



Communication

Activation of trimethylsilyl cyanide by potassium phthalimide for facile synthesis of TMS-protected cyanohydrins

Mohammad G. Dekamin ^{*,1}, Zahra Karimi

College of Chemistry, Iran University of Science and Technology, Resalat Square, Narmak, Tehran 16846-13114, Iran

ARTICLE INFO

Article history:

Received 26 November 2008

Received in revised form 5 January 2009

Accepted 15 January 2009

Available online 21 February 2009

Keywords:

Carbonyl compounds

Cyanosilylation

Potassium phthalimide

Trimethylsilyl cyanide

Organocatalysis

Solvent-free synthesis

ABSTRACT

Potassium phthalimide was found to be a highly effective and easily accessible organocatalyst for the cyanosilylation of various carbonyl compounds under extremely mild conditions. The corresponding cyanohydrin trimethylsilyl ethers were obtained in high to quantitative yields in solvent-free conditions at room temperature using 2.5 mol% catalyst loading.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The addition of cyanide to aldehydes and ketones is one of the oldest known carbon–carbon bond-forming reactions. First reported in 1832 by Winkler, this reaction is the foundation of the Kiliani–Fischer synthesis of carbohydrates [1–3]. Cyanohydrins are of synthetic interest as they can be elaborated into several significant building blocks such as α -hydroxy acids, α -amino acids, α -hydroxy aldehydes or ketones, vicinal diols, β -amino alcohols, 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 [1–51]. However, Preparation of cyanohydrins by the addition of highly toxic HCN to carbonyl group is not a straightforward process and the procedure should be undertaken with caution [3,21]. The other problem which affects the yields of the products stems from the existence of inevitable equilibrium condition between the reactants and the adduct product [2,20]. To overcome these problems, cyanohydrins from carbonyl compounds are generally prepared in *O*-protected form. The cyanosilylation of carbonyl compounds is particularly suitable since the silyl protecting groups can be removed under very mild reaction conditions. The cyanohydrin trimethylsilyl ethers are generally prepared by the addition of trimethylsilyl cyanide (TMSCN), a safe and easily handled reagent

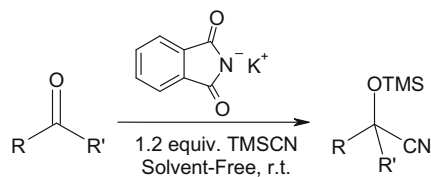
compared to HCN and KCN or NaCN [3–6,21,42], to carbonyl compounds in the presence of Lewis acids [4–19], inorganic Lewis bases [22–25], and double activating [3,26] or bifunctional catalytic systems [27–29]. However, many of these methods suffer from several disadvantages such as use of heavy and expensive metal catalysts [3,12–16], high catalyst loading [6,13,14,22,23], the requirement for an inert atmosphere or anhydrous solvents [11–17,19,21–25] and prolonged reaction times [15,16].

Nowadays, organocatalysis is being vigorously pursued because of its attractive features such as high efficiency, the transition metals-free conditions, experimental simplicity, inexpensive and environmentally benign reagents, potential for large scale reaction and the ease to recover the organocatalysts. Some organocatalysts have been introduced for cyanosilylation of carbonyl compounds in the recent years [1,21,31–51]. Despite improved results, the ideal catalytic system for the practical and broadly applicable synthesis of cyanohydrins remains elusive. On the other hand, green chemistry as applied to chemical processes can be considered as a series of reductions such as energy, auxiliaries, waste, etc. and should always lead to the simplification of the process in terms of the number of chemicals and steps involved. Complete removing or replacement of a safer solvent in a chemical process is likely to often be the greatest reduction and simplification (in the work-up as well as the reaction) that can be achieved [52]. To the best of our knowledge, most of the introduced protocols for cyanosilylation of carbonyl compounds have been reported by using toxic solvents such as DMF [21,43–45], CH_3CN [1,12,23–25], CHCl_3 [40] or CH_2Cl_2 [11–17,19,26,34–39,51] and the number of methods under sol-

* Corresponding author. Tel.: +98 21 7724 0284; fax: +98 21 7749 1204.

E-mail address: mdekamin@iust.ac.ir (M.G. Dekamin).

¹ Previous name: Mohammed G. Dakamin.



R= Aryl, Alkenyl, Alkyl
R'= H, Alkyl

Scheme 1. Cyanosilylation of carbonyl compounds catalyzed by PPI.

vent-free conditions remains quiet limited [5,6,18,33,49]. In continuation of our interest to develop new efficient nucleophilic organocatalysts for cyanosilylation of carbonyl compounds [33–35], we herein disclose the application of potassium phthalimide (PPI) as an efficient organocatalyst for the addition of TMSCN to carbonyl compounds under mild and solvent-free conditions affording various cyanohydrin trimethylsilyl ethers (Scheme 1).

2. Experimental

2.1. General

FT IR spectra were recorded as KBr pellets on a Shimadzu FT IR-8400S spectrometer. ^1H 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 or DMSO 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. All chemicals were purchased from Merck or Aldrich and used as received except for benzaldehyde which a fresh distilled sample was used. The catalyst were powdered and dried at 70°C for 1 h under reduced pressure [51,52]. All reactions were protected from air moisture using a CaCl_2 guard tube. Analytical TLC was carried out using Merck 0.2 mm silica gel 60 F-254 Al-plates. All compounds well characterized by GC analysis, IR and NMR spectral data as compared with those obtained from authentic samples or reported in the literature [4,17,23,24,33,34].

2.2. General procedure for cyanosilylation of carbonyl compounds

TMSCN (1.2 mmol, 0.15 mL) was added to a mixture of 1.0 mmol of a carbonyl compound and PPI (0.025 mmol, 4.6 mg). The obtained solution was stirred at room temperature for 10–120 min. The reaction was monitored by TLC and GC analysis. After the aldehyde or ketone was completely consumed, the reaction mixture was quenched by water (2.5 mL) and the organic materials were extracted with EtOAc (2×2.5 mL). The obtained organic phase was washed with brine followed by water (5.0 mL) and dried over MgSO_4 . The solvent was evaporated on a rotary evaporator to afford the desired products which in some cases were essentially pure cyanohydrin TMS ethers. Further purification of the products was performed by silica gel column chromatography (EtOAc–hexane, 1:10). The isolated yields were in good agreement with those obtained by GC analysis.

2.3. Selected spectroscopic data

2.3.1. 2-(4-Chlorophenyl)-2-(trimethylsilyloxy) acetonitrile (7a)

Yield 96%; ^1H NMR (500 MHz; CDCl_3 ; TMS): δ_{H} 0.28 (s, 9H), 5.53 (s, 1H), 7.41–7.42 (d, $J = 8.50$, 2H), 7.45–7.46 (d, $J = 8.50$, 2H); ^{13}C NMR (125 MHz, CDCl_3 , 25°C , TMS): δ_{C} –0.3, 62.9, 118.8, 127.7, 129.1, 134.8, 135.2.

2.3.2. (2-Nitrophenyl)-2-(trimethylsilyloxy) acetonitrile (7d)

Yield 99%; ^1H NMR (500 MHz; CDCl_3 ; TMS): δ_{H} 0.31 (s, 9H), 6.25 (s, 1H), 7.61–7.65 (t, $J = 8.20$, 1H), 7.79–7.82 (t, $J = 7.80$, 1H), 8.04–8.06 (d, $J = 7.80$, 1H), 8.16–8.18 (d, $J = 8.20$, 1H); ^{13}C NMR (125 MHz, CDCl_3 , 25°C , TMS): δ_{C} 2.0, 60.6, 117.5, 125.9, 129.5, 130.9, 131.0, 134.9, 147.0.

2.3.3. (4-Methoxyphenyl)-2-(trimethylsilyloxy) acetonitrile (7i)

Yield 93%; ^1H NMR (500 MHz; CDCl_3 ; TMS): δ_{H} 0.08 (s, 9H), 3.77 (s, 3H), 5.40 (s, 1H), 6.88–6.90 (d, $J = 8.70$, 2H), 7.37–7.39 (d, $J = 8.70$, 2H); ^{13}C NMR (125 MHz, CDCl_3 , 25°C , TMS): δ_{C} 1.9, 55.5, 63.0, 114.5, 119.4, 127.8, 128.4, 160.5.

2.3.4. (4-Nitrophenyl)-2-(trimethylsilyloxy) propionitrile (7q)

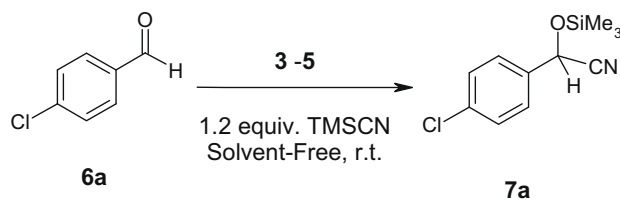
Yield 100%; ^1H NMR (500 MHz; CDCl_3 ; TMS): δ_{H} 0.27 (s, 9H), 1.91 (s, 3H), 7.76–7.78 (d, $J = 8.87$, 2H), 8.29–8.31 (t, $J = 8.87$, 2H); ^{13}C NMR (125 MHz, CDCl_3 , 25°C , TMS): δ_{C} 1.0, 33.4, 70.8, 120.6, 123.9, 125.7, 148.1, 148.9.

3. Results and discussion

Organocatalytic protocols for cyanosilylation of carbonyl compounds have almost shown their catalytic activity by Lewis base catalysis [53,54]. Exceptions are thiourea derivatives [50] or *N*-iodosuccinimide [51]. Although the nitrogen atom, as a suitable Lewis basic site, exists in the structure of the most organocatalysts,

Table 1

Optimization and comparison of the cyanosilylation of 4-chlorobenzaldehyde **6a** catalyzed by various PI alkali-metal salts under solvent-free conditions at room temperature.^a



| Entry | Catalyst | mol% | Time (min) | Conversion ^b (%) | TON ^c | TOF (h ⁻¹) ^d |
|-------|---------------------------|------|------------|-----------------------------|------------------|-------------------------------------|
| 1 | PPI 3 | 1.0 | 100 | 93 | 93.0 | 55.7 |
| 2 | PPI 3 | 2.5 | 30 | 96 | 38.4 | 76.8 |
| 3 | PPI 3 | 3.0 | 25 | 95 | 31.7 | 76.0 |
| 4 | LPI 4 ^e | 2.5 | 75 | 97 | 38.8 | 31.0 |
| 5 | SPI 5 ^f | 2.5 | 50 | 96 | 38.4 | 46.1 |
| 6 | PI 1 | 2.5 | 720 | 0.0 | 0.0 | 0.0 |
| 7 | – | – | 180 | 0.0 | 0.0 | 0.0 |

^a TMSCN (1.2 mmol) was added to a mixture of 4-chlorobenzaldehyde (**6a**, 1.0 mmol) and the catalyst (**3–5**, 2.5 mol%).

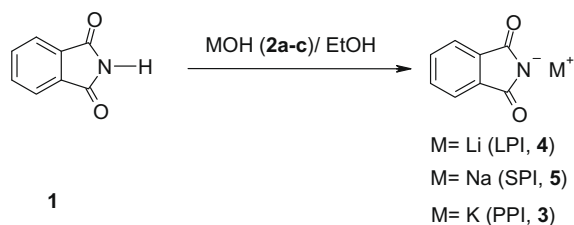
^b Determined by GC analysis.

^c Turnover number: moles of product per mole of catalyst.

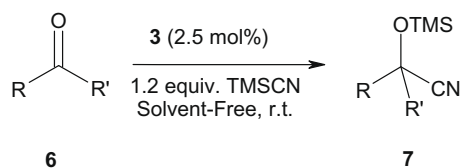
^d Turnover frequency: moles of product per mole of catalyst per hour.

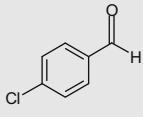
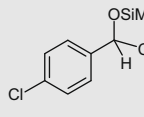
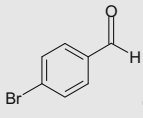
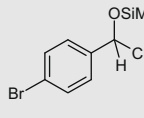
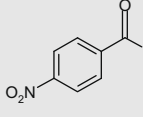
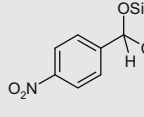
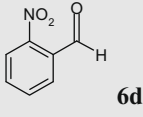
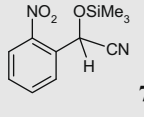
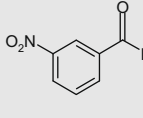
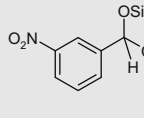
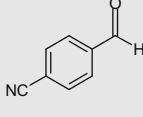
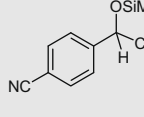
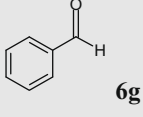
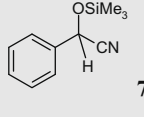
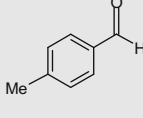
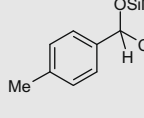
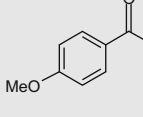
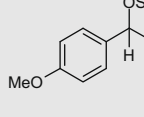
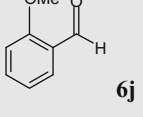
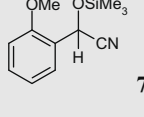
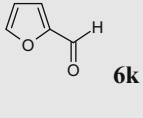
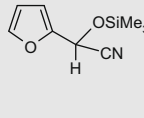
^e Lithium phthalimide.

^f Sodium phthalimide.



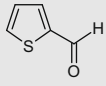
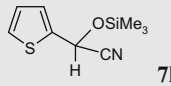
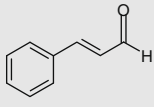
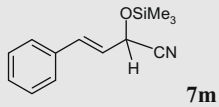
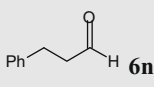
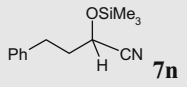
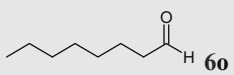
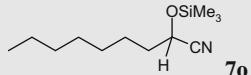
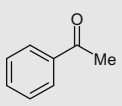
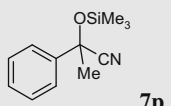
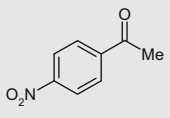
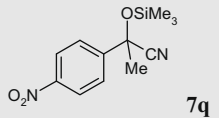
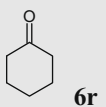
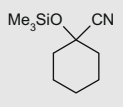
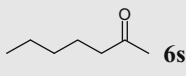
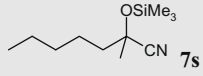
Scheme 2. Different salts of the PI nucleophile (**3–5**) prepared from phthalimide (**1**) and corresponding hydroxide (**2a–c**).

Table 2Potassium phthalimide cyanosilylation of various carbonyl compounds at optimized conditions.^a

| Entry | Substrate | Time (min) | Product | Conversion ^b (yield ^c) (%) |
|-------|---|------------|--|---|
| 1 |  6a | 30 |  7a | 96 (92) |
| 2 |  6b | 45 |  7b | 100 (98) |
| 3 |  6c | 5 |  7c | 99 |
| 4 |  6d | 10 |  7d | 99 (95) |
| 5 |  6e | 15 |  7e | 99 |
| 6 |  6f | 10 |  7f | 96 (93) |
| 7 |  6g | 45 |  7g | 100 (95) |
| 8 |  6h | 45 |  7h | 98 |
| 9 |  6i | 45 |  7i | 96 (93) |
| 10 |  6j | 45 |  7j | 99 (97) |
| 11 |  6k | 70 |  7k | 100 (99) |

(continued on next page)

Table 2 (continued)

| Entry | Substrate | Time (min) | Product | Conversion ^b (yield ^c) (%) |
|-------|---|------------|--|---|
| 12 |  6l | 75 |  7l | 97 |
| 13 |  6m | 120 |  7m | 70 |
| 14 |  6n | 60 |  7n | 100 (99) |
| 15 |  6o | 75 |  7o | 95 |
| 16 |  6p | 120 |  7p | 65 |
| 17 |  6q | 90 |  7q | 100 (99) |
| 18 |  6r | 100 |  7r | 90 |
| 19 |  6s | 120 |  7s | 95 |

^a TMSCN (1.2 mmol) was added to a mixture of appropriate carbonyl compound (**6**, 1.0 mmol) and the catalyst (**3**, 2.5 mol%).

^b Determined by GC analysis.

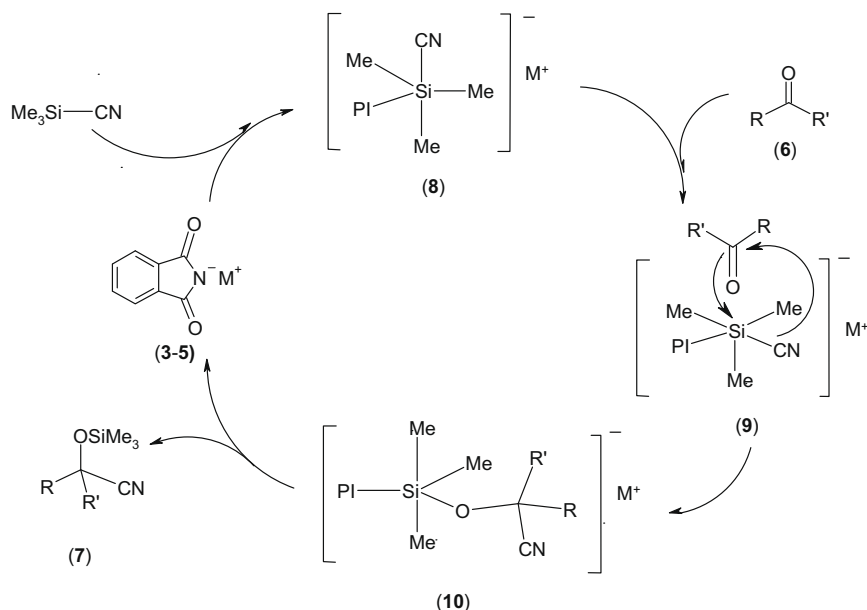
^c Isolated yields.

however other nucleophilic centers such as oxygen, sulfur, phosphorus, and carbon constitute the active sites in these catalytic systems. Examples are tetrabutylammonium dimethylphosphate [21], alkali-metal salts of amino acids [31,32], imidazolium-carbodi-thioate zwitterions [36], different derivatives of phosphazanes [42,43], *N*-heterocyclic carbenes (NHCs) [44–47] or tetrabutylammonium cyanide (TBACN) [48].

Among of different organocatalytic systems, various achiral or chiral tertiary amines have been used as suitable nitrogen-containing nucleophilic catalysts to catalyze cyanosilylation of carbonyl compounds [1,37–39]. However, the most of amine nucleophiles such as DABCO [37] or quaternized DBU [38] have obtained moderate yields in cyanosilylation of carbonyl compounds and only highly basic tetra-substituted guanidines produced excellent yields [37]. On the other hand, potassium phthalimide (PPI) has been extensively used as a suitable nucleophile in the Gabriel synthesis of primary amines [55,56]. However, it has received less attention as a catalyst in organic synthesis [57,58]. Recently, we have reported our discovery of efficient cyclotrimerization of aryl and alkyl isocyanates using imide Lewis basic catalysts such as

potassium phthalimide (PPI) or succinimide (PSI) [58] and sodium saccharin combined with tetrabutylammonium iodide [59] under solvent-free conditions. As part of our ongoing efforts to gain more insight into catalytic activity of phthalimide (PI) anion as a readily available Lewis basic catalyst [57,58], we now wish to disclose a facile PI-catalyzed cyanosilylation between TMSCN and carbonyl compounds.

In the first place, cyanosilylation of model compound 4-chlorobenzaldehyde **6a** was examined using different catalytic amounts of PPI **3**, as a commercially available and inexpensive nucleophilic catalyst, at room temperature under solvent-free conditions. The results have been summarized in Table 1. It was found that the best result in terms of turnover number (TON) and turnover frequency (TOF) could be achieved by using catalyst **3** (2.5 mol% loading) (Table 1, entry 2). On the other hand, It has been reported that inorganic lithium salts such as LiClO₄ [6] and LiCl [7] can promote cyanosilylation of carbonyl compounds as Lewis acidic catalysts in both stoichiometric or catalytic amounts under solvent-free conditions, respectively. Hence, lithium phthalimide (LPI, **4**) and sodium phthalimide (SPI, **5**) were also examined in cyanosilylation



Scheme 3. Proposed catalytic cycle of phthalimide alkali-metal salts catalyzed cyanosilylation of carbonyl compounds.

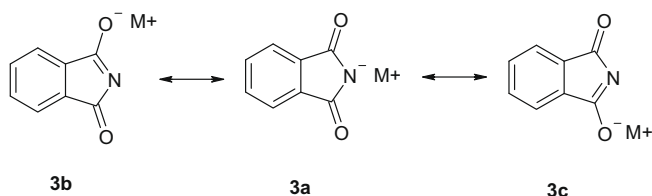


Fig. 1. Possible resonance structures for the phthalimide (PI) anion.

of **6a** at 2.5 mol% catalyst loading under similar reaction conditions (entries 4, 5). However, longer reaction time was required for LPI compared with PPI and SPI. The above results clearly indicate that the reaction is substantially promoted by the PI anion as a Lewis basic organocatalyst. Also, no reaction was observed under similar reaction conditions by using **1** or in the absence of the **3–5** (entries 6, 7). It is noteworthy that **4** and **5** could be easily prepared in quantitative yields by the reaction of phthalimide ($pK_a = 8.3$, **1**) with an equivalent amount of the corresponding metal hydroxide in ethanol under reflux conditions (Scheme 2) [55]. The organocatalysts **3–5** have good lifetimes and were resistant to moisture and air. They could be used for months without loss of performance.

Encouraged by this result, a wide range of aromatic, heterocyclic and aliphatic carbonyl compounds were subjected to cyanosilylation using a catalytic quantity of **3** (2.5 mol%) under optimized reaction conditions (TMSCN/aldehyde = 1.2 equiv., solvent-free, r.t.). Table 2 shows the scope of the reaction wherein high to quantitative yields of cyanohydrin trimethylsilyl ethers **7a–s** were obtained in all the cases studied. No by-products such as products of benzoin condensation or desilylation were observed at all. On the other hand, this protocol is especially suitable for substrates such as furfural, thiophene-2-carbaldehyde and cinnamaldehyde which are decomposed or polymerized under acidic conditions (Table 2, entries 11–13) [6,41]. However, cinnamaldehyde as an α,β -unsaturated aldehyde gave moderate yield of the desired product of 1,2-addition. This result may be associated with a simultaneous interaction of the catalyst with TMSCN (Scheme 3) and carbon–carbon double bond moiety in this substrate. Also, aromatic and aliphatic ketones, such as acetophenone or its 4-nitro

derivative, 2-heptanone and cyclohexanone gave the corresponding cyanohydrins in high to quantitative yields. However, addition of TMSCN to ketones is slower in comparison with aldehydes due to more steric hindrance around the carbonyl group of ketones than of aldehydes (entries 16–19) [5,6].

In general, the reaction conditions are mild and catalyst could be easily separated by aqueous extraction from the reaction mixture. It is noteworthy that the most of organocatalytic cyanosilylations, especially tertiary amines, require column chromatography to separate the catalyst from the reaction mixture [1,38,39]. Therefore, separation of the catalyst by aqueous extraction prior to the purification of the product could lead to the simplification of the process.

The silicon atom expands its coordination sphere with Lewis basic catalysts to give relatively stable penta- or hexacoordinated compounds, or “hypervalent silicates”, due to its vacant 3d-orbital. The obtained extracoordinated species are powerful intermediates with abundant reactivities. Hence, remarkable developments have been made with regard to various organic reactions based on this unique mechanism [60]. Interestingly, the negative charge of the PI anion is delocalized onto the adjacent carbonyl oxygen atoms, consequently it acts as a nucleophile rather than a base (Fig. 1). Oxygen-containing nucleophiles are among more efficient catalysts due to high bond strength as well as the kinetic lability of the silicon–oxygen bond [21,33–35]. Therefore, the trimethylsilylcyanation intermediate in our reactions is assumed to involve an initial penta-coordinate silicon intermediate **8** formed by the interaction of oxygen or nitrogen atoms in the catalyst **3a–c** with TMSCN, analogous to that suggested by Olah and Kobayashi for oxygen-containing [21] or amine [41] nucleophiles. The intermediate **8** may undergo nucleophilic attack by the carbonyl oxygen of the aldehyde or ketone **6** to give rise to the six-coordinate intermediate **9**. This intermediate may then decompose to product **7** and regenerated catalyst **3–5** via the 5-center intermediate **10** (Scheme 3).

4. Conclusion

In summary, potassium phthalimide (PPI) was found as a highly effective organocatalysts to promote the cyanosilylation of a wide

variety of carbonyl compounds under extremely mild conditions. The important features of our method include wide substrate scope, mild reaction conditions, simple work-up, and stable, inexpensive and readily available catalyst. This protocol not only presents a new organocatalytic synthesis of cyanohydrin trimethylsilyl ethers, but also adds a useful entry into the reactions catalyzed by phthalimide nucleophile. Further efforts will be devoted to the application of PI in other reactions using trimethylsilyl reagents.

Acknowledgement

We are grateful for the financial support from the Research Council of Iran University of Science and Technology (IUST), Iran (Grant No. 160/5295).

References

- [1] S.E. Denmark, W. Chung, *J. Org. Chem.* 71 (2006) 4002. and references cited therein.
- [2] R.J.H. Gregory, *Chem. Rev.* 99 (1999) 3649.
- [3] N.H. Khan, R.I. Kureshy, S.H.R. Abdi, S. Agrawal, R.V. Jasra, *Coord. Chem. Rev.* 252 (2008) 593.
- [4] D.H. Ryu, E.J. Corey, *J. Am. Chem. Soc.* 127 (2005) 5384.
- [5] N.H. Khan, S. Agrawal, R. Kureshy, S.H.R. Abdi, S. Singh, R.V. Jasra, *J. Organomet. Chem.* 692 (2007) 4361.
- [6] N. Azizi, M.R. Saidi, *J. Organomet. Chem.* 688 (2003) 283.
- [7] N. Kurono, M. Yamaguchi, K. Suzuki, T. Ohkuma, *J. Org. Chem.* 70 (2005) 6530.
- [8] H. Firouzabadi, N. Iranpoor, A.A. Jafari, *J. Organomet. Chem.* 690 (2005) 1556.
- [9] S. Kataoka, A. Endo, A. Harada, Y. Inagi, T. Ohmori, *Appl. Catal. A Gen.* 342 (2008) 107.
- [10] A. Heydari, L. Ma'Mani, *Appl. Organometal. Chem.* 22 (2008) 12.
- [11] C. Baleizão, B. Gigante, H. Garcia, A. Corma, *Tetrahedron* 60 (2004) 10461.
- [12] S.K. De, R.A. Gibbs, *J. Mol. Catal. A Chem.* 232 (2005) 123.
- [13] Z. Zeng, G. Zhao, P. Gao, H. Tang, B. Chen, Z. Zhou, C. Tang, *Catal. Commun.* 8 (2007) 1443.
- [14] M.L. Kantam, S. Laha, J. Yadav, B.M. Choudary, B. Sreedhar, *Adv. Synth. Catal.* 348 (2006) 867.
- [15] M.S. Yoon, R. Ramesh, J. Kim, D. Ryu, K.H. Ahn, *J. Organomet. Chem.* 691 (2006) 5927.
- [16] W.K. Cho, J.K. Lee, S.M. Kang, Y.S. Chi, H. Lee, I.S. Choi, H.S. Lee, *Chem. Eur. J.* 13 (2007) 6351.
- [17] B. Karimi, L. Ma'Mani, *Org. Lett.* 6 (2004) 4813.
- [18] S.C. George, S.S. Kim, S.T. Kadam, *Appl. Organometal. Chem.* 21 (2007) 994.
- [19] L. Mei, S.W. Wong, H.K. Liang, W.S. Xuan, *Appl. Organometal. Chem.* 22 (2008) 181.
- [20] F.L. Cabiro, A.E.C. Lim, U. Hanefeld, R.A. Sheldon, I.M. Lyapkalo, *J. Org. Chem.* 73 (2008) 2446.
- [21] G.K.S. Prakash, H. Vaghoo, C. Panja, V. Surampudi, R. Kultyshev, T. Mathew, G.A. Olah, *Proc. Natl. Acad. Sci. USA* 104 (2007) 3026.
- [22] B. He, Y. Li, X. Feng, G. Zhang, *Synlett* (2004) 1776.
- [23] S.S. Kim, J. Rajagopal, D.H. Song, *J. Organomet. Chem.* 689 (2004) 1734.
- [24] S.S. Kim, D.H. Song, *Lett. Org. Chem.* 1 (2004) 264.
- [25] S.S. Kim, J.T. Lee, S.H. Lee, *Bull. Korean Chem. Soc.* 26 (2005) 993.
- [26] B.M. Trost, S. Martinez-Sanchez, *Synlett* (2005) 627.
- [27] S. Hun, H. Chen, J.W. Wiench, M. Pruski, V.S. Lin, *Angew. Chem., Int. Ed.* 44 (2005) 1826.
- [28] M. Takamura, K. Yabu, T. Nishi, H. Yanagisawa, M. Kanai, M. Shibasaki, *Synlett* (2003) 353.
- [29] Y. Hamashima, D. Sawada, H. Nogami, M. Kanai, M. Shibasaki, *Tetrahedron* 57 (2001) 805.
- [30] Y. Hamashima, M. Kanai, M. Shibasaki, *Tetrahedron Lett.* 42 (2001) 691.
- [31] X. Liu, B. Oin, X. Zhou, B. He, X. Feng, *J. Am. Chem. Soc.* 127 (2005) 12224.
- [32] S.C. George, S.S. Kim, G. Rajagopal, *Appl. Organometal. Chem.* 21 (2007) 798.
- [33] M.G. Dekamin, M. Farahmand, S. Javanshir, M.R. Naimi-Jamal, *Catal. Commun.* 9 (2008) 1352.
- [34] M.G. Dekamin, S. Javanshir, M.R. Naimi-Jamal, R. Hekmatshoar, J. Mokhtari, *J. Mol. Catal. A Chem.* 283 (2008) 29.
- [35] M.G. Dekamin, J. Mokhtari, M.R. Naimi-Jamal, *Catal. Commun.* 10 (2009) 582.
- [36] A. Blanrue, R. Wilhelm, *Synlett* (2004) 2621.
- [37] L. Wang, X. Huang, J. Jiang, X. Liu, X. Feng, *Tetrahedron Lett.* 47 (2006) 1581.
- [38] I.V.P. Raj, G. Suryavanshi, A. Sudalai, *Tetrahedron Lett.* 48 (2007) 7211.
- [39] S.K. Tian, R. Hong, L. Deng, *J. Am. Chem. Soc.* 125 (2003) 9900.
- [40] S. Kobayashi, Y. Tsuchiya, T. Mukaiyama, *Chem. Lett.* (1991) 537.
- [41] X. Wang, S.K. Tian, *Tetrahedron Lett.* 48 (2007) 6010.
- [42] Z. Wang, B.M. Fetterly, J.G. Verkade, *J. Organomet. Chem.* 646 (2002) 161.
- [43] B.M. Fetterly, J.G. Verkade, *Tetrahedron Lett.* 46 (2005) 8061.
- [44] J.J. Song, F. Gallou, J.T. Reeves, Z. Tan, N.K. Yee, C.H. Senanyake, *J. Org. Chem.* 71 (2006) 1273.
- [45] Y. Fukuda, Y. Maeda, S. Ishii, K. Kondo, T. Aoyama, *Synthesis* (2006) 589.
- [46] Y. Fukuda, K. Kondo, T. Aoyama, *Synthesis* (2006) 2649.
- [47] Y. Suzuki, M.D. Abu Bakar, K. Muramatsu, M. Sato, *Tetrahedron* 62 (2006) 4227.
- [48] I. Amurrio, R. Córdoba, A.G. Csáky, J. Plumet, *Tetrahedron* 60 (2004) 10521.
- [49] X. Wang, S.K. Tian, *Synlett* (2007) 1416.
- [50] S.J. Zuend, E.N. Jacobsen, *J. Am. Chem. Soc.* 129 (2007) 15872.
- [51] S.T. Kadam, S.S. Kim, *Catal. Commun.* 9 (2008) 1342.
- [52] C. Villa, E. Mariani, A. Loupy, C. Grippio, G.C. Grossia, A. Bargagna, *Green Chem.* 5 (2003) 623.
- [53] For a recent review on Lewis base catalysis, see: S.E. Denmark, G.L. Beutner, *Angew. Chem., Int. Ed.* 47 (2008) 1560.
- [54] For a review on selective catalysis by using hard-soft acid and base (HSAB) principle, see: S. Woodward, *Tetrahedron* 58 (2002) 1017.
- [55] P.L. Salzberg, J.V. Supniewski, in: H. Gilman, A.H. Blatt (Eds.), *Organic Synthesis Collection*, vol. 1, John Wiley, New York, 1995.
- [56] M.B. Smith, J. March, *March's Advanced Organic Chemistry Reactions Mechanisms and Structure*, 5th ed., John Wiley, New York, 2001.
- [57] H. Fujisawa, E. Takahashi, T. Mukaiyama, *Chem. Eur. J.* 12 (2006) 5082.
- [58] F.M. Moghaddam, M.G. Dekamin, G.R. Koozehgari, *Lett. Org. Chem.* 2 (2005) 734.
- [59] F.M. Moghaddam, G.R. Koozehgari, M.G. Dekamin, *Monatsh. Chem.* 135 (2004) 849.
- [60] Y. Orito, M. Nakajima, *Synthesis* (2006) 1391.