Letter

Three-component coupling reactions in ionic liquids: a facile synthesis of α-aminonitriles

Jhillu S. Yadav,* Basi. V. S. Reddy, B. Eshwaraiah, Mende. Srinivas and P. Vishnumurthy

Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India. E-mail: yadav@iict.ap.nic.in; Fax: 91-40-7160512

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Aryl imines, derived *in situ* from aldehydes and amines, smoothly undergo addition with trimethylsilyl cyanide in 1-butyl-3-methylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquids under mild and neutral reaction conditions to afford the corresponding α-aminonitriles in excellent yields. The ionic liquids can be recycled in five to six runs without any apparent loss of activity.

Introduction

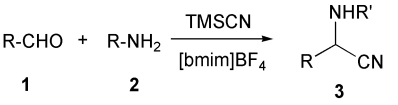
α-Aminonitriles are very useful precursors for the synthesis of α-amino acids,[1] and many nitrogen containing heterocycles[2] such as imidazoles and thiadiazoles, *etc.* The Strecker reaction is one of the most efficient and straightforward synthetic methods for the synthesis of α-aminonitriles.[3] The classical Strecker reaction is generally carried out with alkaline cyanides in aqueous solution. Subsequently, several modifications of the Strecker reaction have been reported using a variety of cyanating agents such as α-trimethylsiloxynitriles, diethyl phosphorocyanidate under various reaction conditions.[4] Trimethylsilyl cyanide is a safe and more effective cyanide anion source for the nucleophilic addition reactions of imines under mild conditions.[5] Recently, one-pot procedures have also been developed for the synthesis of α-aminonitriles from carbonyl compounds, amines and trimethylsilyl cyanide or tributyltin cyanide using lanthanide triflates as novel catalysts.[6] However, many of these methods involve the use of strongly acidic conditions and extended reaction times and also require tedious aqueous work-up leading to the generation of a large amount of toxic waste. Thus, there is still scope to develop a simple and practical method for the cyanation of imines under mild conditions.

One of the prime principles of green chemistry is to develop an alternative reaction medium, which is the basis for the development of many cleaner chemical technologies. In particular, ionic liquids have recently gained recognition as possible environmentally safe and alternative solvents to conventional organic solvents. Ionic liquids, especially those based on the 1-*N*-alkyl-3-methylimidazolium cation, have shown great promise as novel reaction media for various catalytic processes.[7] Due to the great potential of room temperature ionic liquids as environmentally benign media for catalytic processes, much attention has been currently focused on organic reactions promoted by ionic liquids.[8] The unique property of ionic liquids is that they have essentially no vapor pressure, which makes them optimal replacements for volatile organic solvents traditionally used as industrial solvents. Because of distinct advantages of ionic liquids, they can make a great contribution to green chemistry. However, there are no examples on the use of ionic liquids as promoters for the synthesis of α-aminonitriles in a one-pot procedure.

Results and discussion

In view of the emerging importance of ionic liquids as novel reaction media, herein, we wish to report the use of ionic liquids as efficient promoters for the three-component coupling reactions of aldehydes, amines and trimethylsilyl cyanide to produce α-aminonitriles (Scheme 1).

The treatment of benzaldehyde and aniline with TMSCN in 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4 ionic medium afforded the corresponding 2-anilino-2-phenylacetonitrile in 90% yield. Similarly, a variety of aldehydes were coupled with a range of amines and trimethylsilyl cyanide in a one-pot operation by using this procedure to produce α-aminonitriles in 85–93% yields. These three-component coupling reactions proceeded efficiently at ambient temperature with high selectivity. In all cases, no cyanohydrin trimethylsilyl ethers (an adduct between an aldehyde and trimethylsilyl cyanide) are obtained under these reaction conditions. This is due to the rapid formation and activation of the imines by ionic liquids. The reactions are clean and highly selective affording exclusively α-aminonitriles in high yields in a short time. This method is equally effective with aldehydes bearing electron-withdrawing substituents in the aromatic ring. Furthermore, acid sensitive aldehydes such as furfuraldehyde and cinnamaldehyde worked well without any decomposition or polymerization under these reaction conditions. This method does not require any acidic promoters or activators to promote the reaction. The reaction conditions are neither acidic nor basic and are mild enough to perform these reactions in the presence of either acid or base sensitive substrates. Enolizable aldehydes such as 2-phenylacetaldehyde and decanal also produced the corresponding α-aminonitriles in high yields. In this reaction, the activity of the ionic liquid was strongly influenced by the nature of the anion. The reactions of various aldehydes and amines with trimethylsilyl cyanide were carried out in hydrophilic [bmim]BF_4 and hydrophobic [bmim]PF_6 ionic liquids. Among these ionic liquids, [bmim]BF_4 was found to be superior in terms of conversion and selectivity. The advantage of the use of ionic liquids as promoters for this transformation is that these ionic liquids are easily recovered and recycled in subsequent runs. Since the products were weakly soluble in the ionic



Scheme 1

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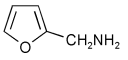
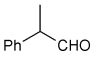
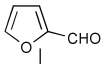
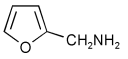
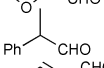
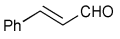
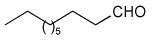
Table 1 Room temperature ionic liquids promoted synthesis of α-amino nitriles

			[bmim]BF_4		[bmim]PF_6	
Entry	Aldehyde	Amine	Time/h	Yield (%)[b]	Time/h	Yield (%)[b]
a)	C_6H_5CHO	$C_6H_5NH_2$	5.0	(92)	6.0	(87)
b)	4-$MeOC_6H_4CHO$	$C_6H_5NH_2$	5.0	(90)	6.5	(85)
c)	3-$PhOC_6H_4CHO$	$C_6H_5NH_2$	5.0	(92)	7.5	(87)
d)	4-ClC_6H_4CHO	$C_6H_5NH_2$	5.5	(89)	8.0	(83)
e)	C_6H_5CHO	$C_6H_4CH_2NH_2$	4.5	(91)	7.5	(85)
f)	2-$EtOC_6H_4CHO$		6.0	(93)	8.5	(82)
g)	C_6H_5CHO	2-$MeC_6H_4NH_2$	5.0	(91)	7.0	(85)
h)	4-$NO_2C_6H_4CHO$	$C_6H_5NH_2$	9.5	(85)	9.0	(75)
i)	4-FC_6H_4CHO	2-$ClC_6H_4NH_2$	6.0	(88)	7.0	(82)
j)	C_6H_5CHO	3-$MeOC_6H_3CH_2NH_2$	6.5	(85)	8.0	(80)
k)		$C_6H_5CH_2NH_2$	4.5	(90)	6.0	(83)
l)			5.5	(92)	6.5	(85)
m)		$C_6H_5NH_2$	6.0	(88)	8.0	(79)
n)		$C_6H_5NH_2$	5.0	(87)	7.5	(82)
o)		$C_6H_5NH_2$	6.5	(89)	9.5	(77)

[a] All products were characterized by ^{1}H NMR, IR and mass spectroscopy. [b] Isolated and unoptimized yields after purification.

phase, they were easily separated by simple extraction with ether. The rest of the ionic liquid was thoroughly washed with ether and dried at 80 °C under reduced pressure and reused four to six times without any loss of activity. The products were of the same purity as in the first run and no decrease in yields was observed in runs carried out using recovered ionic liquid. 1-Butyl-3-methylimidazolium methylsulfate [bmim]-SO_4CH_3 was also equally as effective as [bmim]BF_4 ionic liquid for this conversion. In further reactions, the efficiency of various quaternary ammonium salts was tested. These three-component coupling reactions were not successful in other molten salts such as *n*-tetrabutylammonium chloride (*n*-Bu_4-NCl) or 1-*n*-butyl-3-methylimidazolium chloride [bmim]Cl. This clearly indicates that both cation and anion play an important role as the solvent as well as promoter for this transformation. Furthermore, we have performed the reactions in organic solvents such as CH_3CN and $CHCl_3$ to compare the efficiency of ionic liquids. In these solvents, the reactions took longer (8–22 h) and also the products were obtained in low to moderate yields (35–57%). In contrast to organic solvents, enhanced reaction rates, improved yields and high selectivity are the features obtained in ionic liquids. For example, the treatment of benzaldehyde and aniline with trimethylsilyl cyanide in [bmim]BF_4 ionic liquid for 5.0 h afforded the corresponding α-aminonitrile in 92% yield. This is due to the rapid formation and activation of imines in ionic media. However, the same reaction in refluxing chloroform after 8.0 h gave the desired product in 57% yield along with cyanohydrin trimethylsilyl ether (an adduct between aldehyde and TMSCN). These results clearly show the efficiency of ionic liquids for this conversion. The scope and generality of this process is illustrated with respect to various aldehydes and amines and the results are presented in Table 1.

Conclusion

In summary, we have demonstrated a simple, convenient and practical method for the synthesis of α-aminonitriles through a one-pot three-component coupling of aldehydes, amines and trimethylsilyl cyanide using ionic liquids as novel promoters. The simple experimental and product isolation procedures combined with ease of recovery and reuse of this novel reaction medium is expected to contribute to the development of clean and environmentally friendly processes for the synthesis of α-aminonitriles of synthetic importance. The use of ionic liquids as promoters for this transformation avoids the use of moisture sensitive reagents and heavy metal Lewis acids.

Experimental

[Bmim]BF_4, [bmim]SO_4CH_3 and [bmim]PF_6 ionic liquids were prepared according to the procedures reported in the literature.[9]

Melting points were recorded on Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^{1}H-NMR spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. CHN analyses were recorded on a Vario EL analyzer.

General procedure

A mixture of aldehyde (1 mmol), amine (1 mmol), and trimethylsilyl cyanide (1.2 mmol) in 1-butyl-3-methylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium methylsulfate or 1-butyl-3-methylimidazolium hexafluorophosphate (1 mL) was stirred at ambient temperature for an appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the reaction mixture was washed with diethyl ether (3 × 10 mL). The combined ether extracts were concentrated *in vacuo* and the resulting product was directly charged on small silica gel column and eluted with a mixture of ethyl acetate:*n*-hexane (1:9) to afford pure α-aminonitrile. The rest of the viscous ionic liquid was further washed with ether and dried at 80 °C under reduced pressure to retain its activity in subsequent runs. Spectral data for selected products: **3a**: Solid, m.p. 73–74 °C, IR (KBr): *ν* 3369, 3021, 2954, 2236, 1603, 1505, 1464, 1313, 1142, 995, 751. ^{1}H NMR ($CDCl_3$): *δ* 4.05 (d, 1H, J = 8.1 Hz), 5.40 (d, 1H, J = 8.1 Hz), 6.75 (d, 2H, J = 8.0 Hz), 6.90 (t, 1H, J = 7.8 Hz), 7.25 (t, 2H, J = 7.8 Hz), 7.40–7.50 (m, 3H), 7.60–7.70 (m, 2H). ^{13}C

NMR (proton decoupled, $CDCl_3$): δ 50.7, 114.8, 118.9, 120.6, 127.8, 129.7, 130.0, 130.2, 134.5, 145.4. EIMS: m/z: 208 M^+, 180, 116, 91, 77, 51. Anal. Calcd. for $C_{14}H_{12}N_2$ (208.26): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.73; H, 5.84; N, 13.47%.

3b: Solid, m.p. 94–95 °C, IR (KBr): ν 3383, 3053, 2932, 2245, 1601, 1502, 1454, 1298, 1118, 1041, 925, 764. ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H), 3.90 (d, 1H, J = 8.1 Hz), 5.30 (d, 1H, J = 8.1 Hz), 6.75 (d, 2H, J = 8.0 Hz), 6.80 (t, 1H, J = 7.9 Hz), 6.90 (d, 2H, J = 8.0 Hz), 7.25 (t, 2H, J = 7.9 Hz), 7.50 (d, 2H, J = 8.0 Hz). EIMS: m/z: 238 M^+, 211, 181, 167, 141, 104, 77, 51, 40. Anal. Calcd. for $C_{15}H_{14}N_2O$ (238.28): C, 75.61; H, 5.92; N, 11.76. Found: C, 75.63; H, 5.95; N, 11.79%.

3c: Solid, m.p. 64–65 °C, IR (KBr): ν 3424, 2924, 2854, 2231, 1603, 1514, 1460, 1270, 1153, 1034, 798. ^{1}H NMR ($CDCl_3$): δ 4.02 (d, 1H, J = 8.0 Hz), 5.38 (d, 1H, J = 8.0 Hz), 6.78 (d, 2H, J = 7.9 Hz), 6.90 (t, 1H, J = 7.8 Hz), 7.05–7.65 (m, 11H). EIMS: m/z: 300 M^+, 273, 210, 181, 167, 141, 104, 77, 51. Anal. Calcd. for $C_{20}H_{16}N_2O$ (300.34): C, 79.98; H, 5.37; N, 9.33. Found: C, 80.01; H, 5.39; N, 9.35%.

3d: Solid, m.p. 109–112 °C, IR (KBr): ν 3405, 2927, 2239, 1600, 1515, 1457, 1272, 1161, 1098, 791. ^{1}H NMR ($CDCl_3$): δ 4.05 (d, 1H, J = 8.1 Hz), 5.39 (d, 1H, J = 8.1 Hz), 6.75 (d, 2H, J = 8.0 Hz), 6.90 (t, 1H, J = 7.9 Hz), 7.15 (t, 2H, J = 7.9 Hz), 7.40 (d, 2H, J = 8.0 Hz), 7.60 (d, 2H, J = 8.0 Hz). EIMS: m/z: 242 M^+, 213, 149, 114, 91, 73, 59. Anal. Calcd. for $C_{14}H_{11}ClN_2$ (242.70): C, 69.28; H, 4.57; Cl, 14.61; N, 11.54. Found: C, 69.30; H, 4.59; Cl, 14.60; N, 11.55%.

3e: Colorless oil, IR (KBr): ν 3409, 2924, 2234, 1648, 1514, 1401, 1108, 1028, 919, 825, 751. ^{1}H NMR ($CDCl_3$): δ 1.80 (brs, NH), 3.95 (AB q, 2H, J = 13.5 Hz), 4.70 (s, 1H), 6.78 (d, 1H, J = 8.0 Hz), 7.15 (t, 1H, J = 7.8 Hz), 7.25–7.40 (m, 6H), 7.49–7.51 (m, 2H). ^{13}C NMR (proton decoupled, $CDCl_3$): δ 51.7, 53.8, 119.2, 128.1, 128.9, 129.1, 129.5, 130.0, 135.2, 138.5. EIMS: m/z: 222 M^+, 195, 141, 131, 116, 106, 91, 77, 51. Anal. Calcd. for $C_{15}H_{14}N_2$ (222.28): C, 81.05; H, 6.35; N, 12.60. Found: C, 81.07; H, 6.37; N, 12.61%.

3f: Liquid, IR (KBr): ν 34481, 2981, 2895, 2225, 1638, 1598, 1494, 1248, 1118, 1043, 923, 754. ^{1}H NMR ($CDCl_3$): δ 1.37 (t, 3H, J = 6.9 Hz), 3.90 (AB q, 2H, J = 13.5 Hz), 4.15 (q, 2H, J = 6.9 Hz), 4.80 (s, 1H), 6.30 (m, 1H), 6.87 (d, 1H, J = 8.0 Hz), 7.0 (t, 1H, J = 7.8 Hz), 7.30–7.45 (m, 4H). EIMS: m/z: 256 M^+, 227, 198, 173, 146, 120, 104, 95, 80, 52. Anal. Calcd. for $C_{15}H_{16}N_2O_2$ (256.30): C, 70.29; H, 6.29; N, 10.93. Found: C, 70.31; H, 6.30; N, 10.95%.

3g: Solid, m.p. 72–73 °C, IR (KBr): ν 3365, 2935, 2857, 2237, 1605, 1517, 1461, 1275, 1035, 791. ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 3H), 3.38 (brd, 1H, NH, J = 8.1 Hz), 5.45 (d, J = 8.1 Hz), 6.80 (t, 2H, J = 7.9 Hz), 7.10 (d, 1H, J = 8.0 Hz), 7.20 (d, 1H, J = 7.9 Hz), 7.40–7.50 (m, 3H), 7.50 (d, 2H, J = 8.0 Hz). ^{13}C NMR (proton decoupled, $CDCl_3$): δ 17.8, 50.7, 112.2, 118.9, 120.4, 124.1, 127.7, 127.9, 129.8, 130.0, 131.3, 134.7, 143.4. EIMS: m/z: 222 M^+, 194, 155, 141, 116, 106, 91, 73, 65, 45. Anal. Calcd. for $C_{15}H_{14}N_2$ (222.28): C, 81.05; H, 6.35; N, 12.60. Found: C, 81.03; H, 6. 36; N, 12.63%.

3h: Viscous liquid, IR (KBr): ν 3421, 2920, 2859, 2235, 1600, 1515, 1458, 1271, 1157, 1039, 791. ^{1}H NMR ($CDCl_3$): δ 4.05 (d, 1H, J = 8.0 Hz), 5.35 (d, 1H, J = 8.0 Hz), 6.80 (d, 2H, J = 8.0 Hz), 6.90 (t, 1H, J = 7.9 Hz), 7.20 (t, 2H, J = 7.9 Hz), 7.67 (d, 2H, J = 8.1 Hz), 8.10 (d, 2H, J = 8.1 Hz). EIMS: m/z: 253 M^+, 227, 152, 181, 167, 136, 123, 91,77, 51. Anal. Calcd. for $C_{14}H_{11}N_3O_2$ (253.25): C, 66.40; H, 4.38; N, 16.59. Found: C, 66.42; H, 4.39; N, 16.61%.

3i: Solid, m.p. 95–97 °C, IR (KBr): ν 3410, 2931, 2230, 1610, 1520, 1461, 1269, 1051, 790. ^{1}H NMR ($CDCl_3$): δ 4.65 (d, 1H, J = 8.1 Hz), 5.45 (d, 1H, J = 8.1 Hz), 6.90–6.95 (m, 2H), 7.15–7.35 (m, 4H), 7.58–7.65 (m, 2H). EIMS: m/z: 260 M^+, 234, 135, 100, 75. Anal. Calcd. for $C_{14}H_{10}ClFN_2$ (260.69): C, 64.50; H, 3.87; Cl, 13.60; F, 7.29; N, 10.75. Found: C, 64.51; H, 3.89; Cl, 13.62; F, 7.31; N, 10.73%.

3j: Liquid, IR (KBr): ν 3400, 2941, 2890, 2241, 1616, 1527, 1471, 1283, 1160, 1045, 789. ^{1}H NMR ($CDCl_3$): δ 1.85 (brs, NH), 3.80 (s, 3H), 3.95 (AB q, 2H, J = 13.0 Hz), 4.70 (d, 1H, J = 8.0 Hz), 6.80–6.95 (m, 3H), 7.25 (t, 1H, J = 7.9 Hz), 7.30–7.55 (m, 4H). EIMS:m/z: 252 M^+, 225, 122, 91, 77, 51. Anal. Calcd. for $C_{16}H_{16}N_2O$ (252.31): C, 76.17; H, 6.39; N, 11.10. Found: C, 76.19; H, 6.41; N, 11.13%.

3k: Viscous liquid, IR (KBr): ν 3398, 2927, 2860, 2230, 1609, 1530, 1495, 1275, 1159, 1054, 787. ^{1}H NMR ($CDCl_3$): δ 1.45 (d, 3H, J = 6.9 Hz), 3.10–3.20 (m, 1H), 3.58–3.60 (m, 1H), 3.80 (d, 1H, J = 13.0 Hz), 4.05 (d, 1H, J = 13.0 Hz), 7.20–7.45 (m, 10H). EIMS: m/z: 250 M^+, 223, 145, 105, 91, 77, 51. Anal. Calcd. for $C_{17}H_{18}N_2$ (250.34): C, 81.56; H, 7.25; N, 11.19. Found: C, 81.59; H, 7.27; N, 11.21%.

3l: Liquid, IR (KBr): ν 3406, 2921, 2854, 2220, 1695, 1573, 1460, 1217, 1148, 1012, 938, 759. ^{1}H NMR ($CDCl_3$): δ 2.10 (brs, NH), 3.90 (s, 2H), 4.75 (s, 1H), 6.20–6.35 (m, 4H), 7.35–7.40 (m, 2H). EIMS: m/z: 202 M^+, 150, 125, 111, 95, 81, 69, 57, 43. Anal. Calcd. for $C_{11}H_{10}N_2O_2$ (202.21): C, 65.34; H, 4.98; N, 13.85. Found: C, 65.36; H, 4.98; N, 13.86%.

3m: Solid, m.p. 99–100 °C, IR (KBr): ν 3400, 2967, 2895, 2235, 1601, 1535, 1482, 1280, 1180, 1055, 791. ^{1}H NMR ($CDCl_3$): δ 1.60 (d, 3H, J = 6.9 Hz), 3.20–3.37 (m, 1H), 3.45–3.55 (m, 1H), 4.30–4.45 (m, 1H)), 6.65 (d, 2H, J = 8.0 Hz), 6.85 (t, 1H, J = 7.9 Hz), 7.20–7.45 (m, 7H). EIMS: m/z: 236 M^+, 209, 131, 105, 77, 51. Anal. Calcd. for $C_{16}H_{16}N_2$ (236.31): C, 81.32; H, 6.82; N, 11.85. Found: C, 81.33; H, 6.85; N, 11.87%.

3n: Solid, m.p. 117–119 °C, IR (KBr): ν 3350, 2929, 2233, 1603, 1505, 1461, 1275, 1030, 976, 897, 746. ^{1}H NMR ($CDCl_3$): δ 3.80 (d, 1H, J = 8.1 Hz), 5.05 (m, 1H), 6.30 (dd, 1H, J = 6.9, 17.3 Hz), 6.78 (d, 1H, J = 8.0 Hz), 6.90 (t, 1H, J = 7.9 Hz), 7.08 (dd, 1H, J = 1.7, 17.3 Hz), 7.25–7.45 (m, 8H). EIMS: m/z: 234 M^+, 206, 128, 115, 77, 51. Anal. Calcd. for $C_{16}H_{14}N_2$ (234.30): C, 82.02; H, 6.02; N, 11.96. Found: C, 82.01; H, 6.04; N, 11.98%.

3o: Liquid, IR (KBr): ν 3405, 2925, 2854, 2235, 1600, 1505, 1463, 1279, 1160, 1030, 791. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, J = 6.8 Hz), 1.20–1.40 (m, 12H), 1.50–1.65 (m, 2H), 1.80–1.90 (m, 2H), 3.80 (brs, NH), 4.05–4.15 (m, 1H), 6.60 (d, 2H, J = 8.0 Hz), 6.80 (t, 1H, J = 7.9 Hz), 7.20 (t, 2H, J = 7.9 Hz). EIMS: m/z: 258 M^+, 185, 155, 135, 121, 77,51. Anal. Calcd. for $C_{17}H_{26}N_2$ (258.40): C, 79.02; H, 10.14; N, 10.84. Found: C, 79.04; H, 10.17; N, 10.86%.

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