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Montmorillonite KSF clay catalyzed one-pot synthesis of α-aminonitriles

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Abstract—Aryl imines, formed in situ from aldehydes and amines undergo smoothly nucleophilic addition with trimethylsilyl cyanide on the surface of montmorillonite KSF clay under mild reaction conditions to afford the corresponding α-aminonitriles in excellent yields. The solid acid can be recovered and recycled in subsequent reactions with a gradual decrease of activity.

1. Introduction

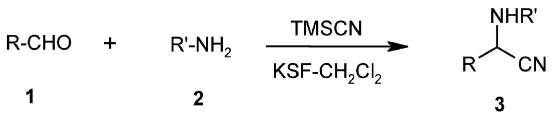
α-Aminonitriles are important intermediates for the synthesis of α-amino acids[1] and various nitrogen containing heterocycles[2] such as imidazoles and thiadiazoles, etc. They are usually prepared by the nucleophilic addition of cyanide anion to the imines.[3] The classical Strecker reaction is generally 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] The use of trimethylsilyl cyanide is a safer and more effective cyanide anion source for the nucleophilic addition reactions of imines under mild conditions.[5] However, many of these methods involve the use of expensive reagents and extended reaction times, harsh conditions and also require tedious aqueous work-up leading to the generation of a large amount of toxic waste.

Furthermore, many of these catalysts are deactivated or some times decomposed by amines and water that exist during imine formation. In order to circumvent some of the problems associated with these procedures recently one-pot procedures have been developed for this transformation.[6] In recent years, the use of solid acid catalysts such as clays, ion-exchange resins and zeolites has received considerable attention in different areas of organic synthesis.[7] Especially, clay catalysts make the reaction process convenient, cost-effective, environmentally benign and act as Brønsted as well as Lewis acids in their natural or ion-exchanged forms, enabling them to function as efficient catalysts for various transformations.[8]

Because of the distinct advantages of solid acids, they can make a great contribution to green chemistry. Although, clay has been used for cyanohydrin formation,[9] there are no examples of the use of clay as catalyst for the synthesis of α-aminonitriles.

2. Results and discussion

In view of the emerging importance of the use of solid acids as environmentally friendly and reusable catalysts,[10] we herein describe a simple and efficient protocol for the three component-coupling reactions of aldehydes, amines and trimethylsilyl cyanide to produce α-aminonitriles using a heterogeneous solid acid catalyst, montmorillonite KSF clay under mild reaction conditions (Scheme 1).



Scheme 1.

The treatment of benzaldehyde and aniline with TMSCN in the presence of KSF clay 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 85–94% yields. These three-component coupling reactions proceeded efficiently at ambient temperature with high selectivity. No cyanohydrin trimethylsilyl ethers (an adduct between an aldehyde and trimethylsilyl cyanide) were

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Keywords: Solid acids; Aryl imines; Trimethylsilyl cyanide; α-Aminonitriles.

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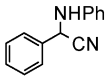
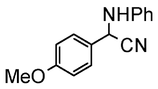
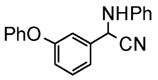
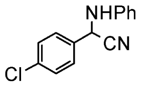
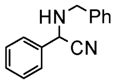
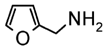
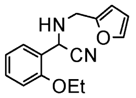
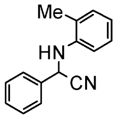
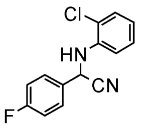
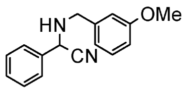
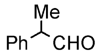
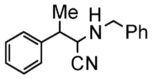
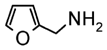
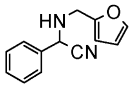
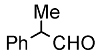
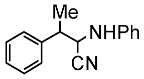
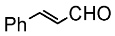
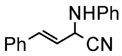
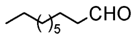
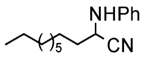
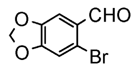
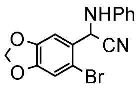
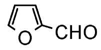
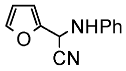
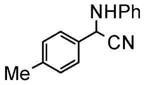
Table 1. Montmorillonite clay promoted synthesis of α-amino nitriles

Entry	Aldehyde (**1**)	Amine (**2**)	Product (**3**)[a]	Reaction time (h)	Yield (%)[b]
(a)	C_6H_5CHO	$C_6H_5NH_2$		3.5	90
(b)	4-$MeOC_6H_4CHO$	$C_6H_5NH_2$		3.0	92
(c)	3-$PhOC_6H_4CHO$	$C_6H_5NH_2$		2.5	89
(d)	4-ClC_6H_4CHO	$C_6H_5NH_2$		3.5	91
(e)	C_6H_5CHO			4.5	87
(f)	2-$EtOC_6H_4CHO$			3.0	92
(g)	C_6H_5CHO	2-$MeC_6H_4NH_2$		4.0	94
(h)	4-FC_6H_4CHO	2-$ClC_6H_4NH_2$		5.0	85
(i)	C_6H_5CHO	3-$MeOC_6H_4CH_2NH_2$		4.5	89
(j)				3.5	91
(k)	C_6H_5CHO			5.5	92
(l)		$C_6H_5NH_2$		5.0	89
(m)		$C_6H_5NH_2$		4.5	85
(n)		$C_6H_5NH_2$		5.5	87
(o)		$C_6H_5NH_2$		5.0	92
(p)		$C_6H_5NH_2$		5.5	89
(q)	4-MeC_6H_4CHO	$C_6H_5NH_2$		5.0	91

Ph=phenyl.

[a] All products were characterized by ^{1}H NMR IR and mass spectroscopy.

[b] Isolated and unoptimized yields after purification.

obtained under these reaction conditions. This is because of the rapid formation and activation of the imines by solid acid clay. Both aromatic and aliphatic aldehydes afforded excellent yields of products whereas ketones did not yield any product under these reaction conditions. The reactions are clean and highly selective affording exclusively α-aminonitriles in high yields in a short reaction 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 additives or stringent reaction conditions to proceed. The reaction conditions 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. The scope and generality of this process is illustrated with respect to various amines and aldehydes including aromatic, α,β-unsaturated, heterocyclic and aliphatic aldehydes and the results are presented in Table 1. Finally, the clay was recovered by filtration, washed with methanol and recycled for use in subsequent reactions (after activation at 120 °C for 4–5 h) with gradual decrease in activity; for example, the reaction of benzaldehyde, aniline and trimethylsilyl cyanide under the present reaction conditions afforded α-aminonitriles in 92, 87 and 82% yields over three cycles.

3. Conclusion

In summary, we describe 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 heterogeneous solid acid KSF clay. The simple experimental and product isolation procedures combined with easy recovery and reuse of this natural clay is expected to contribute to the development of clean and environmentally friendly strategy for the synthesis of α-aminonitriles.

4. Experimental

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. KSF clay was purchased from Aldrich Co.

4.1. General procedure for the preparation of α-aminonitriles

A mixture of aldehyde (1 mmol), amine (1 mmol), trimethylsilyl cyanide (1.2 mmol) and Mont. KSF clay (1.0 g) in dichloromethane (10 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 filtered and washed with dichloromethane (2×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography on silica gel (Merck, 100–200 mesh, ethyl acetate–hexane, 1:9) to afford pure α-aminonitrile. Solid clay portion was washed with methanol, dried at 120° under reduced pressure and could be reused in subsequent reactions.

4.2. Spectroscopic data for products

4.2.1. Compound 3a. White crystalline solid, mp 73–74 °C, IR (KBr): ν 3369, 3021, 2954, 2236, 1603, 1505, 1464, 1313, 1142, 995, 751. ^{1}H NMR ($CDCl_3$): δ 4.0 (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. HRMS calcd for $C_{14}H_{12}N_2$: 208.10004. Found: 208.10105.

4.2.2. Compound 3b. White solid, mp 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). ^{13}C NMR (Proton decoupled, $CDCl_3$): δ 50.0, 55.8, 114.5, 115.0, 118.9, 120.5, 126.3, 129.0, 129.9, 145.1, 160.8. EIMS: *m/z*: 238 M$^+$, 211, 181, 167, 141, 104, 77, 51, 40. HRMS calcd for $C_{15}H_{14}N_2O$: 238.11061. Found: 238.11129.

4.2.3. Compound 3c. Pale yellow solid, mp 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). ^{13}C NMR (Proton decoupled, $CDCl_3$): δ 49.7, 114.1, 117.2, 117.9, 119.1, 119.2, 120.2, 121.5, 123.8, 129.4, 129.8, 130.5, 130.7, 114.4, 156.2, 158.1. EIMS: *m/z*: 300 M$^+$, 273, 210, 181, 167, 141, 104, 77. HRMS calcd for $C_{20}H_{16}N_2O$: 300.12626. Found: 300.12593.

4.2.4. Compound 3d. White solid, mp 109–112 °C, IR (KBr): ν 3405, 2927, 2239, 1600, 1515, 1457, 1272, 1161, 1098, 791. ^{1}H NMR ($CDCl_3$): δ 4.0 (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). ^{13}C NMR (Proton decoupled, $CDCl_3$): δ 49.5, 114.2, 117.8, 120.5, 128.5, 129.4, 129.5, 132.3, 135.5, 144.3. EIMS: *m/z*: 242 M$^+$, 213, 149, 114, 91, 73, 59. HRMS calcd for $C_{14}H_{11}ClN_2$: 242.06107. Found: 242.06152.

4.2.5. Compound 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, 1H, 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, 143.5. EIMS: *m/z*: 222 M$^+$, 195, 141, 131, 116, 106, 91, 77, 51. HRMS calcd for $C_{15}H_{14}N_2$: 222.11569. Found: 222.11603.

4.2.6. Compound 3f. Yellow 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), 1.80 (brs, 1H, NH), 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). ^{13}C NMR (Proton decoupled, CDCl$_3$): δ 14.5, 43.9, 48.9, 63.8, 108.0, 110.1, 111.8, 118.6, 120.6, 122.7, 128.6, 130.3, 142.2, 151.6, 155.9. EIMS: *m/z*: 256 M$^+$, 227, 198, 173, 146, 120, 104, 95, 80, 52. HRMS calcd for $C_{15}H_{16}N_2O_2$: 256.12117. Found: 256.12148.

4.2.7. Compound 3g. Pale yellow solid, mp 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, 1H, 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. HRMS calcd for $C_{15}H_{14}N_2$: 222.11569. Found: 222.11607.

4.2.8. Compound 3h. White crystalline solid, mp 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. HRMS calcd for $C_{14}H_{10}ClFN_2$: 260.05165. Found: 260.05123.

4.2.9. Compound 3i. Yellow liquid, IR (KBr): ν 3400, 2941, 2890, 2241, 1616, 1527, 1471, 1283, 1160, 1045, 789. ^{1}H NMR (CDCl$_3$): δ 1.85 (brs, 1H, NH), 3.80 (s, 3H), 3.95 (AB q, 2H, J=13.0 Hz), 4.70 (d, 1H, J=13.0 Hz), 6.80–6.95 (m, 3H), 7.25 (t, 1H, J=7.9 Hz), 7.30–7.55 (m, 5H). ^{13}C NMR (Proton decoupled, CDCl$_3$): δ 51.4, 53.6, 55.5, 96.5, 113.4, 114.2, 119.0, 120.9, 127.6, 129.3, 130.0, 135.3, 140.0, 160.2. EIMS: *m/z*: 252 M$^+$, 225, 122, 91, 77. HRMS calcd for $C_{16}H_{16}N_2O$: 252.12626. Found: 252.12661.

4.2.10. Compound 3j. Pale yellow oil, 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), 1.95 (brs, 1H, NH), 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. HRMS calcd for $C_{17}H_{18}N_2$: 250.14699. Found: 250.14659.

4.2.11. Compound 3k. Yellow liquid, IR (KBr): ν 3306, 2923, 2851, 2225, 1691, 1575, 1462, 1216, 1141, 1017, 940, 765. ^{1}H NMR (CDCl$_3$): δ 1.80 (brs, 1H, NH), 4.0 (s, 2H), 4.78 (s, 1H), 6.20–6.40 (m, 2H), 7.30–7.55 (m, 6H). EIMS: *m/z*: 212 M$^+$, 186 105, 81, 77 51, 39. HRMS calcd for $C_{13}H_{12}N_2O$: 212.09496. Found: 212.09523.

4.2.12. Compound 3l. Light brown solid, mp 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. HRMS calcd for $C_{16}H_{16}N_2$: 236.13134. Found: 236.13178.

4.2.13. Compound 3m. Pale yellow solid, mp 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. HRMS calcd for $C_{16}H_{14}N_2$: 234.11569. Found: 234.11515.

4.2.14. Compound 3n. Pale yellow 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). ^{13}C NMR (Proton decoupled, CDCl$_3$): δ 48.9, 112.7, 116.3, 116.6, 117.5, 120.4, 120.5, 127.9, 129.0, 129.1, 129.6, 140.4, 161.6, 164.9. EIMS: *m/z*: 258 M$^+$, 185, 155, 135, 121, 77, 51. HRMS calcd for $C_{17}H_{26}N_2$: 258.20959. Found: 258.20906.

4.2.15. Compound 3o. Brown solid, mp 93–94 °C, IR (KBr): ν 3364, 2924, 2855, 2233, 1599, 1499, 1406, 1271, 1239, 1127, 1035, 979, 866, 750. ^{1}H NMR (CDCl$_3$): δ 3.90 (brs, 1H, NH), 5.60 (s, 1H), 6.0 (s, 2H), 6.70 (d, 2H, J=8.0 Hz), 6.90 (t, 1H, J=7.9 Hz), 7.08 (m, 1H), 7.20–7.45 (m, 3H). EIMS: *m/z*: 331 M$^+$, 305, 282, 249, 229, 199, 155, 141, 97, 69, 51, 39. HRMS calcd for $C_{15}H_{11}BrN_2O_2$: 330.00038. Found: 330.00108.

4.2.16. Compound 3p. Dark brown solid, mp 68–70 °C, IR (KBr): ν 3359, 2925, 2235, 1695, 1601, 1501, 1440, 1289, 1248, 1149, 1014, 880, 751. ^{1}H NMR (CDCl$_3$): δ 4.05 (d, 1H, J=8.1 Hz), 5.40 (d, 1H, J=8.1 Hz), 6.40 (m, 1H), 6.55 (m, 1H), 6.80 (d, 2H, J=8.0 Hz), 6.90 (t, 1H, J=7.9 Hz), 7.25 (t, 2H, J=7.9 Hz), 7.40 (m, 1H). EIMS: *m/z*: 198 M$^+$, 169, 155, 141, 115, 106, 92, 77, 51. HRMS calcd for $C_{12}H_{10}N_2O$: 198.07931. Found: 198.07890.

4.2.17. Compound 3q. Yellow solid, mp 76–78 °C, IR (KBr): ν 3306, 2923, 2851, 2225, 1691, 1575, 1462, 1216, 1141, 1017, 940, 765. ^{1}H NMR (CDCl$_3$): δ 2.40 (s, 3H), 3.90 (d, J=8.1 Hz), 5.40 (d, J=8.1 Hz), 6.78 (d, 2H, J=8.0 Hz), 6.90 (t, 1H, J=7.8 Hz), 7.20–7.30 (m, 4H), 7.50 (d, 2H, J=8.0 Hz), 7.50 (d, 2H, J=8.0 Hz). EIMS: *m/z*: 222 M$^+$, 194, 176, 131, 103, 91, 77 41. HRMS calcd for $C_{15}H_{14}N_2$: 222.11569. Found: 222.11508.

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