Ligand-Free Nickel-Catalyzed Conversion of Aldoximes into Nitriles

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Abstract: Catalytic dehydration of aldoximes can be performed efficiently with $NiCl_2$ in acetonitrile under neutral and mild conditions. Under these conditions, various functionalized aldoximes produce the corresponding nitriles in good to excellent yields.

Key words: aldehydes, nickel, nitrile, catalysis, elimination

Nitriles, which serve as precursors in several functional group transformations, are an important class of organic compound. The cyano group is also a known functional motif for hydrogen bonding to certain biological receptors[1] as well as a donating ligand in coordination chemistry.[2] For these reasons, remarkable efforts have been made to develop efficient methods for the preparation of many nitrile compounds. Among the numerous methodologies available, the dehydration of aldoxime or primary amide functionalities appears to be attractive because of the ready availability of the starting materials. A number of reagents have proved to be effective for this transformation.[3] However, the approach suffers from a number of disadvantages such as the use of stoichiometric amounts of reagents, and limitations arising from the sensitivity of some functional groups to the reaction conditions. Thus, the development of metal-catalyzed dehydration of aldoxime has received much attention. A number of catalytic systems are available, such as $Pd(OAc)_2/Ph_3P$,[4] $[(CH_3CH_2CN)_2PtCl_4]$,[5] $[RuCl_2(p\text{-cymene})]_2$,[6] $Ga(OTf)_3$,[7] $Cu(CH_3COO)_2$,[8] $O_3Re(OH)$,[9] iron porphyrin,[10] tungsten–tin mixed hydroxide,[11] $CuCl_2$ under ultrasound conditions,[12] and Raney nickel.[13] Despite the success of these reactions, there is still a strong need for an efficient method for the conversion of aldoximes into nitriles through the use of a simple catalytic system. We report here a catalytic method for this transformation that involves thermal heating of aldoximes in acetonitrile in the presence of catalytic amounts of $NiCl_2{\cdot}2H_2O$.

Initially, the dehydration of benzaldoxime catalyzed by various transition-metal complexes to yield benzonitrile was examined to screen the best catalytic system. Transition-metal complexes associated with polydentate ligands are generally active in catalysis, and we have recently been working with N-donor ligands derived from pyrazole and pyridine such as **pp** (Figure 1).[14] Thus, metal complexes with **pp** ligands were selected as catalysts for the dehydration of aldoximes. In the presence of 5 mol% metal complex and molecular sieves, with acetonitrile as the solvent, benzonitrile was obtained from benzaldoxime under heating for seven hours; the results are summarized in Table 1.

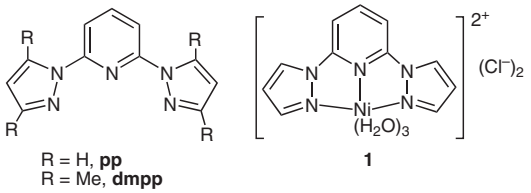

Figure 1 Ligands and nickel complexes

Table 1 Dehydration of Benzaldoxime[a]

Entry	Metal	Ligand	Yield of benzonitrile (%)[b]
1	$FeCl_2$	**pp**	Trace
2	$CoCl_2$	**pp**	38
3	$[Ni(\mathbf{pp})(H_2O)_3]Cl_2$	–	100
4	No metal ions	–	Trace
5	$NiCl_2{\cdot}2H_2O$	**pp**	100
6	$NiCl_2{\cdot}2H_2O$	**dmpp**	71
7	$NiBr_2$	**pp**	70
8	$Ni(NO_3)_2{\cdot}6H_2O$	**pp**	56
9	$Ni(CH_3COO)_2{\cdot}6H_2O$	**pp**	58
10	$FeCl_2$	**pp**	Trace

[a] Reaction conditions: benzaldoxime (0.5 mmol), catalyst (0.025 mmol), MeCN (1 mL), 4 Å MS (0.1 g), reflux, 7 h.
[b] GC yield.

As shown in Table 1, entries 1–3, use of the nickel complex was clearly the best catalyst for this conversion; the corresponding iron complex demonstrated no activity at all. It should be noted that performing the reaction by generating the metal complex in situ gave similar results to those obtained with **1**. However, it appeared that the yield decreased with the use of **dmpp** (entry 6), presumably due to the steric hindrance of this ligand. This catalytic conversion was also influenced by the anion of the nickel

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salts; chloride was established as the best choice (entries 7–9).

Further efforts were then focused on optimizing the reaction conditions; the results are summarized in Table 2. To our surprise, it was found that the activity of nickel dichloride itself was as good as that of complex **1** in the catalytic conversion of benzaldoxime into benzonitrile (Table 2, entry 1). Apparently, the metal ion plays the key role in the catalysis, not the associated ligand, thus, a simple catalyst for the dehydration of oximes is available. Other modified reaction conditions were also examined. When the reaction was carried out in the presence of air, the yield dropped due to decomposition of the metal complexes, as evidenced by the formation of black precipitates (entry 2). The reaction rate was reduced at lower temperatures, and low conversion was observed at 50 °C (<35%). Among several solvents tested, acetonitrile was the medium of choice (entries 6 and 7). Running the reaction under basic conditions did not provide better results (entries 4 and 5).

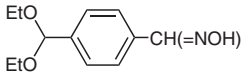
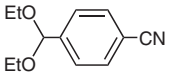
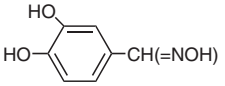
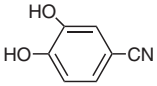
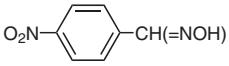
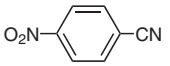
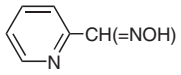
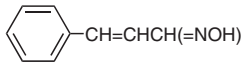
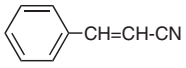
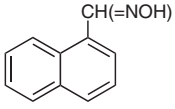
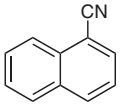
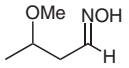
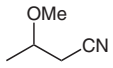
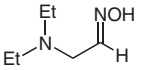
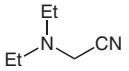
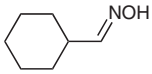
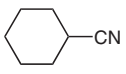
Table 2 Conversion of Benzaldoxime into Benzonitrile[a]

Entry	Conditions and additives	Yield (%)[b]	
		$NiCl_2$ + **pp**	$NiCl_2$
1	–	76	82
2	under air	52	57
3	50 °C	34	30
4	Cs_2CO_3 (0.025 mmol)	26	38
5	DBU (0.025 mmol)	27	27
6	EtOH as solvent	NR[c]	NR[c]
7	toluene as solvent	NR[c]	NR[c]
8	microwave (150 W), 10 min	21	Trace
9	without molecular sieves	68	65

[a] Reaction conditions: benzaldoxime (0.5 mmol), catalyst (0.025 mmol), MeCN (1 mL), 4 Å MS (150 mg), reflux, 3 h.
[b] GC yield.
[c] NR: no reaction.

The generality of this method was demonstrated by the conversion of various kinds of aldoximes into the corresponding nitriles, as illustrated in Table 3. The reactions were carried out at reflux temperature for seven hours with the use of 5 mol% nickel chloride in the presence of 4 Å molecular sieves. Substituent variation on the aromatic ring did influence the efficiency (entries 1–6), and a moderate yield was obtained from the reaction of a sterically congested oxime (entry 2). Conversion of 3,4-dihydroxybezaldoxime and 2-pyridylaldoxime into the corresponding nitriles were quite poor because of chelation of these substrates with metal ions. Cinnamaldoxime was smoothly converted into the corresponding nitrile (entry 9). However, a strong electron-withdrawing group in the aromatic ring caused a decrease in the yield of the desired product (entry 7) accompanied by the formation of *p*-nitrobenzamide as a side product. The present method is also applicable to the preparation of aliphatic nitriles (entries 11–14). Thus, butyaldoxime was quantitatively converted into butanenitrile, as was cyclohexanecarbaldoxime. Neither an amino- nor an alkoxy substituent in the aliphatic substrate affected the efficiency. For example, 3-methoxybutylaldoxime and 2-dimethylaminopropionaldoxime were both smoothly converted into 3-methoxybutanenitrile and 2-dimethylaminopropanenitrile, respectively (Table 3, entries 12 and 13).

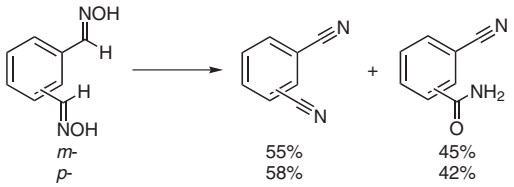
Table 3 Conversion of Aldoximes into Nitriles[a]

Entry	Substrate	Product	Yield (%)
1	PhCH(=NOH)	PhCN	100
2	*o*-$MeC_6H_4CH(=NOH)$	*o*-MeC_6H_4CN	46
3	*p*-$MeOC_6H_4CH(=NOH)$	*p*-$MeOC_6H_4CN$	82
4	*p*-$BrC_6H_4CH(=NOH)$	*p*-BrC_6H_4CN	78
5			57
6			16
7			54[b]
8		–	–
9			100
10			80
11	$CH_3(CH_2)_2CH(=NOH)$	$CH_3(CH_2)_2CN$	100
12			100
13			79
14			100

[a] Reaction conditions: aldoxime (0.5 mmol), catalyst (0.025 mmol), MeCN (1 mL), 4 Å MS (150 mg), reflux, 3 h.
[b] *p*-Nitrobenzamide (24%) was also obtained.

When aromatic bis-aldoxime compounds were treated under the same conditions, a mixture of bis-nitrile and amide–nitrile products were obtained (Equation 1). Presumably, the cyano group formed in the first stage acts an electron-withdrawing group, which affects the dehydra-

tion on the second group. This electronic effect is consistent with the observed dehydration of *p*-nitrobenzaldoxime (Table 3, entry 7).



Equation 1

As shown in Figure 2, complete conversion of benzaldoxime into benzonitrile was accomplished within seven hours; however, the catalytic reaction did not proceed in the first 20 minutes, i.e., there was an induction period for the catalysis. This indicates that the nickel dichloride complex is not the active catalyst. It has been proposed that the Pd(II)-catalyzed dehydration of aldoxime proceeds through an oxidative addition of N–O bond to the Pd(0).[4] In addition, treatment of aldoximes with Raney nickel led to dehydration to afford nitriles.[13] We suspected that reduction of nickel took place under the reaction conditions, and that the lower oxidation state nickel species were responsible for the catalysis. This explains why superior results were obtained when the reaction was carried out under a nitrogen atmosphere. In a separate experiment, it was found that the dehydration of benzaldoxime proceeded in the presence of $[Ni(COD)_2]$ as the catalyst under similar conditions. However, this Ni(0) complex is quite air-sensitive and thus not easy to handle.

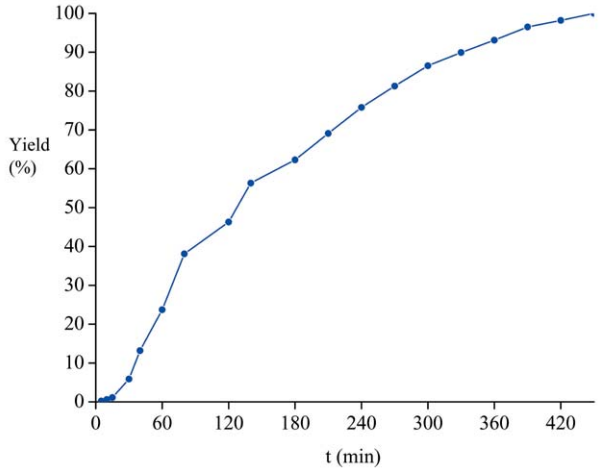
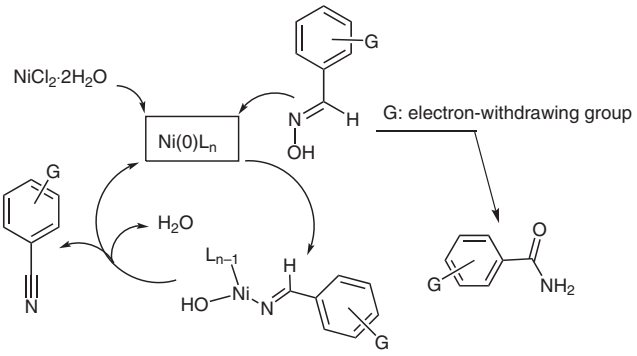


Figure 2 Reaction profile for the dehydration of benzaldoxime. *Reagents and conditions*: benzaldoxime (1 mmol), $NiCl_2 \cdot 2H_2O$ (0.05 mmol), 4 Å MS, MeCN (1 mL), 80 °C.

The catalytic pathway is depicted in Scheme 1. Accordingly, formation of the nitrile involves the oxidative addition of oxime followed by β-elimination, which yields the final product by de-coordination of nitrile from the metal center. When the aromatic aldoxime contains a strong electron-withdrawing substituent, Beckmann rearrangement competes with the dehydration process to yield the amide product. However, nickel(II) ions acting as a Lewis acid to assist the dehydration is an alternative pathway.



Scheme 1 Pathway for catalysis

In summary, the efficient dehydration of a range of aldoximes into nitriles by using a nickel(II) dichloride/acetonitrile system under mild conditions was developed. The advantages of this method are the general applicability to aldoximes, the good to excellent yields obtained, the inexpensive catalyst, and the mild reaction conditions. A detailed study on the mechanistic pathway is currently under investigation.

NMR spectra were recorded in $CDCl_3$ with a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million (ppm) relative to TMS for ^1H NMR. Infrared spectra were measured with a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pellets, unless otherwise noted. Chemicals and solvents were of analytical grade and used as received unless otherwise stated.

Nickel Complex 1

A mixture of $NiCl_2$ (61.4 mg, 0.47 mmol) and **pp** (100 mg, 0.47 mol) in THF (10 mL) was heated at reflux overnight. The reaction mixture was centrifuged and the residue was washed with THF (2 × 2 mL) and Et_2O (2 mL). The obtained light-blue solid was recrystallized from MeOH to give **1**.

Yield: 70 mg (69%); blue-green crystals.

IR: 1619, 1589 cm^{-1}.

Anal. Calcd. for $C_{11}H_{15}Cl_2NiN_5O_3$: C, 33.46; H, 3.83; N, 17.74. Found: C, 33.72; H, 3.89; N, 17.52.

General Procedure

A mixture of aldoxime (0.5 mmol), Ni complex (0.025 mmol) and 4 Å molecular sieves (150 mg) in MeCN (1 mL) was placed in a reaction tube under a nitrogen atmosphere. The mixture was stirred and heated to 80 °C. After the completion of the reaction, brine (3 mL) and CH_2Cl_2 (5 mL) were added, and the organic layer was separated, dried over $MgSO_4$ and concentrated. Products obtained in this work are all known compounds and were characterized by standard spectroscopic methods, particularly NMR ($CDCl_3$) and IR; the data were consistent with those reported.

***o*-Methylbenzonitrile[15]**

IR (KBr): 2226 (CN) cm^{-1}.

^1H NMR (400 MHz): δ = 2.54 (s, 3 H), 7.23–7.30 (m, 2 H), 7.46 (t, *J* = 7.2 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 113.2, 118.4, 126.5, 130.2, 133.0, 142.2.

MS (EI): *m*/*z* = 117 [M]$^+$.

p-Methoxybenzonitrile[16]
IR (KBr): 2217 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 3.85 (s, 3 H, OCH_3), 6.93 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 56.8, 104.3, 115.8, 119.4, 134.1, 163.0.

MS (EI): *m*/*z* = 113 [M]$^+$.

p-Bromobenzonitrile[17]
IR (KBr): 2224 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 7.58 (d, *J* = 8.2 Hz, 2 H), 7.63 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 111.5, 118.2, 128.1, 132.5, 134.0.

MS (EI): *m*/*z* = 181 [M]$^+$, 183 [M + 2]$^+$.

p-Nitrobenzonitrile[16]
Solid; mp 149–151 °C.

IR (KBr): 2232 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 7.86 (d, *J* = 8.0 Hz, 2 H), 8.34 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 50.2, 134.1, 125.0, 118.4, 116.5.

MS (EI): *m*/*z* = 148 [M]$^+$.

p-Nitrobenzamide[18]
IR (KBr): 1685 (CO) cm^{-1}.

^{1}H NMR (400 MHz): δ = 7.96 (d, *J* = 8.4 Hz, 2 H), 8.29 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 124.6, 130.0, 141.4, 149.2, 168.2.

MS (EI): *m*/*z* = 166 [M]$^+$.

4-(Diethoxymethyl)benzonitrile[19]
IR (KBr): 2229 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.24 (t, *J* = 7.0 Hz, 6 H), 3.50–3.63 (m, 4 H), 5.52 (s, 1 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 15.6, 61.3, 100.1, 109.1, 118.4, 127.1, 131.6, 143.7.

MS (EI): *m*/*z* = 205 [M]$^+$.

3,4-Dihydroxylbenzonitrile[20]
IR (KBr): 2217 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 90 (d, *J* = 8.8 Hz, 1 H), 7.10 (d, *J* = 6.8 Hz, 2 H), 7.13 (s, 1 H).

^{13}C NMR (100 MHz): δ = 103.0, 115.5, 118.2, 119.3, 125.8, 144.3, 148.8.

MS (ESI): *m*/*z* = 136 [M + 1]$^+$.

1-Naphthonitrile[21]
IR (KBr): 2222 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 7.46–7.50 (m, 1 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.84–7.89 (m, 2 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz): δ = 110.0, 117.5, 124.8, 125.1, 127.7, 128.5, 128.6, 132.2, 132.5, 132.8, 133.2.

MS (EI): *m*/*z* = 153 [M]$^+$.

***trans*-Cinnamonitrile**[22]
IR (KBr): 2217 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 5.86 (d, *J* = 16.8 Hz, 1 H), 7.35–7.43 (m, 6 H).

^{13}C NMR (100 MHz): δ = 96.3, 118.2, 127.2, 130.0, 131.1, 133.5, 150.4.

MS (EI): *m*/*z* = 129 [M]$^+$.

***n*-Butyronitrile**[23]
IR (KBr): 2260 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.06 (t, *J* = 7.4 Hz, 3 H), 1.68 (m, 2 H), 2.30 (t, *J* = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz): δ = 13.1, 19.0, 19.3, 119.9.

MS (EI): *m*/*z* = 69 [M]$^+$.

3-Methoxybutanenitrile[24]
IR (KBr): 2251 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.28 (d, *J* = 6.0 Hz, 3 H), 2.49 (d, *J* = 5.6 Hz, 2 H), 3.47 (s, 3 H), 3.58–3.62 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.5, 24.9, 56.7, 72.5, 117.

MS (EI): *m*/*z* = 99 [M]$^+$.

***N*,*N*-Diethylaminoacetonitrile**[25]
IR (KBr): 2174 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.08 (t, *J* = 7.0 Hz, 6 H), 2.56 (d, *J* = 6.8 Hz, 4 H), 3.58 (s, 2 H).

^{13}C NMR (100 MHz): δ = 13.6, 40.8, 48.1, 114.5.

MS (EI): *m*/*z* = 112 [M]$^+$.

Cyclohexanecarbonitrile[26]
IR (KBr): 2228 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 1.38–1.58 (m, 4 H), 1.66–1.76 (m, 4 H), 1.81–1.86 (m, 2 H), 2.59–2.61 (m, 1 H).

^{13}C NMR (100 MHz): δ = 24.2, 25.3, 28.1, 29.6, 122.7.

MS (EI): *m*/*z* = 109 [M]$^+$.

1,4-Dicyanobenzene[27]
IR (KBr): 2212 (CN) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.9, 117.0, 132.8.

MS (EI): *m*/*z* = 128 [M]$^+$.

***p*-Cyanobenzamide**[28]
^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.65 (br, 1 H), 7.92 (d, *J* = 7.6 Hz, 2 H), 8.00 (d, *J* = 7.6 Hz, 2 H), 8.02 (br, 1 H).

^{13}C NMR (100 MHz): δ = 114.6, 118.9, 129.1, 133.8, 139.5, 169.0.

IR (KBr): 2207 (CN), 1698 (CO) cm^{-1}.

MS (EI): *m*/*z* = 146 [M]$^+$.

1,3-Dicyanobenzene[29]
IR (KBr): 2233 (CN) cm^{-1}.

^{1}H NMR (400 MHz): δ = 7.64 (t, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 7.94 (s, 1 H).

^{13}C NMR (100 MHz): δ = 114.2, 116.9, 130.5, 136.1, 136.8.

MS (EI): *m*/*z* = 128 [M]$^+$.

***m*-Cyanobenzamide**[30]
^{1}H NMR (400 MHz): δ = 7.63 (br, 1 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.99 (d, *J* = 7.6 Hz, 1 H), 8.15–8.17 (m, 2 H), 8.26 (s, 1 H).

^{13}C NMR (100 MHz): δ = 111.8, 128.1, 129.4, 131.0, 132.4, 134.5, 135.6, 166.5.

MS (EI): *m*/*z* = 146 [M]$^+$.

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