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Indium trichloride catalyzed one-step synthesis of α-amino nitriles by a three-component condensation of carbonyl compounds, amines and potassium cyanide

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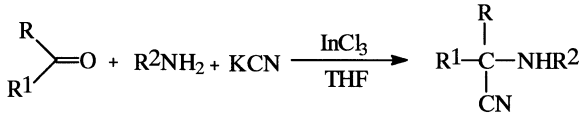
Abstract—A simple and general method has been developed for the synthesis of α-aminonitriles by a one-pot three-component condensation of aldehydes or ketones, amines and potassium cyanide in THF in presence of a catalytic amount of indium trichloride.

1. Introduction

The synthesis of α-amino nitriles has been the subject of considerable current interest as these molecules serve as useful intermediates towards preparation of α-amino acids.[1] The classical procedure, known as the Strecker reaction for their synthesis involves the treatment of an aldehyde or a ketone with alkaline cyanides and salts of amines, and was discovered a century and a half ago.[2] The reaction is usually carried out in aqueous solution and the work-up procedure is also tedious. Thus, several modifications of the Strecker reaction have been reported[3] using a variety of cyanide reagents, such as α-trimethylsiloxynitriles,[3b] diethyl phosphorocyanidate,[3a] under different reaction conditions. However, many of these reagents are not easily accessible due to their high cost and thus there is a need for a more simple, straight-forward and cost-effective method for the synthesis of these useful compounds.

Recently, indium(III) chloride has emerged as a powerful Lewis acid catalyst in a variety of organic transformations.[4] Our own work[5] also found $InCl_3$ to be a very efficient catalyst for two and three component condensation reaction involving addition of a nucleophile to the imine generated in situ from a carbonyl compound and an amine. This prompted us to explore the addition of a cyanide ion to an imine under indium(III) chloride catalysis and we have discovered an excellent modification of the Strecker synthesis by a one-pot procedure (Scheme 1).



Scheme 1.

2. Results and discussion

In a typical general procedure, a mixture of a carbonyl compound (aldehyde or ketone), an amine and potassium cyanide in THF was stirred (for aldehydes) or refluxed (in case of ketones) in presence of indium(III) chloride (30 mol%) for a certain period of time (TLC). Extraction with ether and purification by column chromatography over silica gel furnished the pure product. A wide range of structurally varied aldehydes and ketones were coupled with a variety of aliphatic and aromatic amines and potassium cyanide by this procedure through a single step operation to produce the corresponding α-amino nitriles. The results are summarized in Table 1. It was found that aldehydes, in general, including aromatic, aliphatic and heterocyclic units participate readily using this procedure, whereas only cyclic ketones produced satisfactory results. Acyclic ketones largely remained inert; longer reaction times and greater amounts of indium trichloride also failed to make a significant improvement. Conjugated aldehydes and ketones react by this procedure to furnish mainly tarry material. On the other hand, aliphatic and aromatic primary amines and cyclic secondary amines like pyrrolidine and morpholine are readily coupled. Although the amount of catalyst has been optimized to 30 mol%, lesser amount (10–20 mol%) also worked with longer reaction times. In general, the reactions are considerably fast. No undesired side product was isolated. The yields are reasonably good for a three-component coupling reaction. Notably, this reaction has

Keywords: α-amino nitriles; one-pot three-component condensation; indium trichloride.

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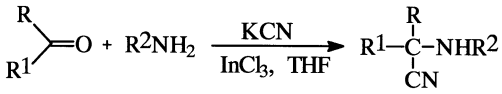
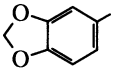
Table 1. Synthesis of α-amino nitriles



Entry	R	R^1	R^2	Time (h)	Yield (%)[a]
1	Ph	H	Ph	6	75
2	Ph	H	$PhCH_2$	5	73
3	Ph	H	$CH_3(CH_2)_3$	5	69
4	Ph	H	$(CH_3)_2CH$	5	70
5	Ph	H		4	74
6	Ph	H	*o*-(CH_3)–C_6H_4	5	82
7	Ph	H	Pyrrolidine	4	89
8	Ph	H	Morpholine	4	82
9	*m*-(OCH_3)–C_6H_4	H	$CH_3(CH_2)_3$	5	75
10	*m*-(OCH_3)–C_6H_4	H	Ph	5	87
11	*m*-(OCH_3)–C_6H_4	H	$PhCH_2$	5	93
12		H	$PhCH_2$	8	62
13		H	$PhCH_2$	8	47
14		H	$PhCH_2$	5	84
15	$(CH_3)_2CH$	H	$PhCH_2$	5	80
16	$(CH_3)_2CH$	H	Pyrrolidine	5	78
17	$CH_3(CH_2)_2$	H	Pyrrolidine	5	60
18	Cyclohexanone		$PhCH_2$	14	66
19	Cyclohexanone		$CH_3(CH_2)_3$	14	64
20	3-Methyl cyclohexanone		$PhCH_2$	14	66
21	3-Methyl cyclohexanone		Pyrrolidine	4	70
22	3-Methyl cyclohexanone		Morpholine	4	70

[a] Yields refer to those of pure isolated products fully characterised by spectral data.

been carried out under Lewis acid catalysis unlike many conventional procedures using basic conditions.[2,3]

3. Conclusion

The present procedure using indium trichloride provides an efficient synthesis of α-amino nitriles by a one-pot three component coupling of carbonyl compound, amine and cyanide. The significant features of this methodology are: (a) operational simplicity; (b) use of cheap commercially available reagents (c) general applicability to different types of aldehydes and amines and (d) high yields of products. We believe, this procedure will make a practical alternative to the existing ones in the literature.[2,3]

4. Experimental

4.1. General

Melting points were determined on a glass disk with an electrical bath and are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were run in $CDCl_3$ solutions. IR spectra were taken as neat for liquid compounds and as KBr plates for solids. Elemental analyses were done by a Perkin–Elmer autoanalyzer. Column chromatography was performed on silica gel (60–120 mesh, SRL, India). The aldehydes, ketones, amines are all commercially available and were distilled before use. Potassium cyanide (SD, India) and indium(III) chloride (Aldrich) were used as such. THF was distilled over potassium-benzophenone before use.

4.1.1. General procedure for the synthesis of α-amino nitriles. Representative procedure for the coupling of benzyldehyde, benzyl amine and potassium cyanide (entry 2, Table 1). A mixture of benzaldehyde (212 mg, 2 mmol), benzyl amine (235 mg, 2.2 mmol) and potassium cyanide (198 mg, 3.0 mmol) in dry THF (6 mL) was stirred in presence of indium trichloride (132 mg, 0.6 mmol, 30 mol%) at room temperature (28–30°C) under a $CaCl_2$ moisture guard tube for the time required to complete the reaction (TLC). THF was then distilled off under vacuum and the residue was taken up in ether. The ether solution was washed with brine, dried (Na_2SO_4) and evaporated to leave the crude product which was purified by column chromatography over silica gel (hexane–ether 92:8) to furnish pure product, 2-(*N*-benzylamino)-2-phenylacetonitrile as a colourless oil (324 mg, 73%); IR (neat) 3325, 2233 cm^{-1}; ^{1}H NMR δ 7.52–7.49 (m, 2H), 7.41–7.26 (m, 6H), 7.18 (t, J=7.9 Hz, 1H), 6.78 (d, J=8.1 Hz, 1H), 4.71 (s, 1H), 3.94 (AB q, J=13.4 Hz, 2H); ^{13}C NMR δ 138.5, 135.1, 130.0 (2C), 129.5 (2C), 129.1 (2C), 128.9 (2C), 128.1 (2C), 119.1, 53.9, 51.7. Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.86; H, 6.24; N, 12.34.

This procedure is followed for all the reactions enlisted in Table 1. However, the reactions were carried out under reflux in case of ketones. The products were identified by their IR, ^{1}H and ^{13}C NMR spectral data and elemental analysis. These data are presented below in order of their entries in Table 1.

4.1.2. 2-(*N*-Anilino)-2-phenylacetonitrile[3a] (entry 1). Pale yellow crystal (75%); mp 84–85°C; IR (KBr) 3336, 2237 cm^{-1}; ^{1}H NMR δ 7.49 (m, 2H), 7.36 (m, 3H), 7.23 (t, J=7.9 Hz, 2H), 6.84 (t, J=7.4 Hz, 1H), 6.69 (d, J=7.9 Hz, 2H), 5.33 (s, 1H), 4.07 (br s, 1H); ^{13}C NMR δ 145.3, 134.5, 130.1 (2C), 130.0, 129.8 (2C), 127.8 (2C), 120.7, 118.9, 114.7 (2C), 50.6.

4.1.3. 2-(*N*-*n*-Butylamino)-2-phenylacetonitrile (entry 3). Colourless oil (69%); IR (neat) 3319, 2229 cm^{-1}; ^{1}H NMR δ 7.72–7.68 (m, 2H), 7.35 (m, 3H), 4.75 (s, 1H), 2.77 (m, 2H), 1.49–1.26 (m, 4H), 0.91 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 135.5, 129.4, 129.3 (2C), 127.7 (2C), 119.3, 54.9, 47.5, 32.2, 20.7, 14.3. Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88. Found: C, 76.39; H, 8.42; N, 14.75.

4.1.4. 2-(*N*-Isopropyl)-2-phenylacetonitrile (entry 4). Colourless oil (70%); IR (neat) 3319, 2223 cm^{-1}; ^{1}H NMR δ 7.52–7.48 (m, 2H), 7.43–7.34 (m, 3H), 4.75 (s, 1H), 3.21 (m, 1H), 1.14 (d, J=6.2 Hz, 6H); ^{13}C NMR δ 135.9, 129.4 (2C), 129.3, 127.7 (2C), 119.4, 52.6, 47.6, 21.9, 20.7. Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.56; H, 8.08; N, 15.82.

4.1.5. 2-(*N*-Cyclohexylamino)-2-phenylacetonitrile (entry 5). Colourless crystal (74%); mp 57–58°C; IR (KBr) 3311, 2229 cm^{-1}; ^{1}H NMR δ 7.53–7.48 (m, 2H), 7.41–7.32 (m, 3H), 4.82 (s, 1H), 2.86 (m, 1H), 1.97–1.18 (m, 10H); ^{13}C NMR δ 130.7, 129.4 (2C), 129.3, 127.7 (2C), 119.8, 55.3, 52.1, 34.3, 32.4, 26.4, 25.1, 24.7. Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.37; H, 8.33; N, 12.86.

4.1.6. 2-[*N*-(2-Methylanilino)]-2-phenylacetonitrile (entry 6). Colourless crystal (82%); mp 72–73°C; IR (KBr) 3361, 2235 cm^{-1}; ^{1}H NMR δ 7.70–7.67 (m, 2H), 7.53–7.51 (m, 3H), 7.25 (m, 2H), 6.89 (t, J=7.8 Hz, 2H), 5.50 (d, J=8.3 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR δ 143.3, 134.7, 131.2, 130.0, 129.9 (2C), 127.8, 127.7 (2C), 124.1, 120.4, 118.9, 112.2, 50.5, 17.9. Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.82; H, 6.11; N, 12.42.

4.1.7. 2-Phenyl-2-(*N*-pyrrolidino)acetonitrile (entry 7). Colourless oil (89%); IR (neat) 2223 cm^{-1}; ^{1}H NMR δ 7.53–7.49 (m, 2H), 7.43–7.31 (m, 3H), 5.03 (s, 1H), 2.71–2.58 (m, 4H), 1.89–1.75 (m, 4H); ^{13}C NMR δ 134.7, 129.2 (2C), 129.1, 128.0 (2C), 116.5, 59.7, 50.7 (2C), 23.9 (2C). Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.12; H, 7.42; N, 14.91.

4.1.8. 2-(*N*-Morpholino)-2-phenylacetonitrile[3a] (entry 8). Colourless crystal (82%); mp 68–69°C; IR (KBr) 2223 cm^{-1}; ^{1}H NMR δ 7.53–7.34 (m, 5H), 4.81 (t, J=4.4 Hz, 4H), 2.57 (t, J=4.5 Hz, 4H); ^{13}C NMR δ 132.9, 129.9, 129.3 (2C), 128.4 (2C), 115.6, 62.1 (2C), 62.8, 50.4 (2C).

4.1.9. 2-(*N*-*n*-Butylamino)-2-(3-methoxyphenyl)acetonitrile (entry 9). Colourless oil (75%); IR (neat) 3319, 2223 cm^{-1}; ^{1}H NMR δ 7.27 (t, J=9.8 Hz, 1H), 7.11–7.06 (m, 2H), 6.89 (dd, J=2.5, 8.2 Hz, 1H), 4.74 (s, 1H), 3.73 (s, 3H), 2.82 (m, 2H), 1.50 (m, 4H), 0.92 (t, J=7.1 Hz, 3H); ^{13}C NMR δ 161.1, 132.9, 130.4, 119.8, 119.4, 114.9, 113.2, 55.7, 54.9, 47.5, 32.1, 20.7, 14.3. Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.32; H, 8.27; N, 12.61.

4.1.10. 2-(*N*-Anilino)-2-(3-methoxyphenyl)acetonitrile (entry 10). Colourless crystal (87%); mp 60–61°C; IR (KBr) 3355, 2223 cm^{-1}; ^{1}H NMR δ 7.29 (t, J=7.6 Hz, 1H), 7.23–7.09 (m, 4H), 6.94–6.84 (m, 2H), 6.73 (d, J=7.6 Hz, 2H), 5.34 (d, J=8.4 Hz, 1H), 4.13 (broad d, J=8.4 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR δ 160.7, 147.2, 135.9, 130.9, 130.0 (2C), 120.7, 119.8, 118.7, 115.6, 114.6 (2C), 113.2, 55.9, 50.5. Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.67. Found: C, 75.34; H, 5.90; N, 11.61.

4.1.11. 2-(*N*-Benzylamino)-2-(3-methoxyphenyl)acetonitrile (entry 11). Colourless oil (93%); IR (neat) 3323, 2223 cm^{-1}; ^{1}H NMR δ 7.38–7.26 (m, 6H), 7.23 (m, 2H), 6.86 (dd, J=2.5, 9.4 Hz, 1H), 4.66 (s, 1H), 3.94 (AB q, J=13.0 Hz, 2H), 3.77 (s, 3H), 1.84 (braod s, 1H); ^{13}C NMR δ 160.5, 138.6, 136.7, 130.4, 128.9 (2C), 129.8 (2C), 128.4, 119.9, 119.1, 114.9, 113.4, 55.7, 53.8, 51.6. Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.86; H, 6.32; N, 11.02.

4.1.12. 2-(*N*-Benzylamino)-2-thiophenylacetonitrile (entry 12). Colourless oil (62%); IR (neat) 3325, 2227 cm^{-1}; ^{1}H NMR δ 7.41–7.22 (m, 7H), 6.99–6.96 (m, 1H), 4.93 (s, 1H), 3.98 (AB q, J=13.0 Hz, 2H), 2.05 (broad s, 1H); ^{13}C NMR δ 138.7, 138.3, 129.1 (2C), 128.9, 128.8 (2C), 128.2, 127.2, 126.8, 118.4, 51.3, 49.7. Anal. Calcd for $C_{13}H_{12}N_2S$: C, 68.39; H, 5.30; N, 12.27. Found: C, 68.24; H, 5.19; N, 12.14.

4.1.13. 2-(*N*-Benzylamino)-2-furfurylacetonitrile (entry 13). Colourless oil (47%); IR (neat) 3325, 2227 cm^{-1}; ^{1}H NMR δ 7.48–7.19 (m, 7H), 6.30 (m, 1H), 4.75 (s, 1H), 3.95 (AB q, J=12.9 Hz, 2H), 1.98 (braod s, 1H); ^{13}C NMR δ 147.8, 143.9, 138.1, 128.8 (2C), 128.6 (2C), 127.7, 127.5, 111.1, 109.5, 51.3, 47.6. Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.57; H, 5.70; N, 13.20. Found: C, 73.38; H, 5.61; N, 13.14.

4.1.14. 2-(*N*-Benzylamino)-2-piperonylacetonitrile (entry 14). Colourless crystal (84%); mp 62–63°C; IR (KBr) 3315, 2227 cm^{-1}; ^{1}H NMR δ 7.28 (m, 6H), 6.99 (s, 1H), 6.81 (s, 1H), 5.97 (m, 2H), 4.64 (s, 1H), 3.97 (AB q, J=12.9 Hz, 2H), 1.79 (broad s, 1H); ^{13}C NMR δ 148.8, 138.7, 129.2 (2C), 129.1, 129.0, 128.9 (2C), 128.2, 121.4, 119.3, 108.9, 108.4, 102.0, 53.7, 51.7. Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.14; H, 5.30; N, 10.41.

4.1.15. 2-(*N*-Benzylamino)-2-isopropylacetonitrile (entry 15). Colourless oil (80%); IR (neat) 3347, 2223 cm^{-1}; ^{1}H NMR δ 7.36–7.23 (m, 5H), 4.06 (d, J=13.0 Hz, 1H), 3.79 (d, J=13.0 Hz, 1H), 3.25 (d, J=6.0 Hz, 1H), 1.98 (m, 1H), 1.55 (broad s, 1H), 1.08 (d, J=6.8 Hz, 3H), 1.07 (d, J=6.7 Hz, 3H); ^{13}C NMR δ 138.3, 128.5 (2C), 128.4

(2C), 127.4, 119.2, 56.2, 51.7, 31.5, 19.2, 18.2. Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88. Found: C, 76.48; H, 8.52; N, 14.71.

4.1.16. 2-Isopropyl-2-(*N*-pyrrolidino)acetonitrile (entry 16). Colourless oil (78%); IR (neat) 2222 cm^{-1}; ^1H NMR δ 3.29 (d, J=10.1 Hz, 1H), 2.61 (m, 4H), 1.92 (m, 1H), 1.82 (m, 4H), 1.12 (d, J=6.6 Hz, 3H), 1.02 (d, J=6.6 Hz, 3H); ^{13}C NMR δ 117.8, 63.2, 50.5 (2C), 31.1, 23.9 (2C), 20.4, 19.7. Anal. Calcd for $C_9H_{16}N_2$: C, 71.01; H, 10.59; N, 18.40. Found: C, 71.12; H, 10.35; N, 18.26.

4.1.17. 2-*n*-Propyl-2-(*N*-pyrrolidino)acetonitrile (entry 17). Colourless oil (60%); IR (neat) 2221 cm^{-1}; ^1H NMR δ 3.74 (t, J=7.8 Hz, 1H), 2.67 (m, 4H), 1.85–1.68 (m, 6H), 1.49 (m, 2H), 0.97 (t, J=7.9 Hz, 3H); ^{13}C NMR δ 94.2, 53.1, 47.9 (2C), 32.7, 21.4 (2C), 17.36, 11.50. Anal. Calcd for $C_9H_{16}N_2$: C, 71.01; H, 10.59; N, 18.4. Found: C, 71.08; H, 10.38; N, 18.29.

4.1.18. 1-(*N*-Benzylamino)-1-cyanocyclohexane (entry 18). Colourless oil (66%); IR (neat) 3313, 2219 cm^{-1}; ^1H NMR δ 7.40–7.30 (m, 5H), 3.92 (s, 2H), 2.07–1.54 (m, 10H); ^{13}C NMR δ 139.8, 128.9 (2C), 128.8 (2C), 127.8, 122.6, 57.8, 49.0, 36.5 (2C), 25.57, 22.72 (2C). Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.35; H, 8.42; N, 13.00.

4.1.19. 1-(*N*-*n*-Butylamino)-1-cyanocyclohexane (entry 19). Colourless oil (64%); IR (neat) 3315, 2218 cm^{-1}; ^1H NMR δ 2.73 (t, J=6.6 Hz, 2H), 2.34 (t, J=6.4 Hz, 1H), 2.04–1.24 (m, 13H), 0.93 (t, J=6.9 Hz, 3H); ^{13}C NMR δ 122.7, 57.6, 43.9, 36.4 (2C), 32.6, 25.5, 22.6 (2C), 20.7, 14.2. Anal. Calcd for $C_{11}H_{20}N_2$: C, 73.28; H, 11.18, N, 15.54. Found: C, 73.38; H, 11.01; N, 15.49.

4.1.20. 1-(*N*-Benzylamino)-1-cyano-3-methylcyclohexane (entry 20). Colourless oil (66%); IR (neat) 3313, 2223 cm^{-1}; ^1H NMR δ 7.39–7.28 (m, 5H), 3.94 (s, 2H), 2.09–1.11 (m, 9H), 0.98 (d, J=6.4 Hz, 3H); ^{13}C NMR δ 139.8, 129.0 (2C), 128.9 (2C), 127.8, 122.5, 58.6, 49.0, 44.8, 36.4, 34.6, 29.8, 23.1, 22.4. Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.79; H, 8.81; N, 12.01.

4.1.21. 1-Cyano-1-(*N*-pyrrolidino)-3-methylcyclohexane (entry 21). Colourless oil (70%); IR (neat) 2216 cm^{-1}; ^1H NMR δ 2.79–2.66 (m, 4H), 2.17–2.04 (m, 2H), 1.82–1.57 (m, 8H), 1.37–1.10 (m, 3H), 0.96 (d, J=6.4 Hz, 3H); ^{13}C NMR δ 199.6, 63.3, 48.3 (2C), 44.5, 36.1, 33.7, 29.7, 23.6 (2C), 23.3, 22.1. Anal. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57. Found: C, 74.85; H, 10.42; N, 14.37.

4.1.22. 1-Cyano-1-(*N*-morpholino)-3-methylcyclohexane (entry 22). Yellowish white crystal (70%); mp 56–57°C; IR (KBr) 2216 cm^{-1}; ^1H NMR δ 3.74 (t, J=4.6 Hz, 4H), 2.69–2.62 (m, 4H), 2.27–2.17 (m, 2H), 1.87–1.59 (m, 5H), 1.30–1.21 (m, 2H), 0.97 (d, J=6.2 Hz, 3H); ^{13}C NMR δ 120.1, 68.2 (2C), 63.3, 48.5 (2C), 43.0, 34.7, 34.6, 30.7, 23.9, 23.3. Anal. Calcd for $C_{12}H_{20}N_2O$: C, 69.19; H, 9.68; N, 13.45. Found: C, 69.12; H, 9.59; N, 13.23.

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