

Synthesis of cyanohydrin trimethylsilyl ethers catalyzed by potassium *p*-toluenesulfinate

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Abstract

Potassium *p*-toluenesulfinate was found to be an effective and easily accessible Lewis basic catalyst for the facile cyanosilylation of carbonyl compounds in high to quantitative yields under solvent-free conditions at room temperature.

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1. Introduction

Cyanohydrins and their trimethylsilyl ethers are key building blocks for the one-step synthesis of many biologically active compounds [1–3], ferroelectrics and liquid crystals [4] that are otherwise only obtained with difficulty. They can easily be converted into various functionalized α -hydroxy acids, α -hydroxy aldehydes, β -amino alcohols and other polyfunctional compounds [5]. Among various cyanating reagents such as KCN or NaCN and HCN, trialkylsilyl cyanide compounds are safe and more effective cyanide sources for nucleophilic addition to carbonyl compounds under mild conditions [6,7]. However, trimethylsilyl cyanide (TMSCN) has been used in particular for this purpose [4–8].

On the other hand, as a consequence of the necessity to minimize the amount of toxic waste and by-products from chemical processes, there is a need to develop new and more environmentally friendly synthetic methods in which fewer toxic substances are used. Nowadays in the development of new syntheses, ecological points of view must also be taken into consideration and apportioned due to impor-

tance in the assessment of viability. Many organic solvents are flammable, toxic, and volatile compounds or hazardous air pollutants [9–11]. Therefore, solvent-free synthesis is highly becoming more popular, especially in industry, because it may be both more environmentally benign and more economically feasible [12]. 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 [13,14], CH₃CN [15], CHCl₃ [16] or CH₂Cl₂ [6,17] and the number of methods under solvent-free conditions remains quiet limited [4]. Also, the transfer of a cyano group from TMSCN to carbonyl compounds can be catalyzed by a plethora of nucleophilic catalysts such as trisaminophosphines [7], *N*-heterocyclic carbenes [8,13,14,18], fluoride sources [15], triethylamine, tributylphosphine, triphenylarsine, triphenylantimony [13], imidazolium-carbodithioate zwitterions [17], guanidine [19], and tetrabutylammonium cyanide [20]. However, most of these catalytic systems suffer from drawbacks such as multi-step preparation, using strong alkoxide base, high catalyst to substrate mole ratios, long reaction times, toxicity, being hygroscopic, instability under ambient conditions and tedious work-up procedures. Therefore, development of new efficient and mild catalysts which operate under solvent-free conditions is a very active research effort.

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2. Experimental

2.1. General

All chemicals were purchased from Merck, Aldrich or Fluka and used as received except for benzaldehyde which a fresh distilled sample was used. Catalysts were powdered and dried at 70 °C for 1 h under reduced pressure. All reactions were protected from moisture using a CaCl₂ guard tube. Analytical TLC was carried out using Merck 0.2 mm silica gel 60 F-254 Al-plates. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were obtained using a Bruker DRX-500 AVANCE spectrometer. All NMR spectra were determined in CDCl₃ at ambient temperature. FT IR spectra were recorded as KBr pellets on a Shimadzu FT IR-8400S spectrometer. GC chromatograms were recorded on a Shimadzu 2010 instrument. All compounds were well characterized by GC analysis, IR and NMR spectral data as compared with those obtained from authentic samples or reported in the literature [8,15].

2.2. General procedure for cyanosilylation of carbonyl compounds

To a mixture of an appropriate carbonyl compound (1.0 mmol) and potassium *p*-toluenesulfinate (2.5 mol%, 4.9 mg), TMSCN (1.2 mmol, 0.15 mL) was added and the mixture was stirred at room temperature after reaction period described in Table 1. The reaction was monitored by TLC. Then, the reaction mixture was quenched by water

(2.5 mL) and the organic materials were extracted with EtOAc (2 × 5.0 mL). The obtained organic phase was washed with brine and water (5.0 mL), respectively and dried over MgSO₄. 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 (3a)

Yield 98%; ¹H NMR (500 MHz, CDCl₃): δ 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). ¹³C NMR (125.8 MHz, CDCl₃): δ -0.3, 62.9, 118.8, 127.7, 129.1, 134.8, 135.2.

2.3.2. (2-Nitrophenyl)-2-(trimethylsilyloxy) acetonitrile (3b)

Yield 99%; ¹H NMR (500 MHz, CDCl₃): δ 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); ¹³C NMR (125.8 MHz, CDCl₃): δ 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 (3i)

Yield 100%; ¹H NMR (500 MHz, CDCl₃): δ 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). ¹³C NMR (125.8 MHz, CDCl₃): δ 1.86, 55.47, 62.99, 114.51, 119.39, 127.78, 128.36, 160.54.

Table 1
Cyanosilylation of various carbonyl compounds at optimized conditions

Entry	Carbonyl compound (2)	Time (min)	Product (3)	Yield (%) ^a
1	4-Chlorobenzaldehyde (2a)	45	3a	98
2	2-Nitrobenzaldehyde (2b)	30	3b	99
3	3-Nitrobenzaldehyde (2c)	30	3c	99
4	4-Cyanobenzaldehyde (2d)	45	3d	96
5	4-Bromobenzaldehyde (2e)	120	3e	100
6	Benzaldehyde (2f)	120	3f	98
7	4-Methylbenzaldehyde (2g)	120	3g	98
8	2-Methoxybenzaldehyde (2h)	60	3h	96
9	4-Methoxybenzaldehyde (2i)	150	3i	100
10	Furfural (2j)	75	3j	100
11	Thiophen-2-carbaldehyde (2k)	75	3k	98
12	2-Naphthaldehyde (2l)	120	3l	99
13	3-Phenylpropanal (2m)	120	3m	97
14	Cinnamaldehyde (2n)	150	3n	98
15	Octanal (2o)	150	3o	99
16	Acetophenone (2p)	300	3p	68
17	4-Nitroacetophenone (2q)	150	3q	100
18	2-heptanone (2r)	180	3r	95
19	Cyclohexanone (2s)	180	3s	92

^a Conversions yields.

3. Results and discussions

Oxygen-containing nucleophilic catalysts such as oxoanions, alkoxides, and *N*-oxides [13,21–23] are more efficient catalysts in trimethylsilylated reagents chemistry due to the high bond strength as well as the kinetic lability of the silicon–oxygen bond [24]. However, the high basicity of metal alkoxide and laborious work-up of *N*-oxides has made oxoanions more suitable for these transformations. In particular, carboxylate [21,22,25] or phenoxide [26] salts have been used as suitable catalysts in trimethylsilylated reagents chemistry. Recently, inorganic salts such as K₂CO₃ or phosphate salts have been used in both cyanation [22] and trifluoromethylation [24]. However, the efficiency of sulfinate anion as catalyst for cyanosilylation has been unexplored. We have recently developed a convenient and efficient procedure for the solvent-free synthesis of isocyanurate derivatives using sodium *p*-toluenesulfinate either alone or combined with tetrabutylammonium iodide [27]. In continuation of our interest to improve catalytic scope of oxoanions for various organic transformations

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