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Catalytic oxidative conversion of alcohols, aldehydes and amines into nitriles using KI/I_2–TBHP system

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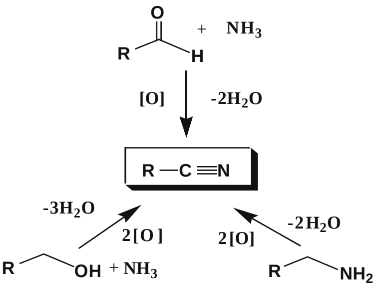
ABSTRACT

The oxidative conversion of alcohols, aldehydes and amines to give corresponding nitriles in excellent yields was easily achieved by the catalytic amount of KI or I_2 in combination with TBHP as an external oxidant. This non-transition metal catalyst is cost effective and provides easy work-up and separation of the product.

Nitriles are useful functional groups in synthetic organic chemistry. The most common and well-known procedure for the preparation of nitriles is the nucleophilic displacement of substrates with suitable leaving groups such as halogen compounds, aryl sulfonates, alcohols, esters, ethers, nitro or amino compounds and diazonium salts with inorganic cyanide ions.[1] The other alternative procedures are dehydration of amides[2] and aldoximes,[3] conversion of alcohols,[4] aldehydes[5] and carboxylic acids[6] to nitriles using various reagents and direct conversion of amines.[7] The conventional methods and several of these reported procedures often require hazardous reagents, severe reaction conditions, expensive catalysts and substrates. To overcome some of these economical and environmental related problems, catalytic methods involving the direct conversion of aldehydes and alcohols to nitriles using commercially available aqueous ammonia or direct conversion primary amines to nitriles via dehydrogenation could be a viable alternative and clean route (Scheme 1). Moreover, this route will eliminate the additional step involved in the preparation of imines, amides and aldoximes. Although several oxidative procedures using stoichiometric reagents are known for the synthesis of nitriles, only a few catalytic methods involving dehydrogenation protocols have been reported.[8]



Scheme 1.

In case of oxidative transformation of primary amines to nitriles, a number of procedures are reported mostly using stoichiometric metal oxidants such as nickel peroxide,[9] copper reagents in combination with oxygen,[10] silver reagents,[11] cobalt peroxide[12] and lead tetraacetates.[13] The catalytic oxidations using $NiSO_4/K_2S_2O_8$,[14] $RuCl_3/O_2$,[15] $RuCl_3/K_2S_2O_8$,[16] and ruthenium complex/O_2,[17] Ru supported on Alumina/O_2[18] have been reported. Nitriles are also obtained by direct electrochemical oxidation[19] or indirect electrochemical oxidations with mediators.[20] Recently, molecular iodine in stoichiometric amount, in combination with aq NH_3 is used for the above transformation.[21]

Molecular halogens and related reagents are well known for oxidations due to their simple operation and low cost. Among them, molecular iodine is an attractive candidate as it is cheap, readily available and less toxic than its counterparts. Several reports appeared recently on the use of iodine for various organic transformations.[21] Moreover, molecular iodine is efficiently utilized for oxidation of aldehydes and alcohols into their correspond-

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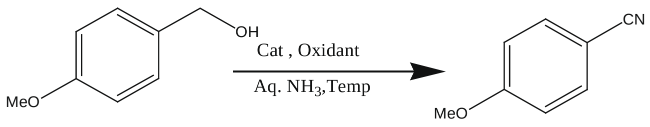
ing nitriles in the presence of aqueous ammonia.[7c,d,8d] One of the limitations of these procedures is the use of more than stoichiometric amount of iodine, which could lead to generation of excess amount of salt as a by-product during work-up. We have recently shown the use of catalytic amount of KI and molecular iodine for the facile oxidative amidation of aldehydes and alcohols to form amides using TBHP as an external oxidant (Eq. 1).[22] Here, as part of our ongoing study on the application of iodine reagents in catalytic oxidative functionalization of alcohols and aldehydes, we would like to present direct oxidative conversion of alcohols, aldehydes and primary amines to the corresponding nitriles (Scheme 1) using potassium iodide or molecular iodine as catalyst and TBHP as the external oxidant.

$$RCHO + R'NH_2 \xrightarrow[\text{Catalyst}]{\text{Oxidant}} RCONHR' + H_2O \qquad (1)$$

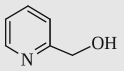
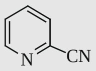
Table 1
Optimization studies for the conversion of alcohol to nitrile[a]



S. No.	Catalyst (mmol)	Oxidant (mmol)	Temp (°C)	Conversion[b] (%)
1	—	TBHP (3.8)	rt	NR
2	KI (0.2)	—	rt	–
3	KI (0.05)	TBHP (2.2)	rt	10
4	KI (0.1)	TBHP (2.2)	rt	17
5	KI (0.2)	TBHP (2.2)	rt	29
6	I_2 (0.1)	TBHP (2.2)	rt	29
7	KI (0.05)	TBHP (2.2)	60	99
8	I_2 (0.025)	TBHP (2.2)	60	99
9	KI (0.05)	H_2O_2 (2.2)	60	–
10	KI (0.05)	NaOCl (2.2)	60	–

[a] Reaction conditions: alcohol (1 mmol), aqueous NH_3 (3 mL), 15 h.
[b] Conversion based on ^1H NMR.

Table 2
KI/I_2–TBHP catalyzed oxidative conversion of alcohols to nitriles[a]

Entry	Substrate	Product	Yield[b] (%)	
			KI (5 mol %)	I_2 (2.5 mol %)
1	*p*-MeO–Ph–CH_2–OH	*p*-MeO–Ph–CN	98	98
2	*o*-MeO–Ph–CH_2–OH	*o*-MeO–Ph–CN	85	78
3	2,6-MeO–Ph–CH_2–OH	2,6-MeO–Ph–CN	98	95
4	*p*-MeS–Ph–CH_2–OH	*p*-MeS–Ph–CN	75	79
5	*o*-Me–Ph–CH_2–OH	*o*-Me–Ph–CN	92	90
6	*p*-Me–Ph–CH_2–OH	*p*-Me–Ph–CN	90	86
7	Ph–CH_2–OH	Ph–CN	75	80
8	*p*-Cl–Ph–CH_2–OH	*p*-Cl–Ph–CN	77	69
9	*o*-Cl–Ph–CH_2–OH	*o*-Cl–Ph–CN	79	75
10	*p*-Br–Ph–CH_2–OH	*p*-Br–Ph–CN	81	78
11	*p*-F–Ph–CH_2–OH	*p*-F–Ph–CN	72	67
12	*p*-NO_2–PH–CH_2–OH	*p*-NO_2–Ph–CN	5 (70)[c]	12
13	1-Octanol	1-Octanonitrile	41[d]	37[d]
14	1-Decanol	1-Decanonitrile	29[d]	30[d]
15	Cinnamyl alcohol	Cinnamonitrile	30	32
16	 N OH	 N CN	36[d]	40[d]

[a] Reaction conditions: alcohol (1 mmol), aqueous NH_3 (3 mL), TBHP (2.2 mmol), 60 °C, 15 h.
[b] Isolated yield.
[c] Reaction at RT with 20 mol % of KI.
[d] Conversion based on ^1H NMR, with 20 mol % of KI or 10 mol % of I_2.

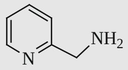
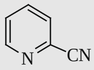
Table 3
KI/I_2–TBHP catalyzed oxidative conversion of aldehydes to nitriles[a]

Entry	Substrate	Product	Conversion[b] (%)	
			KI (5 mol %)	I_2 (2.5 mol %)
1	*p*-MeO–Ph–CHO	*p*-MeO–Ph–CN	92	85
2	*o*-MeO–Ph–CHO	*o*-MeO–Ph–CN	90	73
3	*p*-*i*Pr–Ph–CHO	*p*-*i*Pr–Ph–CN	88	84
4	*p*-Me–Ph–CHO	*p*-Me–Ph–CN	85	87
5	Ph–CHO	Ph–CN	75	70
6	1-Napthaldehyde	1-Napthalenecarbonitrile	65	63
7	*p*-Cl–Ph–CHO	*p*-Cl–Ph–CN	83	72
8	*p*-Br–Ph–CHO	*p*-Br–Ph–CN	85	66
9	*p*-F–Ph–CHO	*p*-F–Ph–CN	73	67
10	*o*-F–Ph–CHO	*o*-F–Ph–CN	68	67
11	*p*-NO_2–Ph–CHO	*p*-NO_2–Ph–CN	Amide	12
12	1-Octanal	1-Octanonitrile	40	42

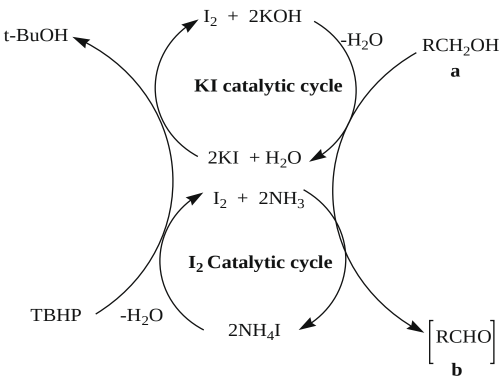
[a] Reaction conditions: aldehyde (1 mmol), aqueous NH_3 (3 mL), TBHP(1.2 mmol), 60 °C, 8 h.
[b] Conversion based on ^1H NMR.

For our initial optimization studies, 4-methoxy benzyl alcohol was chosen as the model substrate. A mixture of 4-methoxy benzyl alcohol and aqueous ammonia solution was stirred under different conditions, and the results are summarized in Table 1. Reactions at room temperature provided lower product formation, but by increasing the catalyst from 5 mol % to 20 mol %, the conversion improved moderately. Under similar reaction conditions, both KI and I_2 have shown same activities. There was no product formation

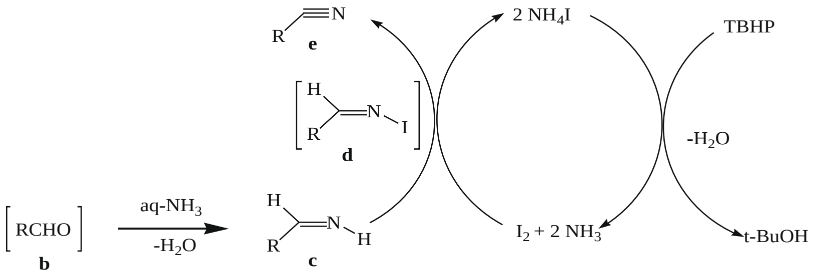
Table 4
KI–TBHP catalyzed oxidative conversion of amines to nitriles[a]

S. No.	Substrate	Product	Conversion[b] (%)
1	Ph–CH_2–NH_2	Ph–CN	73
2	*p*-OMe–Ph–CH_2–NH_2	*p*-OMe–Ph–CN	60
3	*p*-Me–Ph–CH_2–NH_2	*p*-Me–Ph–CN	66
4	*p*-F–Ph–CH_2–NH_2	*p*-F–Ph–CN	60
5	*p*-Cl–Ph–CH_2–NH_2	*p*-Cl–Ph–CN	64
6	CH_3–$(CH_2)_{15}$–NH_2	CH_3–$(CH_2)_{14}$–CN	58(70)[c]
7	CH_3–$(CH_2)_{11}$–NH_2	CH_3–$(CH_2)_{10}$–CN	78
8	CH_3–$(CH_2)_{17}$–NH_2	CH_3–$(CH_2)_{16}$–CN	38
9	 N NH_2	 N CN	59

[a] Reaction conditions: amine (1 mmol), H_2O (3 mL), KI (0.20 mmol), TBHP(1.1 mmol), RT, 8 h.
[b] Conversion based on GC.
[c] CH_3CN used as the solvent.



Scheme 2a. KI/I_2 catalyzed oxidation of alcohol to aldehydes.



Scheme 2b. KI/I_2 catalyzed oxidation of aldehydes to nitrile with ammonia.

in the absence of either catalysts or oxidant. Further, increasing the temperature and decreasing the amount of catalyst led to the quantitative conversion of benzyl alcohol to nitrile. We have also examined the role of other commercially available oxidants such as H_2O_2 and NaOCl on the model reaction, but we could not observe any notable conversions.

The general applicability of this method was further evaluated for structurally diverse alcohols under optimized reaction conditions using KI or I_2 as catalyst (Table 2).[23] The reactivity depends on the nature of alcohols used. Thus benzyl alcohols having electron-donating groups were smoothly converted to the corresponding nitriles in good yields (Table 1, entries 1–6), while benzyl alcohols with electron-withdrawing groups have shown slightly lower yield (Table 1, entries 8–11).

In case of (*p*-methylsulfanyl-benzyl alcohol) (Table 2, entry 4), apart from the desired *p*-methylsulfanyl-benzonitrile, we have also observed *p*-methanesulfinyl-benzonitrile as a minor product (10% by GC analysis). The reaction with *p*-nitro-benzyl alcohol under optimized condition resulted in the formation of *p*-nitro-benzamide as the major product, but when we carried out the reaction at room temperature with 20 mol % of KI as catalyst, 70% of desired product was obtained (Table 2, entry 12). In the case of primary aliphatic alcohols such as 1-octanol and 1-decanol, the reactions under optimized condition provided very lower conversions, however, increasing the amount of catalyst by 20 mol % led to moderate conversions (Table 2, entries 13 and 14). Similarly the reaction with cinnamyl alcohol led to cinnamonitrile in 30% isolated yield. In the case of hetero-aromatics, we have tested the reaction with 2-pyridyl carbinol which provided amide as the major product along with the required nitrile product which was analyzed by ^{1}H NMR and further confirmed by GC and GC–MS.

The present catalytic system was further examined for the direct conversion of aldehydes to nitriles, and the results are summarized in Table 3. We obtained a very good conversion irrespective of the electronic nature of the aldehydes. Moreover, these reactions were found to be faster when compared to alcohols. In case of *p*-nitro benzaldehyde, amide was observed as the major product.

Next, the catalytic studies were extended for the direct conversion of primary amines to nitriles, and the products were analyzed by GC and were confirmed by GC–MS. In a typical experiment, benzyl amine was treated with 5 mol % of KI, 1.1 mmol of TBHP at room temperature in water, which led to 73% of the desired nitrile product. Further we examined the feasibility of this reaction for various substrates, and the results are summarized in Table 4. We observed the formation of nitrile products for both aromatic and aliphatic amines, however, the conversion was low for aliphatic amines, which may be due to solubility problem of the long chain aliphatic amines.

Based on the present results, we tentatively propose the following mechanism as shown in Scheme 2. In the case of alcohol **a**, formation of aldehyde **b** could be an intermediate, which can be achieved by using either KI or I_2 as a catalyst (Scheme 2a). This was similar to our earlier results on the oxidative amidation of alcohols with amines.[22] Aldehyde **b** thus formed reacts with ammonia to form an imine **c**. Imine further reacts with iodine to form N-iodo aldimine **d**, which finally transforms into nitrile **e** by β-elimination of HI with ammonia (Scheme 2b). In case of direct conversion of primary amines to nitrile, a similar mechanism via imine and N-iodo aldimine was expected.[4c] It has been proposed earlier that under alkaline conditions, iodine involves in multiple equilibriums, in which hypoiodous acid is one of the possible intermediates.[24a] Similar intermediate was also proposed under acidic conditions with NaI and H_2O_2 for the alpha-iodination of ketones.[24b]

Since the aromatic nitriles are very useful and expensive products, the feasibility of the present catalytic system on multi-gram scale was examined for the synthesis of 4-methoxy-benzonitrile. Reaction of 4-methoxy-benzyl alcohol (5 g, 36.2 mmol) with 20 mol % of KI and 3.2 equiv of TBHP at 60 °C provided pure nitrile product quantitatively after 24 h.[25]

In summary, a simple and convenient method has been developed for the direct conversion of alcohols, aldehydes and primary amines to their corresponding nitriles selectively using catalytic amount of KI or iodine in combination with TBHP as an external oxidant. The present method avoids the use of expensive metal catalysts and hypervalent iodine reagents. Moreover, the present non-transition metal catalytic system also provides an easy scale-up and separation protocol.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.02.057.

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23. *General procedure for the synthesis of nitriles from alcohols*: To a solution of alcohol (1.0 mmol), potassium iodide (0.05 mmol) in 3 mL of aq NH_3 was added, a solution of 70% aqueous TBHP (3.8 mmol) was added dropwise over a period of 30 min and stirred at 60 °C. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was quenched with saturated aqueous $Na_2S_2O_3$, washed with brine, extracted with ethyl acetate and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded the crude product, which was purified by column chromatography using hexane/ethyl acetate (9:1) mixture and was analyzed by ^1H NMR, GC and GC–MS. Similar procedure was followed for synthesis of nitriles from aldehydes but with lesser amount of TBHP (2.2 mmol).
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25. *Gram scale preparation of 4-methoxy benzonitrile*: To a suspension of alcohol (5.0 g, 36.2 mmol) in 115 mL of aq NH_3 was added KI (20 mol %), and a solution of 70% aqueous TBHP (3.8 equiv) was added dropwise over a period of 30 min and stirred at 60 °C. Progress of the reaction was monitored by TLC. After completion of the reaction (24 h), the mixture was quenched with saturated aqueous $Na_2S_2O_3$, washed with brine, extracted with ethyl acetate and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded the crude product.