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Perfectly Green Organocatalysis: Quaternary Ammonium Base Triggered Cyanosilylation of Aldehydes[†]

Wen, Yeqian(温叶倩) Liang, Mengwei(梁梦伟) Wang, Yiming*(王忆铭)
Ren, Weimin(任伟民) Lü, Xiaobing*(吕小兵)

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, Liaoning 116024, China

Quaternary ammonium bases, such as aqueous $(CH_3)_4NOH$, were found to be an extraordinarily efficient catalyst for cyanosilylation of aldehydes. The addition reaction of trimethylsilyl cyanide (TMSCN) to equivalent aldehydes could proceed smoothly with turnover frequency (TOF) up to 3000000 h^{-1} and in near 100% yield under solvent-free conditions. These organic catalysts also tolerated various aldehydes including aromatic, aliphatic and *α*,*β*-unsaturated aldehydes. This process perfectly conforms to the features of green chemistry: no waste regarding side-products and unconverted reactants, solvent-free, excellent catalytic activity, and no requirement for separation.

Keywords organocatalysis, green chemistry, cyanosilylation, quaternary ammonium base, solvent-free

Introduction

In the past decades, we have witnessed notable advances in organic synthesis. The resultant chemicals concern almost every aspect of our lives and significantly improve the quality of the lives of the billions of individuals who now inhabit the planet. However, the manufacturing processes of these useful chemicals usually need the use of a large amount of organic solvents, and also produce undesired byproducts. These substances, as well as the inactive catalysts and unconverted reactants have substantial negative effects on human health and the environment. In fact, the greatest release of hazardous waste to the environment is the chemical industry.[1] Unfortunately, it wasn't until 1990s that the environmental impact of chemical substances had been fully recognized as a serious problem.[2]

Along with the increasing concern about the global problem of pollution, 'Green chemistry', which suggests developing green chemical methods for pollution prevention rather than end-of-pipe control,[3] was proposed and rapidly become a significant area of organic synthetic chemistry.[4] Along with the conception of 'Green chemistry', several other topics, such as atomic economic reaction,[5] green solvent,[6] phase transfer catalysis,[7] ionic liquid,[8] and water-based reaction,[9] were also put forward. An ideal reaction is expected to proceed efficiently under solvent-free condition with very low catalyst loading, short reaction time and selective for target compounds with a 100% yield without any production of waste.[10] The process should be economical, safe, energy-efficient, environmentally benign, and easily capable of being scaled up.[11] Herein, we report a highly efficient organocatalysis: quaternary ammonium base triggered cyanosilylation of aldehydes at mild conditions (Figure 1). This process perfectly conforms to the features of green chemistry: no waste regarding side-products and unconverted reactants, solvent-free, excellent catalytic activity with a TOF up to 3 000 000 h^{-1}, and no requirement for separation. Furthermore, two chiral quaternary ammonium bases **I** and **II** derived from cinchonine were also synthesized for investigating the effect of the cation on the reaction (Scheme 1).

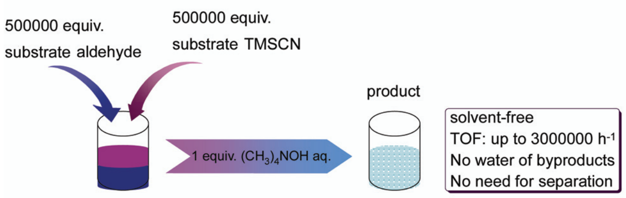

Figure 1 $(CH_3)_4NOH$ triggered cyanosilylation of aldehydes with equimolar TMSCN.

Experimental

General information

^1H, and ^{13}C NMR spectra were recorded on a Varian

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* E-mail: chemwym@dlut.edu.cn; lxb-1999@163.com; Tel.: 0086-0411-84986255; Fax: 0086-0411-84986256
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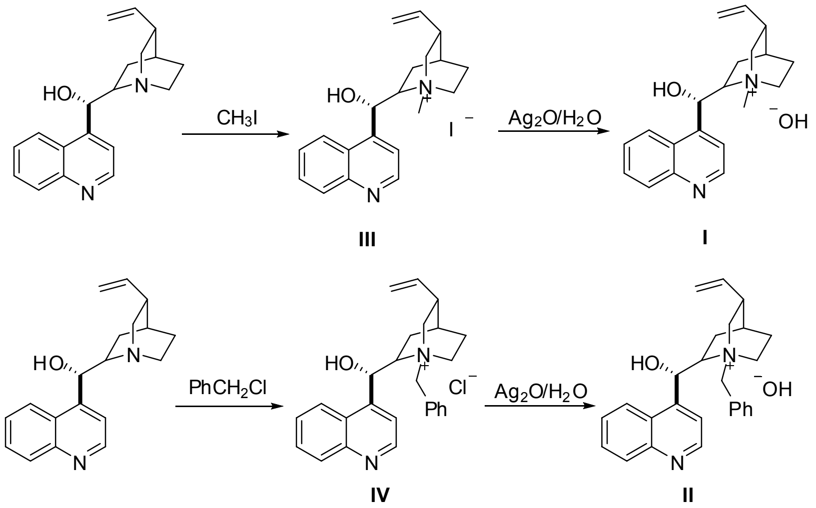
Scheme 1



INOVA-400 MHz type (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shift at δ 0 for ^{1}H NMR and against the solvent, chloroform-*d* at δ 77.0 for ^{13}C NMR, respectively. High Resolution Mass Spectrometry (HRMS) was performed on a Micromass Q-Tof (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray). Fourier Transform Infrared spectroscopy (FTIR) was performed on Nicolet NEXUS FT-IR spectrophotometer equipped with a liquid cell (Harrick Scientific Corporation). All aldehydes were freshly distilled before use. $(CH_3)_4OH$ and $(n\text{-Bu})_4OH$ were bought from Sinipharm Chemical Reagent Co., Ltd.

Representative procedure for the cyanosilylation of aldehydes

A 150-mL two-necked flask was equipped with a Teflon-coated magnetic stirring bar. The flask was charged with freshly distilled benzaldehyde (0.125 mol), and 1% $(CH_3)_4NOH$ aq. (2.3 μL, 2.5×10^{-7} mol, 2×10^{-6} equiv.), respectively. Then TMSCN (0.125 mol, 1 equiv.) was added into the mixture with constant-pressure drop funnel at ambient temperature, and the exothermic reaction immediately began. After stirring for 20 min, the solution was changed into colorless. NMR analyses confirmed the complete transformation of all substrates to the corresponding cyanosilylation product, 2-phenyl-2-trimethylsilyloxyacetonitrile.

Synthesis of quaternary ammonium bases derived from cinchonine

Compound III To a suspension of cinchonine (0.44 g, 1.50 mmol) in methanol (50 mL) in a 100 mL flask wrapped in aluminum foil, CH_3I (0.14 mL, 2.25 mmol) was added. The resulting mixture stirred for 24 h at room temperature before removing the solvent. The crude product was purified by column chromatography on silica gel, eluting with dichloromethane/methanol (V : V=10 : 1) to afford compound **III** as a light yellow solid (0.50 g, 76%). ^{1}H NMR (400 MHz, CD_3OD) δ: 8.93 (d, J=4.8 Hz, 1H), 8.20 (d, J=8.4 Hz, 1H), 8.11 (d, J=8.4 Hz, 1H), 7.90 (s, 1H), 7.83—7.87 (m, 1H), 7.77—7.81 (m, 1H), 6.36 (s, 1H), 6.02—6.11 (m, 1H), 5.27—5.34 (m, 2H), 4.47—4.52 (m, 1H), 3.74—3.83 (m, 2H), 3.54—3.65 (m, 2H), 3.47 (s, 3H), 2.84—2.90 (m, 1H), 2.38—2.44 (m, 1H), 2.02—2.06 (m, 2H), 1.88—1.93 (m, 1H), 1.02—1.07 (m, 1H).

Compound I A mixture of compound **III** (0.22 g, 0.50 mmol), H_2O (9 μL, 0.50 mmol) and Ag_2O (0.09 g, 0.38 mmol) in methanol (50 mL) in a 100 mL flask wrapped in aluminum foil was stirred for 24 h at room temperature. Then the mixture was filtered to remove solid, and the filtrate was collected and the solvent was removed. The residue was purified by column chromatography on aluminum oxide (neutral) column, eluting with dichloromethane/methanol (V : V=20 : 1) to afford compound **I** as a white solid (0.15 g, 92%). m.p. 256—259 ℃; ^{1}H NMR (400 MHz, D_2O) δ: 8.63 (d, J=4.8 Hz, 1H), 7.84 (d, J=7.6 Hz, 1H), 7.79 (d, J=7.6 Hz, 1H), 7.60—7.63 (m, 2H), 7.49—7.53 (m, 1H), 6.16 (s, 1H), 5.77—5.86 (m, 1H), 5.09—5.10 (m, 1H), 5.06—5.07 (m, 1H), 4.14—4.20 (m, 1H), 3.41—3.45 (m, 2H), 3.28—3.36 (m, 2H), 3.22 (s, 3H), 2.60—2.67 (m, 1H), 2.01—2.07 (m, 1H), 1.78—1.79 (m, 2H), 1.52—1.57 (m, 1H), 0.68—0.72 (m, 1H); ^{13}C NMR (100 MHz, D_2O) δ: 150.1, 146.8, 145.9, 145.8, 136.8, 130.5, 128.9, 128.1, 124.5, 122.7, 119.8, 117.3, 66.7, 65.8, 61.5, 59.8, 48.6, 37.6, 26.6, 23.9, 20.1. HRMS calcd for $C_{20}H_{25}N_2O$ $[M-OH]^+$ 309.1967, found 309.1975.

Compound IV Benzyl chloride (1.2 mL, 10.5 mmol) was added to a solution of cinchonine (2.0 g, 7.0 mmol) in ethanol (50 mL), DMF (60 mL) and chloroform (2.0 mL), and the mixture was stirred at 100 ℃ for 10 h. After cooling to room temperature, the mixture was added with Et_2O and pink solid precipitated. The precipitate was filtered and washed with additional Et_2O to give the product **IV** (2.8 g, 95%). ^{1}H NMR (400 MHz, CD_3OD) δ: 8.96 (d, J=4.8 Hz, 1H), 8.30 (d, J=8.0 Hz, 1H), 8.13 (d, J=7.6 Hz, 1H), 7.97 (d, J=4.8 Hz, 1H), 7.85—7.90 (m, 1H), 7.79—7.83 (m, 1H), 7.72—7.74 (m, 2H), 7.59—7.61 (m, 3H), 6.64 (s, 1H), 6.03—6.12 (m, 1H), 5.26—5.31 (m, 2H), 5.01—5.08 (m, 2H), 4.40—4.46 (m, 1H), 4.02 (t, J=10.0 Hz, 1H), 3.88 (t, J=10.4 Hz, 1H), 3.64 (t, J=11.2 Hz, 1H), 3.07—3.15 (m, 1H), 2.60—2.67 (m, 1H), 2.47—2.53 (m, 1H), 1.96 (s, 1H), 1.81—1.89 (m, 2H), 1.08—1.13 (m, 1H).

Compound II The synthesis of compound **II** was the same procedure of compound **I**. m.p. 258—260 ℃; ^{1}H NMR (400 MHz, CD_3OD) δ: 8.96 (d, J=4.8 Hz, 1H), 8.30 (d, J=8.0 Hz, 1H), 8.13 (d, J=7.6 Hz, 1H), 7.97 (d, J=4.4 Hz, 1H), 7.87 (t, J=7.2 Hz, 1H), 7.81 (t, J=6.8 Hz, 1H), 7.72—7.74 (m, 2H), 7.59—7.61 (m, 3H), 6.64 (s, 1H), 6.03—6.11 (m, 1H), 5.26—5.31 (m, 2H), 5.01—5.08 (m, 2H), 4.40—4.45 (m, 1H), 4.02 (t, J=9.6 Hz, 1H), 3.85—3.91 (m, 1H), 3.64 (t, J=11.2 Hz, 1H), 3.07—3.14 (m, 1H), 2.60—2.67 (m, 1H), 2.47—2.53 (m, 1H), 1.96 (s, 1H), 1.81—1.89 (m, 2H), 1.05—1.12 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ: 151.0, 148.7, 147.4, 137.7, 134.9, 131.7, 131.1, 130.4, 130.2, 129.1, 128.8, 126.1, 124.4, 121.2, 117.7, 69.0, 66.9, 64.96, 58.1, 55.8, 38.9, 28.5, 24.7, 22.3; HRMS (ESI) calcd for $C_{26}H_{29}N_2O$ $[M-OH]^+$ 385.2280, found 385.2290.

Results and Discussion

Cyanohydrins are versatile synthetic intermediates in organic chemistry, which can be transformed into a variety of valuable functional compounds, such as α-hydroxy acids, α-hydroxy aldehydes, β-hydroxy amines, and α-amino acid derivatives.[12] The addition reaction of trimethylsilyl cyanide (TMSCN) to carbonyl compounds has been well-known as one of the most effective methods for synthesizing cyanohydrins.[13] Numerous catalyst systems, including Lewis acids,[14] Lewis bases,[15-20] *N*-heterocyclic carbenes,[21] quaternary ammonium or phosphonium salts,[22-25] metal complexes,[26] inorganic salts,[27] and bifunctional catalysts,[28-30] have been developed for this transformation. Notably, solvent-free cyanosilylation of aldehydes was realized in some systems.[31]

The present study started with an accidental discovery that when tetrahydrofuran (THF) stored in sodium was used as solvent, the cyanosilylation of benzaldehyde could finish in 1 h without any external catalyst,[32] while no reaction was observed in the systems with the use of untreated solvent or distilled THF. It is tentatively ascribed to the trace amount of sodium hydroxide generated from sodium with the adventurous water in THF. Further studies found that various inorganic bases including LiOH, NaOH and KOH dissolved in THF could effectively catalyze this reaction. Detailed optimization experiments found that organic quaternary ammonium bases were shown to be the most effective. Subsequently, we adopted the simplest quaternary ammonium base $(CH_3)_4NOH$ instead of inorganic base as catalyst to make sure the function of anion. To our delight, the reaction proceeded within 10 min at a substrate-to-catalyst molar ratio as high as 10000 under solvent-free condition. There was no influence on reaction rate and yield even using equivalent TMSCN and benzaldehyde. Considering the hydrophilic property of quaternary ammonium base, we tried to use 25% $(CH_3)_4NOH$ aqueous solution as catalyst for this reaction. It was found that the simple catalyst system was still effective under the same conditions, indicating that the $(CH_3)_4NOH$-catalyzed cyanosilylation reaction was not sensitive to moisture. The high efficiency of the simple catalyst was also observed in the system with a ratio of substrate-to-catalyst to 500000∶1 (Table 1, Entry 1). The reaction was finished within 20 min and the TOF reached up to 1500000 h^{-1}. To the best of our knowledge, this system represents the most efficient catalyst known to date for this reaction. Such a high efficiency is comparable with oxynitrilase.[33] Notably, the system proved to be easily capable of being scaled up. In the presence of 0.36 μL (0.001 mmol) 25% $(CH_3)_4NOH$ aqueous solution, 53.0 g (500 mmol) benzaldehyde and 66.6 mL (500 mmol) TMSCN were completely converted into the corresponding cyanohydrin trimethylsilyl ether with 100% selectivity within 20 min. The ^{1}H NMR spectrum of the resultant product without any purification is very clear and has no difference with that of its pure form (Figure 2). Such a low catalyst concentration and no waste regarding byproducts and unconverted reactants make purification process unnecessary. From an economical as well as an environmental standpoint, this reaction process perfectly embodies economical, resource- and energy-efficient, and environmentally benign characters.

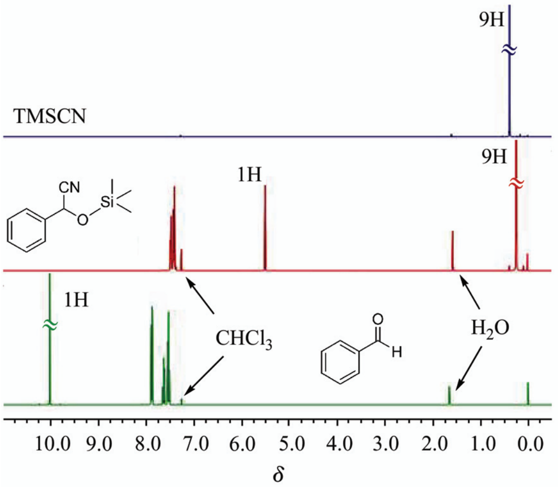


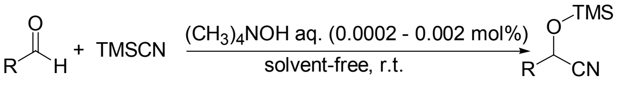
Figure 2 ^{1}H NMR spectra of benzaldehyde, TMSCN, and the untreated reaction mixture of benzaldehyde with equivalent TMSCN using $(CH_3)_4NOH$ as catalyst.

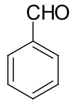
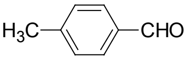
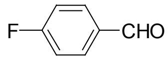
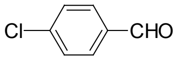
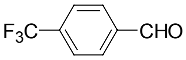
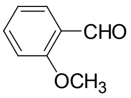
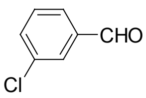
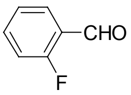
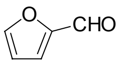
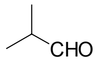
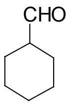
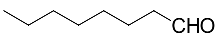
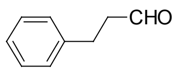
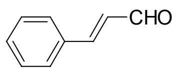
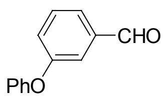
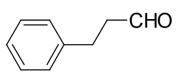
The scope with respect to aldehyde substrates was then explored with 0.0002—0.002 mol% $(CH_3)_4NOH$ loading under solvent-free condition. As shown in Table 1, various aromatic, aliphatic, and α,β-unsaturated aldehydes smoothly underwent the addition reaction and were converted into the corresponding cyanohydrin trimethylsilyl ether with 100% selectivity in excellent yields. The catalyst was particularly effective for aliphatic aldehydes. For example, when isobutylaldehyde or cyclohexanecarboxaldehyde was used as substrate (S/C=500000), the reaction could completed within 10 min and the TOF value is up to 3000000 h^{-1} (Entries 10 and 11). In the system regarding *α,β*-unsaturated aldehyde, only the 1,2-adduct was produced absolutely (Entry 14). The products of the reaction could be used for synthesizing agrochemicals, flavorings, and fragrances, for example, the cyanosilylation product of 3-phenoxybenzaldehyde is an intermediate for industrial production of pyrethroid insecticides (Entry 15). Unfortunately, upon replacing aldehydes with a ketone such as acetophenone, the cyanosilylation proceeded in a very low rate. With 1 mol% catalyst loading, the prolonged reaction time of 48 h gave a yield of 88%.

Similarly, anhydrous or aqueous $(n\text{-Bu})_4NOH$ also exhibited excellent activity for this reaction. For example, with 3-phenylpropanal as substrate, the cyanosilylation reaction was completely finished within 5 min under the same condition as $(CH_3)_4NOH$ (Table 1, Entry 16). For a comparison purpose, we also conducted control experiments using chiral quaternary ammonium bases **I** and **II** derived from cinchonine as catalysts for the cyanosilylation of benzaldehyde. Unfortunately, only racemic product was obtained with a 97% conversion after 15 min (S/C=100000/1), suggesting that the chiral property of the cation has no effect on the nucleophilic attack process.

Because of its easier weighing than $(CH_3)_4NOH$, we chose $(n\text{-Bu})_4NOH$ as model quaternary ammonium base for investigating the catalytic mechanism. Fourier Transform Infrared spectroscopy (FTIR) experiments were studied for the interaction of TMSCN and $(n\text{-Bu})_4NOH$. There is a strong absorption band at 2188 cm^{-1} derived from C≡N in the FTIR spectrum of TMSCN. After 0.2 equiv. of $(n\text{-Bu})_4NOH$ was added into TMSCN, a new band at 2045 cm^{-1} rapidly appeared, along with the decrease in intensity of the original band at 2188 cm^{-1}. The complete disappearance of the band at 2188 cm^{-1} was observed at the addition of equivalent $(n\text{-Bu})_4NOH$ (Figure 3). Prior to our study, Wang and Tian[24] reported the activation of TMSCN by benzyltriphenylphosphonium chloride by FTIR method. They found the appearance of a new cyanide stretching band at 2254 cm^{-1} in the IR spectrum of the 1∶1 mixture, which was different from that for TMSCN (2190 cm^{-1}) and TMSN=C (2088 cm^{-1}). Moreover, when benzaldehyde was introduced into the mixture of $(n\text{-Bu})_4NOH$ and TMSCN with 1∶1 ratio, the absorption peak at 2045 cm^{-1} speedily disappeared, occurring with the formation of the cyanosilylatio product (Figure 4). These results indicate a transition state of pentacoordinated alkylsilicate originated from the coordination of OH^- to silicon atom. Indeed, nu-

Table 1 $(CH_3)_4NOH$ aq.-catalyzed cyanosilylation of aldehydes[a]



Run	Aldehyde	S/C	*t*/min	Conv.[b]/%	TOF/h^{-1}
1		500000	20	100	1500000
2		50000	10	100	300000
3		500000	60	97	490000
4		100000	15	99	400000
5		100000	5	100	1,200,000
6		100000	20	98	290,000
7		100000	20	97	290,000
8		100000	5	100	1,200,000
9		500000	20	100	1,500,000
10		500000	10	100	3,000,000
11		500000	10	99	3000000
12		100000	10	100	600000
13		100000	5	100	1200000
14		100000	30	99	200000
15		30000	20	99	89000
16[c]		100000	5	100	1200000

[a] All reactions were conducted with a scale of 0.025 mol aldehydes; *n*(aldehyde)∶*n*(TMSCN)=1∶1. [b] Conversion was determined by ^1H NMR. [c] $(n\text{-Bu})_4NOH$ aq. as catalyst.

cleophilic substitution at silicon in R_3SiX compoundscan be activated by nucleophiles such as RCO_2^-, RO^-, *N*-oxide, resulting in the formation of hypervalent silicon intermediates with penta- or hexacoordination states.[34-36] It is generally known that pentacoordinate allylsilicates are more reactive than tetracoordinate silicon, since σ-π conjugation results in the enhanced nucleophilicity of the *γ*-carbon of the allylsilicates.[37,38]

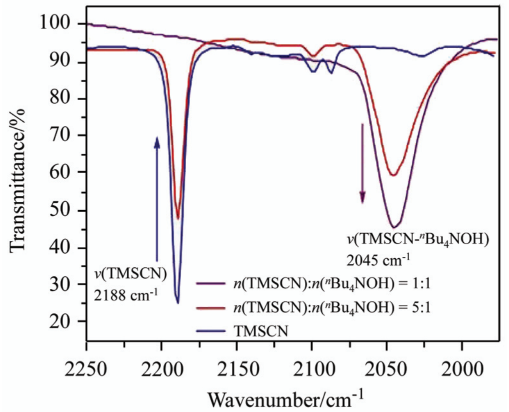


Figure 3 FTIR spectra of the mixture of TMSCN and (n-Bu)$_4$NOH in different ratios.

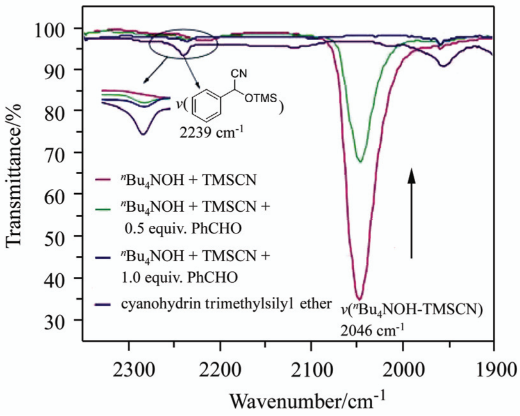
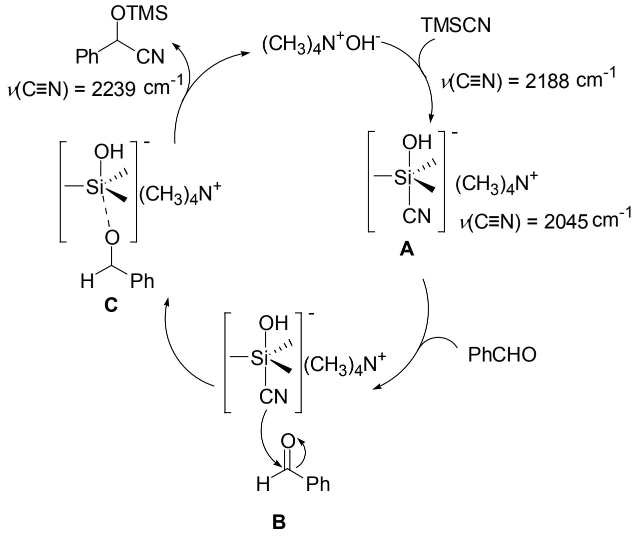


Figure 4 The changes of absorption peak strength of activated C≡N with addition of benzaldehyde to the mixture of TMSCN and (n-Bu)$_4$NOH in FTIR spectra. Procedure: (i) (n-Bu)$_4$NOH (0.52 g, 2.0 mmol) and TMSCN (0.2 g, 2.0 mmol) were dissolved in 0.4 mL THF, (ii) then half of PhCHO (0.1 mL, 1.0 mmol) was added, (iii) finally the other half PhCHO (0.1 mL, 1.0 mmol) was added into the solution.

On the basis of the above observations, a possible mechanism was proposed as shown in Scheme 2. Firstly, OH^- anion coordinates to the Si atom to form the more reactive pentacoordinate silicate (**A**). Then the activated CN^- attacks the carbonyl group of an aldehyde, followed with the generation of the desired product and release of quaternary ammonium base compound. In the catalytic cycle, the cation of quaternary ammonium base perhaps stabilizes the more reactive pentacoordinate silicate through Coulombic interaction, and does not participate in the attack of the nucleophile.

Scheme 2 Possible mechanism of $(CH_3)_4NOH$-catalyzed cyanosilylation of aldehydes



Conclusions

In summary, we have developed an extraordinarily efficient and simple organocatalyst for cyanosilylation of various aldehydes under extremely mild conditions. Aqueous $(CH_3)_4NOH$ triggered addition reaction of trimethylsilyl cyanide (TMSCN) to equivalent aldehydes which could proceed smoothly in a very low catalyst loading, with a turnover frequency (TOF) up to 3000000 h^{-1} and in near 100% yield under solvent-free conditions. This reaction process perfectly conforms to the feature of green chemistry: no waste regarding side-products and unconverted reactants, solvent-free, 100% product selectivity, and no requirement for separation. Furthermore, it represents a rare example of perfect organocatalysis with very low catalyst loading and excellent activity/selectivity.[39,40] Although chiral quaternary ammonium bases **I** and **II** derived from cinchonine as catalysts also exhibited excellent activities for the cyanosilylation of benzaldehyde, the chiral property of the cation has no effect on the nucleophilic attack process and only racemic product was obtained.

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(Zhao, C.)