Copper (II)-catalysed direct conversion of aldehydes into nitriles in acetonitrile

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A mild one-pot method for the direct conversion of aryl, heteroaryl and alkyl aldehydes into nitriles was achieved by forming the corresponding oximes *in situ* with NH_2OH and allowing them to react with CuO and acetonitrile. Yields of the 13 nitriles prepared were moderate to very good (62–91%).

Keywords: nitrile, copper salt, aldehyde, hydroxylamine hydrochloride, acetonitrile

Nitriles are useful organic synthetic intermediates, and play an important role in organic chemistry.[1,2] Nitriles have been widely utilised as synthetic intermediates for pharmaceuticals, agricultural chemicals, dyes and material sciences, and some nitriles have seen direct use as pesticides, perfumes, metal inhibitors and liquid crystal materials.[3–5] For these reasons, much attention has been paid to the development of efficient and practical methods for their synthesis. There are diverse methods for the synthesis of nitrile groups from different organic functional groups. Among these methods, the conversion of an aldehyde into a nitrile using hydroxylamine hydrochloride as the nitrogen source is considered to be one of the most important. Usually, this conversion is achieved via aldoxime dehydration in a two-step process. Direct conversion of an aldehyde into a nitrile has also been reported, either by using high-temperature conditions,[6–14] or by treatment with various dehydrating reagents[15–19] or transition metal catalysts such as red mud (Fe_2O_3, Al_2O_3, SiO_2, Na_2O, TiO_2, MgO and CaO),[20] CuO nanoparticles,[21] Fe_3O_4-CTAB (cetyltrimethyl ammonium bromide) nanoparticles,[22] W-Sn hydroxide[2] or zinc compounds.[23,24] At the same time, we have particularly noticed that the conversion of aldoximes or aldehydes into nitriles catalysed by other copper salts has been reported.[21,25–27] With certain copper salts as catalysts, the transformation of aldoximes to nitriles proceeds smoothly.[25–27] However, the direct conversion of aldehydes into nitriles has been found to be relatively difficult when other copper salts are used as catalysts.[21] According to this report,[21] the direct conversion of an aldehyde into a nitrile was achieved by use of a commercially unavailable copper salt catalyst with the help of microwave irradiation. Therefore, there is still a need for a mild and convenient method for this conversion.

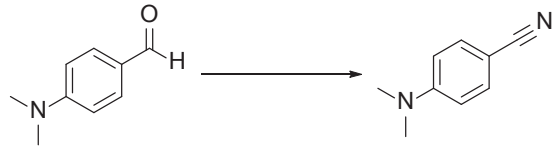
In this paper, we report the development of a mild method for the direct conversion of aldehydes into nitriles by use of a commercially available copper catalyst in acetonitrile.

Results and discussion

For our optimisation studies, we selected 4-(dimethylamino) benzaldehyde as a model substrate to investigate the influence of ratio of reactant, reaction temperature, type of base, various copper salts and solvent on the yields of the reaction. The results are listed in Table 1.

As shown in Table 1, no nitrile product was obtained in the absence of catalyst (entry 1). In this case, the aldehyde was completely converted into the aldoxime. When a catalytic

Table 1 Optimisation of the reaction conditions (catalyst, solvent, temperature, duration of reaction) for the conversion of 4-(dimethylamino)benzaldehyde to 4-(dimethylamino)benzonitrile[a]



Entry	Conditions	Yield[b] (%)
1	$NH_2OH{\cdot}HCl$ (1.0 equiv.), NaOAc (1.0 equiv.), CH_3CN, reflux, 4 h	0
2	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.0 equiv.), NaOAc (1.0 equiv.), CH_3CN, reflux, 4 h	70
3	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), NaOAc (1.5 equiv.), CH_3CN, reflux, 4 h	91
4	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), NaOAc (1.5 equiv.), CH_3CN, 50°C, 4 h	23
5	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), NaOAc (1.5 equiv.), CH_3CN, 25 °C, 8 h	0
6	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), NaOH (1.5 equiv.), CH_3CN, reflux, 4 h	55
7	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), Na_2CO_3 (0.75 equiv.), CH_3CN, reflux, 4 h	16
8	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), pyridine (1.5 equiv.), CH_3CN, reflux, 4 h	12
9	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), triethylamine (1.5 equiv.), CH_3CN, reflux, 4 h	0
10	$Cu(OAc)_2$ (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), NaOAc (1.5 equiv.), CH_3CN, reflux, 4 h	86
11	$CuSO_4{\cdot}5H_2O$ (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), NaOAc (1.5 equiv.), CH_3CN, reflux, 4 h	74
12	$CuCl_2{\cdot}2H_2O$ (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), NaOAc (1.5 equiv.), CH_3CN, reflux, 4 h	25
13	CuO (0.05 equiv.), $NH_2OH{\cdot}HCl$ (1.5 equiv.), triethylamine (1.5 equiv.), EtOH, reflux, 4 h	0

[a]Reaction conditions: a stirred mixture of 4-(dimethylamino)-benzaldehyde (2.0 equiv.), hydroxylamine hydrochloride (1.0 or 1.5 equiv.), base (0.75–1.5 equiv.), and a Cu(II) salt (0.05 equiv.) in a solvent (6 mL) was reacted at various temperatures and for various times.

[b]Isolated yield.

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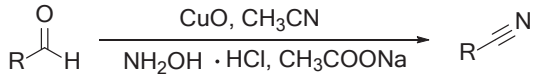
amount of copper oxide was added into the reaction system, the yield of 4-(dimethylamino)benzonitrile drastically increased to 70% (entry 2). It is worth noting that some 4-(dimethylamino) benzaldehyde was recovered unchanged. When we increased the amounts of $NH_2OH{\cdot}HCl$ and NaOAc to 1.5 equiv. each, the yield went up to 91% (entry 3). Decreasing the reaction temperature to 50 °C resulted in a decreased yield, while at 25 °C the reaction was hampered (entries 4 and 5). The influence of bases such as NaOAc, NaOH, Na_2CO_3, pyridine and triethylamine was examined. It is clear that NaOAc gave the best result (entry 3); a lower yield was obtained using NaOH, Na_2CO_3 or pyridine (entries 6–8). No 4-(dimethylamino) benzonitrile was detected in the case of triethylamine (entry 9). The various copper salts listed in Table 1 appear to efficiently catalyse the reaction (entries 3, 10 and 11), and it was shown that copper oxide (CuO) and cupric acetate ($Cu(OAc)_2$) were much more efficient than copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) and copper(II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$). We also compared the catalytic activity of copper oxide (CuO) and cupric acetate ($Cu(OAc)_2$). Cupric acetate has similar catalytic activity to copper oxide, but copper oxide features higher catalytic selectivity and less by-product (amide). Use of ethanol in place of acetonitrile resulted in no product. Therefore, we thought that acetonitrile may be involved in the reaction.

On the basis of the above results, we can conclude that increasing the amounts of hydroxylamine hydrochloride and base will improve the yield of the product and using CuO, $NH_2OH{\cdot}HCl$ and NaOAc in acetonitrile at refluxing temperature is the optimum conditions for the conversion of an aldehyde into a nitrile. This procedure was subsequently applied to various aromatic aliphatic and heterocyclic aldoximes and the results are shown in Table 2.

Various aldehydes including aromatic aldehydes (entries 1–8), an aliphatic aldehyde (entry 9) and heterocyclic aldehydes (entries 10–12) were converted into the corresponding nitriles in moderate to good yields. Aldehydes bearing an electron-donating group reacted more effectively than substrates with an electron-withdrawing group (entries 1 and 5) and gave the corresponding nitriles in good yields and in a relatively shorter time (entries 1–3). In contrast, electron-withdrawing groups on the aromatic rings decreased the speed of the reaction and nitriles were obtained in slightly lower yields (entries 5 and 6). The sterically hindered *o*-substituted aldehydes were slow to react and the reaction time needed to be increased to 10 h (entries 7 and 8). In the case of an aliphatic aldehyde (entry 9), there was a smooth conversion into the corresponding nitrile in a good yield. Heterocyclic aldehydes with a heteroatom lone pair positioned *ortho* to the aldehyde group showed high reactivity and the reactions were completed after a relatively short reaction time of 3 h. However, in these cases, the corresponding nitriles were obtained in relatively low yields and the yield of the corresponding amide was appreciable (26–34%; entries 11 and 12).

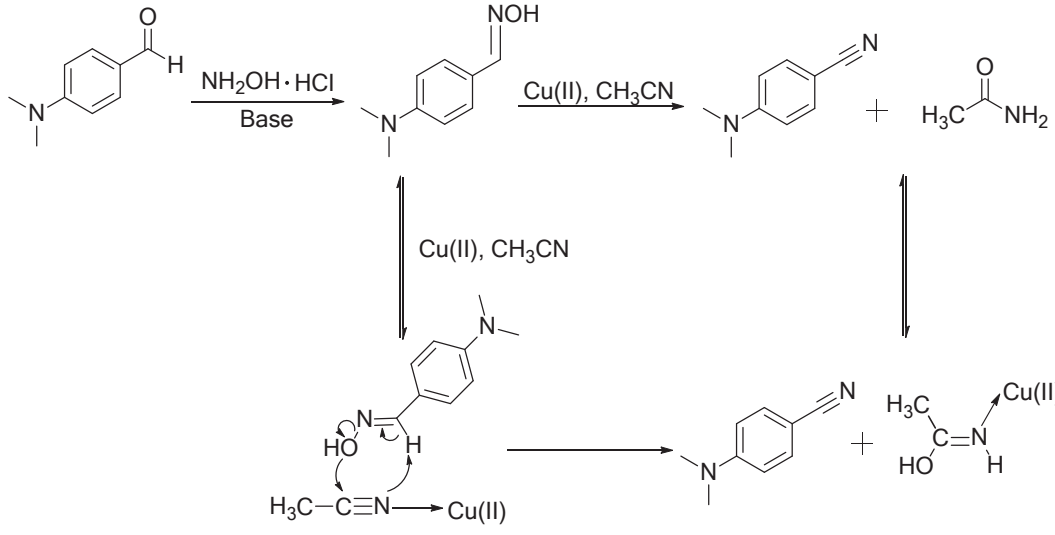
As can be seen from Table 1, no nitrile product was detected when ethanol was used in place of acetonitrile as solvent (entry 13); therefore, we thought that acetonitrile not only serves as a solvent but also participates in the reaction. Indeed, we thought that the mechanism of the conversion of aldoximes to nitriles was likely to be similar to the mechanism reported in the literature.[26,27] A possible reaction pathway is presented in Scheme 1. The coordination of acetonitrile to copper ion results in an enhanced electrophilicity of the nitrile carbon facilitating the nucleophilic addition of 4-(dimethylamino)benzaldehyde

Table 2 Yields of a series of nitriles (R = various) prepared by reaction of an aldehyde (R = various) with hydroxylamine and CuO in MeCN[a]



Entry	R	Time (h)	Yield[b] (%)
1	4-MeO-C_6H_4	4	90
2	4-OH-C_6H_4	4	88
3	3-MeO-4-MeO-5-MeO-C_6H_2	5	86
4	Ph	5	87
5	4-NO_2-C_6H_4	6	78
6	4-Cl-C_6H_4	6	83
7	2-Cl-4-Cl-C_6H_3	10	87
8	2-Cl-C_6H_4	10	88
9	*n*-$C_{11}H_{23}$	6	85
10	4-pyridyl	6	75
11	2-furyl	3	62(34)[c]
12	2-thienyl	3	69(26)[c]

[a]Reaction conditions: a stirred mixture of an aldehyde (2 mmol), $NH_2OH{\cdot}HCl$ (3 mmol), NaOAc (3 mmol), CuO (0.1 mmol) in MeCN (6 mL) was refluxed for various times.
[b]Isolated yield.
[c]Yield of the corresponding amide is given in brackets.



Scheme 1 Proposed mechanism for nitrile synthesis reaction.

oxime. The reaction proceeds smoothly *via* a six-membered intermediate to yield the hydrated product, acetamide and the dehydrated product, 4-(dimethylamino)benzonitrile. The yield of the by-product amide depends on the hydrolytic lability of the product nitrile. The by-product of this reaction, acetamide, was identified in the crude by extract by LC-MS.

In conclusion, we disclose a simple method for the direct conversion of aldehydes into nitriles using an inexpensive copper salt catalyst in acetonitrile. Both the catalyst and the reagents are commercially available and the reactions were carried out under relatively mild reaction conditions. In this method, aromatic, heterocyclic and aliphatic aldehydes were converted into the corresponding nitriles in moderate to good yields.

Experimental

Reagent grade chemicals were purchased from Aladdin Reagent (Shanghai, China) and were used without further purification. ^{1}H NMR spectra were obtained on a Bruker DPX-500 or a Bruker DPX-400 MHz spectrometer in DMSO-d_6 or $CDCl_3$ using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) are given in Hz. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. Yields refer to the isolated yields of the products after purification by silica-gel column chromatography (300 mesh).

Synthesis of nitriles; general procedure

An aldehyde (2 mmol), CuO (0.1 mmol), $NH_2OH{\cdot}HCl$ (3 mmol), NaOAc (3 mmol) and acetonitrile (6 mL) were added to a 25 mL round-bottom flask equipped with magnetic stirrer. The mixture was heated to reflux for 3–10 h. After cooling to r.t., acetonitrile was distilled off under reduced pressure. Water (15 mL) and ethyl acetate (30 mL) were added to the reaction mixture, and the organic layer was washed with saturated aqueous sodium bicarbonate (1 × 15 mL) and water (1 × 15 mL). The organic layer was dried with Na_2SO_4, evaporated and the residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane) to give the corresponding nitriles. All the nitriles are commercially available and were characterised by ^{1}H NMR spectra, which are available in the ESI.

Identification of acetamide as a by-product

4-(Dimethylamino)benzonitrile was synthesised using the method described above. After cooling to r.t., the reaction mixture was filtered and the filtrate was concentrated under reduced pressure to provide the crude product. The crude product was analysed by LC-MS. From the LC-MS spectra, we found that acetamide was generated. In addition to the product 4-(dimethylamino)benzonitrile, 4-(dimethylamino) benzamide, 4-(dimethylamino)benzaldehyde and 4-(dimethylamino) benzoic acid were also detected.

Acetamide: MW: 59.07; found: 60.1 (M + 1).

4-(Dimethylamino)benzonitrile: MW: 146.19; found: 147.1 (M + 1).

4-(Dimethylamino)benzamide: MW: 164.21; found: 165.1 (M + 1).

4-(Dimethylamino)benzaldehyde: MW: 149.19; found: 150.2 (M + 1).

4-(Dimethylamino)benzoic acid: MW: 165.19; found: 166.2 (M + 1).

4-(Dimethylamino)benzonitrile (Table 1, entry 3): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:10) to give 4-(dimethylamino)benzonitrile as: White solid; yield 266 mg (91%): m.p. 70–71 °C (lit.[20] 69–71 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.04 (s, 6H), 6.63 (m, 2H), 7.47 (m, 2H). Data are in good agreement with the literature.[28]

4-Methoxybenzonitrile (Table 2, entry 1): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:4) to give 4-methoxybenzonitrile as: White solid; yield 239 mg (90%); m.p. 56–58 °C (lit.[20] 57–59 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.86 (s, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H). Data are in good agreement with the literature.[29]

4-Hydroxybenzonitrile (Table 2, entry 2): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:3) to give 4-hydroxybenzonitrile as: White solid; yield 209 mg (88%); m.p. 109–111 °C (lit.[14] 108–110 °C); ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.89 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.61 (m, 2H), 10.64 (s, 1H). Data are in good agreement with the literature.[30]

3,4,5-Trimethoxylbenzonitrile (Table 2, entry 3): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:3) to give 3,4,5-trimethoxybenzonitrile as: White solid; yield 323 mg (86%); m.p. 92–94 °C (lit.[8] 93 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (s, 6H), 3.89 (s, 3H), 6.86 (s, 2H). Data are in good agreement with the literature.[31]

Benzonitrile (Table 2, entry 4): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:15) to give benzonitrile as: Colourless liquid; yield 179 mg (87%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (m, 2H), 7.63 (m, 1H), 7.67 (m, 2H). Data are in good agreement with the literature.[32]

4-Nitrobenzonitrile (Table 2, entry 5): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:5) to give 4-nitrobenzonitrile as: White solid; yield 231 mg (78%); m.p. 147–148 °C (lit.[20] 146–149 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (m, 2H), 8.37 (m, 2H). Data are in good agreement with the literature.[32]

4-Chlorobenzonitrile (Table 2, entry 6): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:15) to give 4-chlorobenzonitrile as: White solid; yield 228 mg (83%); m.p. 92–94 °C (lit.[20] 91–93 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H). Data are in good agreement with the literature.[33]

2,4-Dichlorobenzonitrile (Table 2, entry 7): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:15) to give 2,4-dichlorobenzonitrile as: White solid; yield 299 mg (87%); m.p. 58–60 °C (lit.[8] 59 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H). Data are in good agreement with the literature.[28]

2-Chlorobenzonitrile (Table 2, entry 8): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:10) to give 2-chlorobenzonitrile as: White solid; yield 242 mg (88%); m.p. 43–44 °C (lit.[8] 42 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (m, 1H), 7.56 (m, 2H), 7.69 (m, 1H). Data are in good agreement with the literature.[33]

Dodecanenitrile (Table 2, entry 9): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:15) to give dodecanenitrile as: Colourless liquid; yield 308 mg (85%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.27–1.33 (m, 14H), 1.45 (m, 2H), 1.66 (m, 2H), 2.34 (t, *J* = 7.2 Hz, 2H). Data are in good agreement with the literature.[34]

Isonicotinonitrile (Table 2, entry 10): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:1) to give isonicotinonitrile as: White solid; yield 156 mg (75%); m.p. 76–78 °C (lit.[20] 76 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (m, 2H), 8.82 (m, 2H). Data are in good agreement with the literature.[31]

Furan-2-carbonitrile (Table 2, entry 11): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:15 and 2:1) to give furan-2-carbonitrile as: Colourless liquid; yield 115 mg (62%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.55 (m, 1H), 7.12 (m, 1H), 7.60 (m, 1H). Data are in good agreement with the literature.[35] Furan-2-carboxamide was obtained as a by-product: White solid; yield 75 mg (34%; m.p. 139–141 °C (lit.[36] 140–142 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.81 (d, 1H, *J* = 0.8 Hz), 7.79 (br. s, 1H), 7.40 (br. s, 1H), 7.10 (d, 1H, *J* = 3.2 Hz), 6.61 (m, 1H). Data are in good agreement with the literature.[36]

Thiophene-2-carbonitrile (Table 2, entry 12): The residue was purified by column chromatography on silica gel (ethyl acetate/*n*-hexane = 1:15 and 2:1) to give thiophene-2-carbonitrile as: Colourless liquid; yield 150 mg (69%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (m, 1H), 7.62 (m, 1H), 7.65 (m, 1H). Data are in good agreement with the literature.[32] Thiophene-2-carboxamide was obtained as a by-product: White solid; yield 66 mg (26%); m.p. 178–179 °C (lit.[37] 179.1–180.2 °C); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.97 (br. s, 1H), 7.74 (d, 2H, *J* = 4.0 Hz), 7.39 (br. s, 1H), 7.13 (t, 1H, *J* = 4.0 Hz). Data are in good agreement with the literature.[37]

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