from 2 to 3 mol%, the reaction yield and time did not alter remarkably (entry 4). On the other hand, decreasing the catalyst loading to 1 mol% required longer time for completion of the reaction (entry 5). In addition, no reaction was observed in the absence of any dithiocarbamate anions **1–3** (entry 6). Accordingly, 2 mol% catalyst loading under solvent-free conditions at room temperature was found to be the optimal

Table 1. Optimization of cyanosilylation of 4-cholorobenzaldehyde **4a** catalyzed by different dithiocarbamate anions under solvent-free conditions and ambient temperature[a]



Entry	Catalyst	(Mol%)	Time (min)	Yield[b] (%)	TON[c]	TOF[d] (h^{-1})
1	PBPDC, **1**	2	10	98	49	294
2	SPIDC, **2**	2	25	88	44	106
3	SDEDC, **3**	2	40	84	42	63
4	PBPDC, **1**	3	6	95	32	317
5	PBPDC, **1**	1	45	93	93	124
6	–	–	180	0	0	0

[a] A 1.2 mmol aliquot of TMSCN was added to a mixture of 1.0 mmol of 4-cholorobenzaldehyde and 0.02 mmol of PBPDC.
[b] Determined by GC analysis.
[c] Turnover number: moles of product per mole of catalyst.
[d] Turnover frequency: moles of product per mole of catalyst per hour.

Table 2. Addition of TMSCN to aldehydes and ketones mediated by potassium 4-benzylpiperidinedithiocarbamate (PBPDC) at optimal conditions[a]

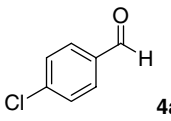
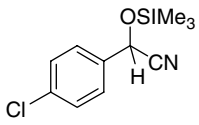
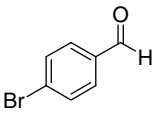
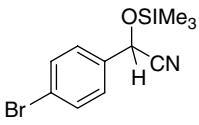
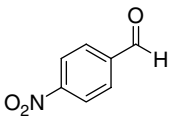
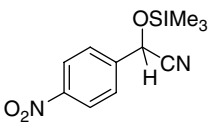
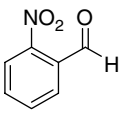
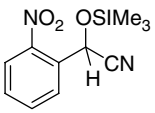
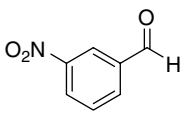
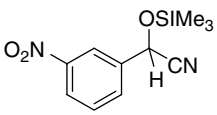
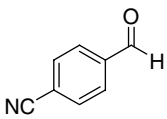
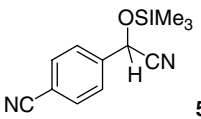
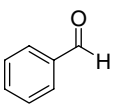
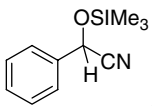
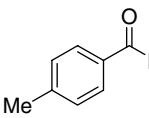
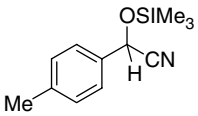
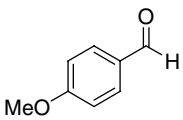
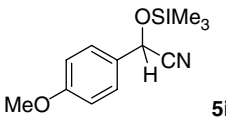
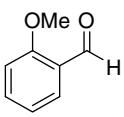
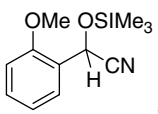
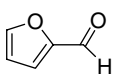
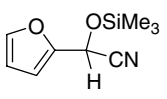
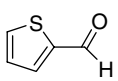
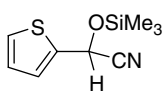
Entry	Carbonyl compound	Time (min)	Product[b]	Conversion (%)[c]
1	 **4a**	10	 **5a**	98
2	 **4b**	15	 **5b**	100
3	 **4c**	5	 **5c**	99
4	 **4d**	5	 **5d**	99
5	 **4e**	10	 **5e**	98
6	 **4f**	7	 **5f**	99
7	 **4g**	15	 **5g**	100
8	 **4h**	15	 **5h**	96
9	 **4i**	15	 **5i**	95
10	 **4j**	10	 **5j**	96
11	 **4k**	15	 **5k**	100
12	 **4l**	20	 **5l**	92

Table 2. (*Continued*)

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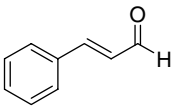
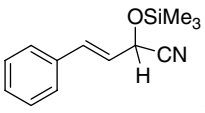
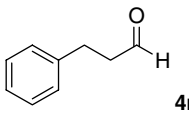
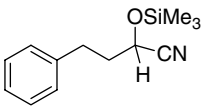
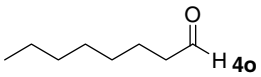
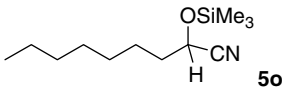
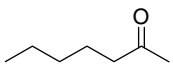
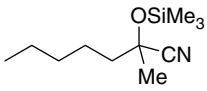
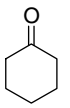
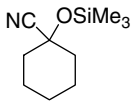
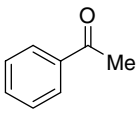
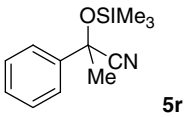
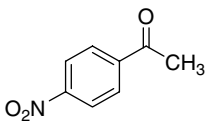
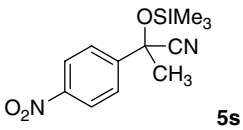
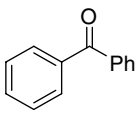
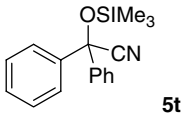
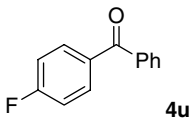
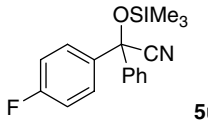
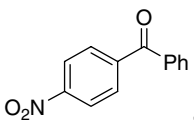
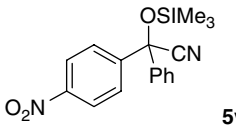
13	 **4m**	25	 **5m**	98
14	 **4n**	35	 **5n**	100
15	 **4o**	60	 **5o**	98
16	 **4p**	180	 **5p**	94
17	 **4q**	120	 **5q**	97
18	 **4r**	180	 **5r**	62
19	 **4s**	150	 **5s**	100
20	 **4t**	240	 **5t**	75
21	 **4u**	180	 **5u**	94
22	 **4v**	150	 **5v**	96

[a] A 1.2 mmol aliquot of TMSCN was added to a mixture of 1.0 mmol of carbonyl compound and 0.02 mmol of PBPDC under solvent-free conditions at room temperature.
[b] All products are known and were well-characterized by IR and NMR spectral data as compared with those obtained from authentic samples or reported in the literature.[9,12,17,18,20,21,35,50,54,70]
[c] Determined by GC analysis.

conditions in terms of obtained turnover number (TON) and turnover frequency (TOF).

The optimized reaction conditions were applicable for a wide range of representative carbonyl compounds with excellent to quantitative yields and short reaction times. The results have been summarized in Table 2. The data illustrated in Table 2 clearly demonstrates that a variety of aryl and alkyl aldehydes may be employed in the PBPDC-catalyzed process to afford the corresponding cyanohydrin trimethylsilyl ethers in 92–100% yields (entries 1–15). Upon completion of the reactions, the catalyst was removed from the reaction mixture simply by extraction to the aqueous phase used for quenching of any intact TMSCN. Aldehydes bearing electron-withdrawing groups such as NO_2– or CN–(entries 3–6), were more active than those

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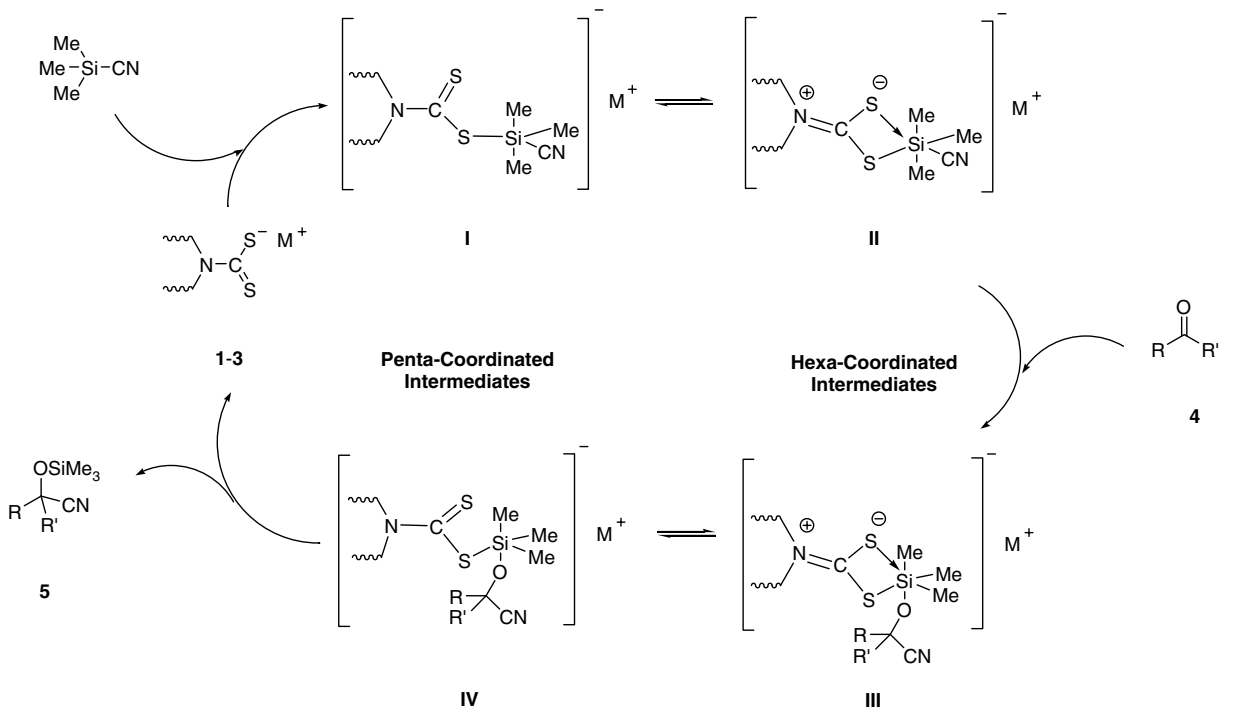

Scheme 2. Plausible mechanism for cyanosilylation of carbonyl compounds catalyzed by PBPDC.

Table 3. Comparison of some of the results obtained by cyanosilylation of aldehydes ketones with TMSCN in the presence of PBPDC (1), with some of those reported by imidazolium-carbodithioate zwitterions (2), K_2CO_3 (3), triethanolamine *N*-oxide combined with dibenzyldimethylammonium bromide (4), monobenzyloctahydropyrimido(1,2:a)azepinium bromide (5) and different lanthanide–nitrogen complexes (6) at room temperature

		Method [equivalent of TMSCN : TOF (h^{-1})]					
Entry	Substrate	1[a]	2[52] b	3[24] c	4[47] b	5[56] b	6[17] b
1	Benzaldehyde	1.2 : 200	2.0 : 0.62	1.2 : 55	–	1.2 : 4.2	2.2 : 0.62
2	4-Chlorobenzaldehyde	1.2 : 294	–	1.2 : 110	–	–	2.2 : 0.61
3	4-Methoxylbenzaldehyde	1.2 : 190	2.0/0.15	1.2 : 5.2	–	1.2 : 4.3	–
4	Cinnamaldehyde	1.2 : 118	–	1.2 : 9.1	–	1.2 : 12	–
5	3-Phenylpropanal	1.2 : 86	–	–	–	1.2 : 16	–
6	Acetophenone	1.2 : 10	–	1.2 : 0.13	2.0 : 2.5	–	2.2 : 0.26
7	Cyclohexanone	1.2 : 24	–	1.2 : 0.55	2.0 : 2.5	–	–

[a] The reactions were carried out under solvent-free conditions.
[b] The reactions were carried out in CH_2Cl_2 as solvent.
[c] The reactions were carried out in Et_2O as solvent.

with electron-donating groups (entries 8–12). Interestingly, this catalytic system well tolerated acid-labile substrates such as the furfural, thiophen-2-carbaldehyde and cinnamaldehyde to provide the corresponding products in excellent yields (entries 11–13). In addition, only 1,2-addition product was observed for α,β-unsaturated aldehyde (entry 13).[10–12] The reaction with aromatic and heterocyclic aldehydes afforded the corresponding products in shorter reaction times compared with aliphatic aldehydes (entries 13–15). It is of particular interest to note that by-products such as those which could be produced by desilylation or benzoin condensation were not observed in all of the reactions studied.[58,59]

In the next step, the procedure was further explored by conversion of aliphatic or aromatic ketones into their corresponding cyanohydrin trimethylsilyl ethers (**5p**–**v**) in high yields within short reaction time (entries 16–22). In general, ketones required longer reaction times compared with aldehydes due to increasing the steric hindrance around the carbonyl functional group.[20,21]

The following Lewis basic mechanism may be proposed for cyanosilylation of carbonyl compounds with TMSCN catalyzed by different dithiocarbamate nucleophiles as organocatalysts (Scheme 2). Therefore, the bidentate dithiocarbamate organocatalyst can interact with TMSCN to produce the pentacoordinate intermediate **I**. It is noteworthy that the catalytic activity of different nucleophilic catalytic systems, such as fluoride ion,[25,26] as well as oxygen-containing[47–51] or sulfur-containing nucleophiles,[52] can be correlated with the dissociation energies of the formed bonds between Si and the nucleophilic centers to produce pentacoordinate silicon complexes.[5,65] The catalytic activity of dithiocarbamate anions may be intensified by the presence of second nucleophilic centers to form hexacoordinated silicon com-

plexes analogous to that suggested by Olah and co-workers for carbonate anion (intermediate **II**).[23] Interestingly, formation of the later silicon complex could be facilitated by the presence of the nitrogen atom in the proximity of the second nucleophilic sulfur atoms. This pattern of reactivity could be attributed to the vacant 3d-orbital in silicon atom.[57] The cyanide nucleophile can then add to the carbonyl compound, and the resulting alkoxide anion can coordinate to the silicon atom of the coordination sphere. Again a penta- or hexacoordinated intermediate (**III** or **IV**) is possible. Collapsing the later intermediates affords the desired cyanohydrin trimethylsilyl ethers (**5**) with the regeneration of the catalysts.

To illustrate the efficiency of the new method, Table 3 compares our results with some of those reported in the literature.[17,24,47,52,56]

Conclusion

In conclusion, potassium 4-benzylpiperidinedithiocarbamate (PBPDC) was found to be a mild and efficient nucleophilic organocatalyst for promoting cyanosilylation of carbonyl compounds under solvent-free conditions. The excellent functional group tolerance, high to quantitative yields, availability of inexpensive starting materials together with the simplicity of the reaction and green methodology provide a convenient and practical method for the preparation of cyanohydrin trimethylsilyl ethers after short reaction time.

Acknowledgments

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