Metal-Free One-Pot Conversion of Electron-Rich Aromatics into Aromatic Nitriles

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Abstract: Various electron-rich aromatics could be smoothly converted into the corresponding aromatic nitriles in good to moderate yields by treatment of electron-rich aromatics with $POCl_3$ and DMF, followed by treatment with molecular iodine in aqueous ammonia. The present reaction is a novel metal-free one-pot method for the preparation of aromatic nitriles from electron-rich aromatics.

Key words: aromatics, aromatic *N*,*N*-dimethyliminium salt, aromatic nitrile, Vilsmeier–Haack reaction, molecular iodine, aqueous ammonia

Aromatic nitriles are one of the most important synthetic transformation precursors because they can be easily converted into esters, amides, carboxylic acids, amines, and nitrogen-containing heterocycles, and aromatic nitriles are also used as synthetic intermediates for agricultural chemicals, pharmaceuticals, and functional materials.[1] Moreover, Citalopram hydrobromide® (treatment of alcohol dependency), Periciazine® (antipsychotic drug), Fadrozole® (oncolytic drug), and Letrozole® (breast cancer therapy) are pharmaceutically important aromatic nitriles.[2] The most typical methods for the preparation of aromatic nitriles are the dehydration of aromatic amides with $SOCl_2$, TsCl–Py, P_2O_5, $POCl_3$, $COCl_2$, $(EtO)_3P$–I_2, or Ph_3P–CCl_4, the condensation of carboxylic acids with NH_3–silica gel or NH_3–ethyl polyphosphate, the reaction of esters with Me_2AlNH_2,[3] and the Sandmeyer reaction of aromatic diazonium ion with toxic CuCN.[3,4] On the other hand, the preparation of aromatic nitriles from aromatics generally requires many steps as follows. The first typical preparation method of aromatic nitriles from aromatics is the halogenation of aromatics to give the aromatic halides, the formation of the Grignard reagents with the aromatic halides, treatment of the Grignard reagents with CO_2, the formation of aroyl halides by reacting aromatic carboxylic acids with thionyl chloride, treatment of the aroyl halides with aqueous ammonia, and finally the dehydration of aromatic amides to provide aromatic nitriles. The second typical preparation method of aromatic nitriles from aromatics is the nitration of aromatics, the reduction of the nitro group to the amino group, treatment of aromatic amines with $NaNO_2$ and hydrochloric acid, and the reaction of aromatic diazonium chlorides with CuCN to give aromatic nitriles (the Sandmeyer reaction). Recently, the direct conversion of aromatic bromides into the corresponding aromatic nitriles, i.e., cyanodehalogenation, has been actively studied with CuCN at DMF refluxing temperature (the Rosenmund–von Braun reaction),[5a] $Pd(OAc)_2$·$K_4[Fe(CN)_6]$ at 120 °C,[5b] Pd·(binaphthyl)P(*t*-Bu)$_2$·$Zn(CN)_2$·Zn at 80–95 °C,[5c] $Pd_2(dba)_3$·$Zn(CN)_2$·DPPF at 80–120 °C,[5d] $Pd(tmhd)_2$·$K_4[Fe(CN)_6]$ at 80 °C,[5e] $Zn(CN)_2$·$Pd_2(dba)_3$ at 100 °C,[5f] Pd/C·CuI·$K_4[Fe(CN)_6]$·$3H_2O$ at 130–140 °C,[5g] CuI·alkylimidazole·Pd/C·CuI·$K_4[Fe(CN)_6]$ at 140–180 °C,[5h] $Zn(CN)_2$·$Pd_2(dba)_3$· dppf·Zn·$ZnBr_2$ at 95 °C,[5i] and CuO·Pd·$K_4[Fe(CN)_6]$ at 120 °C,[5j] all of which require toxic metal cyanides. More recently, the direct and catalytic cyanation of aromatics containing 2-pyridyl group via C–H bond cleavage with $Cu(OAc)_2$·TMSCN[6a] and $Pd(OAc)_2$·CuBr·CuCN[6b] at 130 °C, which requires toxic metal cyanides again, was reported. Thus, an environmentally benign and economical approach to convert aromatics into aromatic nitriles is in great demand. To the best of our knowledge, studies on the one-pot conversion of aromatics into the corresponding aromatic nitriles using less toxic reagents are extremely limited. One typical method is the reaction of aromatics with chlorosulfonyl isocyanate to form *N*-chlorosulfonyl amides and the subsequent treatment with DMF to provide aromatic nitriles, together with the evolution of SO_3 and HCl.[7] On the other hand, molecular iodine is one of the simplest oxidants currently available. It is highly affordable and has very low toxicity. Considered to be an environmentally benign oxidizing agent for organic synthesis, molecular iodine is used in various organic reactions, including the oxidation of alcohols or aldehydes to esters, the oxidation of sulfides to sulfoxides, the oxidation of cyclohexenones to benzene rings, the introduction of protecting groups, the deprotection of protecting groups, iodocyclization, carbon–carbon bond formation, and the formation of heterocycles.[8]

Here, as part of our ongoing studies on the use of molecular iodine for organic synthesis,[9] we would like to report the one-pot conversion of aromatics into the corresponding aromatic nitriles. Recently, we have reported the direct, efficient, practical, and less toxic oxidative conversion of benzylic halides into the corresponding nitriles using molecular iodine in aqueous ammonia.[9h,i] Moreover, aldehydes could be smoothly converted into the corresponding nitriles with molecular iodine in aqueous ammonia.[9b,g,10] Thus, we planned to perform the metal-free one-pot conversion of aromatics into aromatic nitriles using molecular iodine in aqueous ammonia. The

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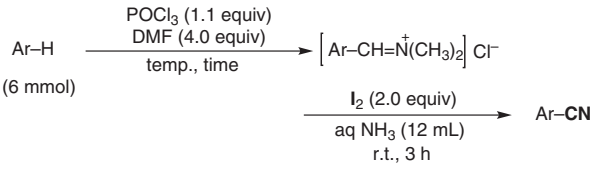
reaction was carried out as follows:[11] To a flask containing aromatics were added $POCl_3$ and DMF at 0 °C. Then, the mixture was warmed at room temperature, 40 °C, 80 °C, or 100 °C, depending on the substrate for a few hours. Then, molecular iodine and aqueous ammonia (28–30%) were added to the reaction mixture and the obtained mixture was stirred for three hours at room temperature to provide the corresponding aromatic nitrile. The results are shown in Table 1. 1,3-Dimethoxybenzene, 1,3,5-trimethoxybenzene, indole, *N*-methylindole, 1-methoxynaphthalene, 2-methoxynaphthalene, 1,5-dimethoxynaphthalene, and *N*,*N*-dimethylaniline gave the corresponding aromatic nitriles as a single isomer in good yields (entries 1, 2, 4–8, and 10).

Table 1 One-Pot Conversion of Aromatics into Aromatic Nitriles through Aromatic *N*,*N*-Dimethyliminium Chlorides



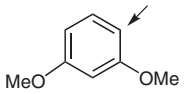
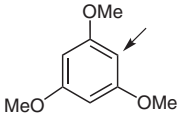
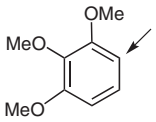
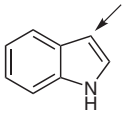
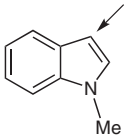
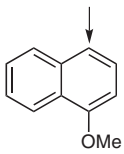
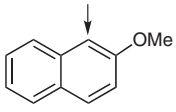
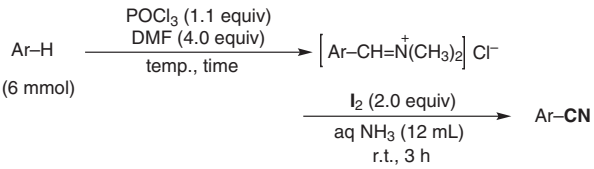
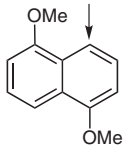
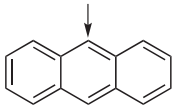
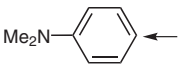
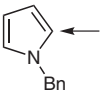
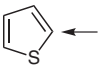
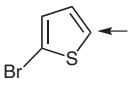
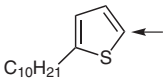
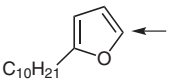
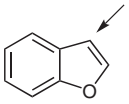
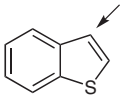
Entry	Ar–H	Temp	Time	Yield of nitrile (%)[a]
1		40 °C	3 h	74
2		40 °C	3 h	99
3		100 °C	4 h	59
4		r.t.	3 h	81
5		40 °C	3 h	99
6		100 °C	2 h	99
7		100 °C	6 h	90

Table 1 One-Pot Conversion of Aromatics into Aromatic Nitriles through Aromatic *N*,*N*-Dimethyliminium Chlorides (continued)



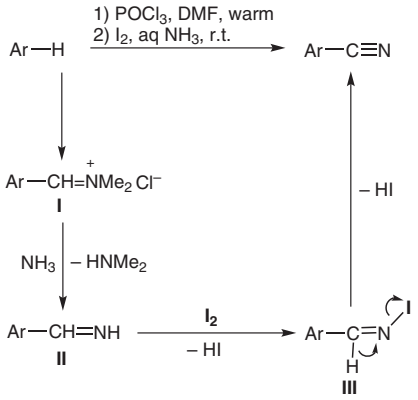
Entry	Ar–H	Temp	Time	Yield of nitrile (%)[a]
8		80 °C	4 h	91
9		100 °C	10 h	67
10		80 °C	2 h	86
11		40 °C	1 h	87 (α/β = 72:25)
12		80 °C	4 h	45
13		100 °C	3 h	13
14		80 °C	2 h	76
15		80 °C	2 h	91
16		100 °C	6 h	12
17		100 °C	6 h	0

[a] Isolated yield.

The same treatment of 1,2,3-trimethoxybenzene, anthracene, and thiophene provided the corresponding aromatic nitriles in moderate yields (entries 3, 9 and 12), although the treatment of 2-bromothiophene gave 5-cyano-2-bromothiophene in low yield (entry 13). *N*-Benzylpyrrole gave a 75:25 mixture of 2-cyano- and 3-cyano-*N*-benzylpyrroles in good yield (entry 11). On the other hand, the same treatment of 2-decylthiophene and 2-decylfuran gave the corresponding heteroaromatic nitriles as a single isomer in good yields (entries 14 and 15). Whereas, 3-cyanobenzofuran was obtained in low yield by the same treatment of benzofuran (entry 16), 3-cyanobenzothiophene was not obtained at all even at 100 °C in the

first step (entry 17). The reason is as follows: the initial formation of aromatic *N*,*N*-dimethyliminium chloride by the reaction of benzothiophene with $POCl_3$ and DMF did not occur at all, because the electron density on the aromatics was not sufficiently high. Moreover, 1-cyanonaphthalene, 4-cyanobiphenyl, and 2,5-dimethoxybenzonitrile were not formed at all by the present method with naphthalene, biphenyl, and 1,4-dimethoxybenzene, respectively, even at 100 °C in the first step. Practically, the Vilsmeier–Haack reaction of benzothiophene, naphthalene, biphenyl, and 1,4-dimethoxybenzene did not occur at all.

The plausible reaction mechanism is shown in Scheme 1. The initial step involves the Vilsmeier–Haack reaction to form aromatic *N*,*N*-dimethyliminium salt **I**. Once the aromatic *N*,*N*-dimethyliminium salt **I** is formed, it reacts smoothly with ammonia to form the corresponding aromatic imine **II**, which further reacts with molecular iodine to generate the corresponding aromatic *N*-iodoimine **III**. The elimination of HI from aromatic *N*-iodoimine **III** rapidly occurs in aqueous ammonia to provide the corresponding aromatic nitrile.[9]



Scheme 1 Possible reaction pathway for nitrile

In conclusion, various electron-rich aromatics, such as 1,3-dimethoxybenzene, 1,3,5-trimethoxybenzene, 1-methoxynaphthalene, 2-methoxynaphthalene, 1,5-dimethoxynaphthalene, aniline, indole, thiophene, furan, and pyrrole, could be smoothly converted into the corresponding aromatic nitriles in good yields, by treatment with $POCl_3$ and DMF, followed by the reaction with molecular iodine in aqueous ammonia. The present reaction is a novel metal-free one-pot conversion of aromatics into the corresponding aromatic nitriles, although the reaction is limited to electron-rich aromatics. The advantages of the present reaction are operational simplicity, low cost, low toxicity, and easy availability of reaction materials. Therefore, we believe that the present reactions are a useful and environmentally benign method for the preparation of aromatic nitriles from aromatics directly. Further synthetic study of the present method is underway in this laboratory.

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(11) **Typical Experimental Procedure**: To a flask containing 1,3,5-trimethoxybenzene (1009.1 mg, 6 mmol) were added $POCl_3$ (1011.9 mg, 6.6 mmol) and DMF (1754.1 mg, 24 mmol) at 0 °C. After being stirred for 3 h at 40 °C, I_2 (3045.7 mg, 12 mmol) and aq ammonia (12 mL, 28–30%) were added to the reaction mixture. The obtained mixture was

stirred for 3 h at r.t. After the reaction, the mixture was poured into aq sat. Na_2SO_3 solution and extracted with $CHCl_3$ (3 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated to provide almost pure 2,4,5-trimethoxybenzonitrile (1156.1 mg) in 99% yield. If it was necessary, it was recrystallized from a mixture of hexane and EtOAc (1:1).

Most aromatic nitriles mentioned in this work are commercially available and were identified by comparison with the authentic samples.

2,4-Dimethoxybenzonitrile: mp 93–94 °C (commercial, mp 93–94 °C). IR: 2219 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.90 (s, 3 H), 6.46 (s, 1 H), 6.51 (d, *J* = 8.5 Hz, 1 H), 7.48 (d, *J* = 8.5 Hz, 1 H).

2,4,6-Trimethoxybenzonitrile: mp 139–140 °C (commercial, mp 143–145 °C). IR: 2212 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 3.89 (s, 6 H), 6.07 (s, 2 H).

2,3,4-Trimethoxybenzonitrile: mp 55–56 °C (commercial, mp 56–57 °C). IR: 2226 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 3.92 (s, 3 H), 4.06 (s, 3 H), 6.70 (d, *J* = 8.7 Hz, 1 H), 7.29 (d, *J* = 8.7 Hz, 1 H).

3-Cyanoindole: mp 177–179 °C (commercial, mp 179–182 °C). IR: 2227 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.28–7.36 (m, 2 H), 7.48 (d, *J* = 7.6 Hz, 1 H), 7.73 (s, 1 H), 7.78 (d, *J* = 7.3 Hz, 1 H), 8.91 (s, 1 H).

***N*-Methyl-3-cyanolindole**: mp 60–61 °C (lit. [12] mp 60.5–61.5 °C). IR: 2219 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.75 (s, 3 H), 7.25 (t, *J* = 6.4 Hz, 1 H), 7.28–7.35 (m, 2 H), 7.44 (s, 1 H), 7.68 (d, *J* = 7.9 Hz, 1 H).

4-Methoxy-1-cyanonaphthalene: mp 100–102 °C (commercial, mp 100–102 °C). IR: 2213 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.07 (s, 3 H), 6.84 (d, *J* = 8.2 Hz, 1 H), 7.59 (t, *J* = 8.2 Hz, 1 H), 7.69 (t, *J* = 8.2 Hz, 1 H), 7.86 (d, *J* = 8.2 Hz, 1 H), 8.17 (d, *J* = 8.2 Hz, 1 H), 8.32 (d, *J* = 8.2 Hz, 1 H).

2-Methoxy-1-cyanonaphthalene: mp 96–97 °C (lit.[13] mp 95–96 °C). IR: 2211 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.08 (s, 3 H), 7.28 (d, *J* = 8.7 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 7.64 (t, *J* = 8.0 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 8.04 (d, *J* = 8.7 Hz, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H).

4,8-Dimethoxy-1-cyanonaphthalene: mp 126–129 °C. IR: 2211 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.05 (s, 6 H), 6.85 (d, *J* = 8.2 Hz, 1 H), 6.99 (d, *J* = 7.7 Hz, 1 H), 7.47 (t, *J* = 7.7 Hz, 1 H), 7.86 (d, *J* = 8.2 Hz, 1 H), 7.89 (d, *J* = 7.7 Hz, 1 H). HRMS (ESI): *m/z* calcd for $C_{13}H_{11}O_2N$: 213.0784; found: 21.0780.

4-Cyano-*N*,*N*-dimethylaniline: mp 74–75 °C (commercial, mp 75 °C). IR: 2210 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.04 (s, 6 H), 6.64 (d, *J* = 9.1 Hz, 2 H), 7.47 (d, *J* = 9.1 Hz, 2 H).

9-Cyanoanthracene: mp 173–175 °C (commercial, mp 173–177 °C). IR: 2212 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.59 (t, *J* = 8.5 Hz, 2 H), 7.73 (t, *J* = 8.5 Hz, 2 H), 8.09 (d, *J* = 8.5 Hz, 2 H), 8.43 (d, *J* = 8.5 Hz, 2 H), 8.69 (s, 1 H).

2-Cyano-*N*-benzylpyrrole: oil. IR: 2215 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.19 (s, 2 H), 6.19 (dd, *J* = 2.9, 2.7 Hz, 1 H), 6.80–6.86 (m, 2 H), 7.18 (d, *J* = 7.4 Hz, 2 H), 7.31–7.38 (m, 3 H). HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{12}H_{11}N_2$: 183.0922; found: 183.0927.

3-Cyano-*N*-benzylpyrrole: oil. IR: 2224 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.06 (s, 2 H), 6.44 (d, *J* = 1.7 Hz, 1 H), 6.65 (s, 1 H), 7.11–7.17 (m, 3 H), 7.33–7.41 (m, 3 H). HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{12}H_{11}N_2$: 183.0922; found: 183.0927.

2-Cyanothiophene: oil. IR: 2222 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.14 (dd, *J* = 5.2, 3.7 Hz, 1 H), 7.62 (d, *J* = 5.2 Hz, 1 H), 7.64 (d, *J* = 3.7 Hz, 1 H).

5-Decyl-2-cyanothiophene: oil. IR: 2218 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 3 H), 1.23–1.38 (m, 14 H), 1.67 (quint, *J* = 7.5 Hz, 2 H), 2.83 (t, *J* = 7.5 Hz, 2 H), 6.78 (d, *J* = 3.6 Hz, 1 H), 7.43 (d, *J* = 3.6 Hz, 1 H). HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{15}H_{24}NS$: 250.1629; found: 250.1636.

5-Decyl-2-cyanofuran: oil. IR: 2229 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3 H), 1.21–1.38 (m, 14 H), 1.65 (quint, *J* = 7.1 Hz, 2 H), 2.66 (t, *J* = 7.1 Hz, 2 H), 6.11 (d, *J* = 3.4 Hz, 1 H), 6.99 (d, *J* = 3.4 Hz, 1 H). HRMS (FAB): *m/z* $[M + H]^+$ calcd for $C_{15}H_{24}NO$: 234.1858; found: 234.1861.

3-Cyanobenzofuran: mp 90–91 °C (commercial, mp 93 °C). IR: 2211 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.35 (t, *J* = 7.5 Hz, 1 H), 7.44 (s, 1 H), 7.48–7.56 (m, 2 H), 7.67 (d, *J* = 9.1 Hz, 1 H).

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