Direct Oxidative Conversion of Alcohols, Aldehydes and Amines into Nitriles Using Hypervalent Iodine(III) Reagent

Chenjie Zhu, Chengguo Sun, Yunyang Wei*

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. of China Fax +86(25)84317078; E-mail: ywei@mail.njust.edu.cn

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Abstract: An efficient, facile, and high-yielding procedure for the direct oxidative conversion of alcohols, aldehydes, and primary, secondary, and tertiary amines into the corresponding nitriles using the hypervalent iodine(III) reagent hydroxy(tosyloxy)iodobenzene in combination with ammonium acetate as a nitrogen source is reported. The oxidation proceeded in mixed solvent to afford nitriles in excellent yields and high selectivity even at room temperature. Selective oxidation of primary amines in the presence of secondary amines and tertiary amines was also achieved. A possible mechanism for the oxidation is proposed.

Key words: alcohols, aldehydes, amines, hypervalent iodine, oxidations

Nitriles are of considerable interest as an integral part of dyes, herbicides, natural products, and pharmaceuticals.¹ Moreover, the cyanide group plays a crucial role in organic synthesis as it can be easily converted into a variety of functional groups, such as acids, amides, ketones, oximes, and amines.² The most typical synthetic procedure for the preparation of nitriles is by nucleophilic displacement from substrates containing suitable leaving groups, such as alkyl halides.³ Other methods, such as by dehydration of amides⁴ and aldoximes,⁵ have been traditionally employed to accomplish this transformation. The direct conversion of alcohols,⁶ aldehydes,⁷ carboxylic acids,⁸ amines,⁹ azides,¹⁰ pyridine N-oxides,¹¹ and boronic acids,¹² into nitriles has also been explored. Of the one-pot preparative methods developed in recent years, the use of ammonia combined with an appropriate oxidant, such as in the following systems NH₃/O₂/CuCl₂·H₂O/MeONa,¹³ NH₃/Pb(OAc)₄,¹⁴ NH₃/I₂/MeONa,¹⁵ NH₃/S₈/NaNO₂,¹⁶ NH₃/H₂O₂/CuCl,¹⁷ NH₃/I₂,¹⁸ NH₃/CAN,¹⁹ NH₃/NBS,²⁰ NH₃/TBHP/KI(I₂),^{6g} or NH₃/IBX,²¹ is considered to be an expedient method for this transformation. However, ammonia used as the nitrogen source in these procedures may cause environmental problems because ammonia has an undesirable smell and is a common and undesirable contaminant in waste water and biomass cultivation media. The adverse effects of ammonia have promoted the development of various techniques for its removal.²² Previously, ammonium acetate has also been developed, as a good cyanide source in the system ammonium acetate/ iodine.²³ One of the limitations of this procedure is the use

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of more than a stoichiometric amount of iodine, which could lead to the generation of excess amounts of salts as byproducts during workup and the transformation of aliphatic compounds often gave unsatisfactory yields.

On the other hand, hypervalent iodine(III) reagents have drawn considerable attention as mild and highly chemoselective oxidizing reagents for various organic transformations.²⁴ As a result of their nontoxic nature, affordability, and safety profile, hypervalent iodine(III) reagents are nowadays popular reagents for the formation of carbon– carbon bonds, carbon–heteroatom bonds, and heteroatom–heteroatom bonds. Activation of carbon–hydrogen bonds, rearrangements, and fragmentations can be also induced by these reagents. Therefore, hypervalent iodine compounds offer high potential for the improvement of known reactions, not only from an environmental point of view, they are also potentially interesting reagents for the development of completely new synthetic transformations.

In continuation of our efforts to develop new applications of hypervalent iodine compounds,²⁵ herein, we would like to report a facile procedure for the direct oxidation of alcohols, aldehydes, and amines to the corresponding nitriles with [hydroxy(tosyloxy)iodo]benzene [HTIB, PhI(OH)OTs, Koser's reagent] using ammonium acetate as the nitrogen source.

To the best of our knowledge, direct oxidative conversion of an alcohol into the corresponding nitrile in one-pot manner is extremely limited,⁶ and there is no report on the use of hypervalent iodine(III) reagents as an oxidant for the preparation of nitriles. The initial experiments were carried out using 4-nitrobenzyl alcohol as the model substrate (Table 1). Initially, a range of hypervalent iodine reagents such as PhIO, PhICl₂, PhIO₂, PhI(OAc)₂, and HTIB were used as the oxidant in the reaction, it was found that using PhI(OAc)₂ and HTIB as the oxidant gave 4-nitrobenzonitrile in 17% and 36% yields, respectively (entries 1–5). Encouraged by these results, we examined the effects of nitroxyl radicals, 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) and N-hydroxyphthalimide (NHPI), on the reaction, with the aim of promoting the initial oxidation of the alcohol to an intermediate aldehyde and thus facilitating the formation of the final product. Fortunately, TEMPO serves as a good catalyst and enhances the reaction remarkably (entry 6); the catalytic activity of NHPI was much lower (entry 8). Ammonium salts other than ammonium acetate were also used as a nitrogen source,

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but lower yields were obtained (entries 9-11). Next, an investigation of the effects of the solvent on the reaction showed that dichloromethane, chloroform, and ethyl acetate were equally efficient for the reaction, whereas the reaction did not proceed well using methanol or ethanol as the solvent (entries 12-16). These results demonstrated that protic solvents cannot be used as a solvent for this reaction, regardless of the polarity of the solvent. However, the use of water as a co-solvent is beneficial to the reaction, which may be explained by the improvement of the dissolution of ammonium acetate (entry 17). Addition of zinc oxide or 3Å molecular sieves to accelerate the dehydration of in situ formed aldimines to nitriles in the reaction medium did not improve the reaction (entries 18 and 19). It is noteworthy that the reaction can also proceed smoothly even at room temperature, albeit a longer reaction time was required (entry 20).

In order to evaluate the versatility of this novel catalytic system, we applied the procedure to the oxidation of a wide range of alcohols (Table 2). Excellent chemoselectivity was observed with the optimized oxidation conditions. We detected no phenol oxidation products, which are known to form in reactions with aryl- λ^3 -iodanes (entry 5).²⁶ Allylic alcohols such as cinnamyl alcohol (entry 6) were also oxidized efficiently without any observable reaction at the double bond functionality. The electronic properties of the substituents in the aromatic ring had a remarkable influence on the rate of the oxidation of benzyl alcohols. Strong electron-withdrawing groups, such as the nitro group, improve the rate of the oxidation of the alcohol (entry 2). Strong electron-donating groups, such as methoxy, lowered the reaction rate (entry 3). This differs from previously reported procedures, where the methoxy group favors the oxidation of the alcohol.^{6g} It is worth

Table 1	Optimization	Studies for	the Conversion	of 4-Nitrobenzyl Alcohola
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O ₂ N	A OH oxida additi	nt, catalyst, NH ₄ X ive, solvent, temp	→ _{O2N}	O ₂ N			
Entry	Oxidant	NH_4X	Solvent	Catalyst	Additive	Temp (°C)	Yield (%)
1	PhIO	NH ₄ OAc	MeCN	_	_	80	_
2	PhCl ₂	NH ₄ OAc	MeCN	_	_	80	-
3	PhIO ₂	NH ₄ OAc	MeCN	-	_	80	-
4	PhI(OAc) ₂	NH ₄ OAc	MeCN	_	_	80	17
5	HTIB	NH ₄ OAc	MeCN	-	-	80	36
6	HTIB	NH ₄ OAc	MeCN	TEMPO	_	80	91
7	HTIB	-	MeCN	TEMPO	_	80	82 ^b
8	HTIB	NH ₄ OAc	MeCN	NHPI	_	80	46
9	HTIB	NH ₄ Cl	MeCN	TEMPO	-	80	27
10	HTIB	NH ₄ HCO ₃	MeCN	TEMPO	-	80	-
11	HTIB	HCO_2NH_4	MeCN	TEMPO	_	80	58
12	HTIB	NH ₄ OAc	EtOH	TEMPO	_	80	<10
13	HTIB	NH ₄ OAc	MeOH	TEMPO	_	80	<10
14	HTIB	NH ₄ OAc	CH_2Cl_2	TEMPO	_	80	81
15	HTIB	NH ₄ OAc	CHCl ₃	TEMPO	_	80	78
16	HTIB	NH ₄ OAc	EtOAc	TEMPO	_	80	85
17	HTIB	NH ₄ OAc	MeCN	TEMPO	H2O	80	96°
18	HTIB	NH ₄ OAc	MeCN	TEMPO	ZnO	80	87
19	HTIB	NH ₄ OAc	MeCN	TEMPO	3 Å MS	80	90
20	HTIB	NH ₄ OAc	MeCN	TEMPO	H2O	r.t.	92 ^d

CN

^a Reactions conditions: 4-nitrobenzyl alcohol (1 mmol), oxidant (2.5 mmol), NH_4X (10 mmol), catalyst (0.2 mmol), solvent (4 mL), 80 °C, 3 h, unless otherwise noted.

^b Yield of 4-nitrobenzaldehyde.

^cH₂O (1 mL) was added.

^d Reaction was carried out at r.t. for 24 h.

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mentioning that, together with the good results with benzylic alcohols, the yields obtained from the oxidation of aliphatic alcohols under the same conditions are also quite high (entries 8–10). In view of the fact that the oxidation of aliphatic alcohols is much more difficult than the oxidation of benzylic alcohols, results obtained with this procedure were very satisfactory.

Table 2 Oxidation Conversion of Alcohols into Nitriles with HTIB/
TEMPO/NH $_4$ OAc a



^a Reaction conditions: alcohol (1 mmol), HTIB (2.5 mmol), TEMPO (0.2 mmol), NH₄OAc (10 mmol), MeCN-H₂O (4:1, 5 mL), 80 °C.
 ^b Yields of isolated products unless otherwise noted.

^c Yields were determined by GC.

The oxidation of alcohols to nitriles using HTIB/TEMPO/ NH₄OAc is believed to proceed via the intermediate formation of aldehydes (Table 1, entry 7). Further studies show that structurally diverse aldehydes, including benzylic, allylic, heterocyclic, and aliphatic aldehydes, can also be smoothly oxidized to the corresponding nitriles in excellent yield with the HTIB/NH₄OAc system in the absence of TEMPO (Table 3). 2-Ethylhexanal, an α branched aliphatic aldehyde, was also oxidized to 2-ethylhexanenitrile efficiently (entry 13). The effect of the electronic nature of the aldehyde was similar to that found in the oxidation of alcohols. Additionally, steric hindrance had a relatively minor influence on the oxidation of aldehydes (entries 2 and 3). As expected, the conversion of aldehydes into nitriles did not need the presence of TEMPO, and proceeded faster than the oxidation of alcohols under similar conditions.

Table 3 Oxidation Conversion of Aldehydes into Nitriles with $HTIB/NH_4OAc^a$

Entry	Substrate	Product	Time (h)	Yield ^b (%)
1	СНО	CN	2	98
2	O ₂ N CHO	O ₂ N CN	2	97
3	CHO	NO ₂ CN	2	93
4	МеО СНО	MeO	4	90
5	CHO	Br	2	96
6	СІСНО	CI	2	95
7	сно	HO	4	86
8	СНО	CN	3	92
9	СНО	CN CN	2	90
10	СНО	CN	3	91
11	Me(CH ₂) ₆ CHO	Me(CH ₂) ₆ CN	4	90°
12	Me(CH ₂) ₁₀ CHO	Me(CH ₂) ₁₀ CN	4	88°
13	СНО	CN	4	86°

^a Reaction conditions: aldehyde (1 mmol), HTIB (1.5 mmol),

NH₄OAc (10 mmol), MeCN–H₂O (4:1, 5 mL), 80 °C.

^b Yields of isolated products unless otherwise noted.

^c Yields were determined by GC.

To demonstrate the scope and efficiency of this method, the HTIB/NH₄OAc system was extended to the direct conversion of primary, secondary, and tertiary amines into the corresponding nitriles. As shown in Table 4, most amines underwent oxidation to afford the corresponding nitriles in excellent yields. This transformation can also proceed without ammonium acetate (entry 1). Diamines were also converted into the corresponding dinitriles in good yields (entries 8 and 9). When *N*-methyl secondary amines and *N*,*N*-dimethyl tertiary amines were treated with HTIB under the same conditions, the corresponding nitriles could be again obtained in good yields (entries 10–12).

 Table 4
 Oxidation Conversion of Amines into Nitriles with HTIB/ NH₄OAc^a

Entry	Substrate	Product	Time (h)	Yield ^b (%)
1	NH ₂	CN	3	84 (73°)
2	NH ₂	O ₂ N CN	3	94
3	MeO NH2	MeO	5	83
4	CI NH2	CI	3	92
5	NH ₂		3	82
6	NH ₂	CN	4	75
7	Me(CH ₂) ₁₀ CH ₂ NH ₂	Me(CH ₂) ₁₀ CN	5	72 ^d
8	H ₂ N NH ₂	CN CN	3	90 ^e
9	NH ₂ NH ₂	CN CN	5	67 ^e
10	N Me H	CN	3	82 (39°)
11		CN	3	80
12	N Me Me	CN	3	78 (22°)

^a Reaction conditions: amine (1 mmol), HTIB (2.5 mmol), NH₄OAc (10 mmol), MeCN-H₂O (4:1, 5 mL), 80 $^{\circ}$ C.

^b Yields of isolated products unless otherwise noted.

^c NH₄OAc was not used.

^d Yields were determined by GC.

^e Double amount of HTIB was used.

Table 5 shows the results of the competitive oxidation of primary, secondary, and tertiary amines. The competing oxidation of an equimolar mixture of benzylamine and *N*-methylbenzylamine into benzonitrile resulted in 76% conversion of benzylamine and less than 10% conversion of *N*-methylbenzylamine (entry 1). Oxidation of an equimolar mixture of benzylamine and *N*,*N*-dimethylbenzyl-

amine gave 81% conversion of benzylamine and less than 10% conversion of N,N-dimethylbenzylamine, respectively (entry 2). These results suggest that chemoselective oxidation of primary amine in the presence of secondary and tertiary amine is possible with the present system.

 Table 5
 Competitive Oxidation of Primary, Secondary, and Tertiary Amines^a

Entry	Substrate	Time (h)	Conversion ^b (%)
1	+ + Me	2	76 <10
2	+ NKMe	2	81 <10
3	+ N <me Me Me</me 	2	57 36
^a The rea ary, and	ctions were carried out of tertiary amines.	n a 1:1 mixture	of primary, second-

^b Conversion was based on the yield of product by column chromatography isolation.

Based on these results, a plausible reaction pathway for the conversion of alcohols, aldehydes and amines into the corresponding nitriles is depicted in Scheme 1. For the conversion of a primary alcohol into the corresponding nitrile, TEMPO served as the actual oxidant to oxidize the alcohol to the corresponding aldehyde, the role of HTIB is to regenerate TEMPO from TEMPOH. Then, the aldehyde reacts with ammonium acetate to form an aldimine, which undergoes oxidation by HTIB to afford the *N*-I(OTs)Ph aldimine. Elimination of HOTs from the *N*-I(OTs)Ph aldimine gives the final nitrile product. Iodobenzene was detected at the end of the reaction. The oxidation of an amine with HTIB produces the imine initially,²⁷ which is subsequently hydrolyzed to give an aldehyde, further oxidation of the aldehyde will yield a nitrile; aldehyde was detected in the reaction. Another route B not via an aldehyde is also possible, since nitriles were also obtained from the reaction of an amine and HTIB without the presence of ammonium acetate (Table 4, entry 1, 10, and 12).

In conclusion, a simple and efficient method for the conversion of alcohols, aldehydes, primary, secondary, and



Scheme 1 Plausible reaction pathway for the formation of nitriles

tertiary amines into the corresponding nitriles with HTIB using ammonium acetate as the nitrogen source has been developed. A key feature of the oxidation protocol is its inherent simplicity. There is no need for rigorous exclusion of air or moisture in order to effect a clean oxidation, the reaction conditions and reagents are easy to handle and the reaction is applicable to various kinds of alcohols, aldehydes, and amines.

All chemicals (AR grade) were obtained from commercial sources and used without further purification. ¹H NMR spectra were obtained with TMS as internal standard in CDCl₃ using a Bruker DRX 300 (300MHz) spectrometer. Gas chromatography (GC) analysis was performed on an Agilent GC-6820 chromatograph equipped with a 30 m × 0.32 mm × 0.5 µm HP-Innowax capillary column and a flame ionization detector. GC-MS spectra were recorded on Thermo Trace DSQ GC-MS spectrometer using a TRB-5MS (30 m × 0.25 mm × 0.25 µm) column. IR spectra were recorded on a Shimadzu spectrophotometer using KBr discs. Melting points were determined on a Yamato melting point apparatus Model MP-21. Progress of the reactions was followed by TLC (silica gel polygrams SIL G/UV 254 plates). Column chromatography was performed using Silicycle (40–60 mm) silica gel.

Oxidation of Alcohols with HTIB/TEMPO/NH₄OAc; General Procedure

To a soln of alcohol (1 mmol), NH₄OAc (0.77 g, 10 mmol), and TEMPO (0.03 g, 0.2 mmol) in MeCN–H₂O (4:1, 5 mL) was added HTIB (0.95 g, 2.5 mmol). The mixture was stirred at 80 °C for several hours (GLC or TLC monitoring). After completion, aq NaHCO₃ and EtOAc were sequentially added to the residue and then the mixture was stirred vigorously for 10 min. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined EtOAc phases were concentrated under vacuum. The crude product was purified by column chromatography (petroleum ether–EtOAc, 10:1) to provide analytically pure product (¹H NMR and GC/MS).

Oxidation of Aldehydes with HTIB/NH₄OAc; General Procedure

To a soln of aldehyde (1 mmol) and NH₄OAc (0.77 g, 10 mmol) in MeCN–H₂O (4:1, 5 mL) was added HTIB (0.57 g, 1.5 mmol). The mixture was stirred at 80 °C for several hours (GLC or TLC monitoring). After completion, the mixture obtained was treated as above to afford the corresponding pure product.

Oxidation of Amines with HTIB/NH₄OAc; General Procedure To a soln of amine (1 mmol) and NH₄OAc (0.77 g, 10 mmol) in MeCN-H₂O (4:1, 5 mL) was added HTIB (0.95 g, 2.5 mmol). The mixture was stirred at 80 C for several hours (GLC or TLC monitoring). After completion, the mixture obtained was treated as above to afford the corresponding pure product.

Benzonitrile

IR (KBr): 2218 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.45–7.65 (m, 5 H, Ar).

4-Chlorobenzonitrile

IR (KBr): 2237 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.67 (d, *J* = 8.1 Hz, 2 H, Ar), 7.52 (d, *J* = 8.1 Hz, 2 H, Ar).

4-Nitrobenzonitrile

IR (KBr): 2230 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.42 (d, *J* = 8.4 Hz, 2 H, Ar), 7.95 (d, *J* = 8.4 Hz, 2 H, Ar).

4-Methoxybenzonitrile

IR (KBr): 2218 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.57 (d, *J* = 8.7 Hz, 2 H, Ar), 6.94 (d, *J* = 8.7 Hz, 2 H, Ar), 3.85 (s, 3 H, OCH₃).

Cinnamonitrile

IR (KBr): 2223 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.38–7.43 (br s, 6 H, Ar, PhCH), 5.87 (d, *J* = 16.5 Hz, 1 H, CHCN).

Benzyl Cyanide

IR (KBr): 2250 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.27–7.34 (m, 5 H, Ar), 3.67 (s, 2 H, CH₂).

Supporting Information for this article is available online at http://www.thieme-connect.com/ ejournals/toc/synthesis.

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