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Transition-Metal-Free Hydration of Nitriles Using Potassium *tert*-Butoxide under Anhydrous Conditions

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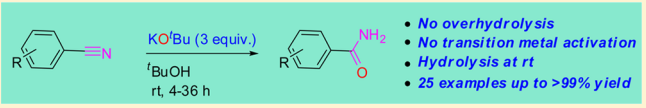
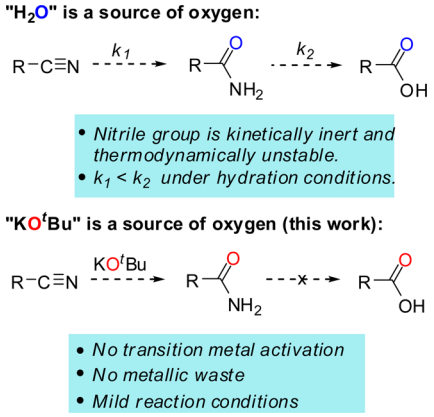
Supporting Information

ABSTRACT: Potassium *tert*-butoxide acts as a nucleophilic oxygen source during the hydration of nitriles to give the corresponding amides under anhydrous conditions. The reaction proceeds smoothly for a broad range of substrates under mild conditions, providing an efficient and economically affordable synthetic route to the amides in excellent yields. This protocol does not need any transition-metal catalyst or any special experimental setup and is easily scalable to bulk scale synthesis. A single-electron-transfer radical mechanism as well as an ionic mechanism have been proposed for the hydration process.



The amide functional group is present in proteins and is essential for sustaining life. It is a synthetically versatile synthon distributed in several biologically active molecules.[1] Amides have also been extensively used in industrial applications.[1,2] One of the most straightforward and atom-economical ways to synthesize amides is the hydration of the corresponding organonitriles. The nitrile group is mechanistically intriguing as it is kinetically inert and thermodynamically unstable.[3] Further, the rate of amide hydrolysis to the corresponding acid is much faster than the rate of hydrolysis of nitrile to the corresponding amide (Scheme 1).[4] These inherent properties make selective hydrolysis of nitriles to the corresponding amides much more challenging. Classically, hydration of nitriles was carried out under acid- and base-catalyzed conditions. However, major limitations of these hydration protocols include (a) the formation of corresponding acids by overhydrolysis, (b) requirement of high temperature and pressure, (c) poor functional group tolerance and narrow substrate scope, and (d) the inability to hydrolyze substrates having more than one nitrile functional group.[5,6]

Scheme 1. Hydration of the Nitriles to the Amides



To circumvent these problems, several catalytic hydration of nitriles have been devised utilizing enzyme catalysis,[7] transition-metal-mediated homogeneous catalysis,[8] heterogeneous catalysis,[9] and nanocatalysis.[10] Various green approaches such as microwave-assisted hydration of nitriles,[11] super basic system DMSO−CsOH,[12] chitosan-supported ruthenium catalyst,[13] and hydroxide-promoted[14] hydrolysis of nitriles have been reported. Although these processes offer improved yields and selectivity, each of these protocols has its own set of disadvantages. There is a need for the development of an ideal reaction condition, which can be performed at room temperature in a metal-free environment and scalable for industrial applications. As part of our ongoing research program toward the development of economically sustainable green synthetic methodologies,[15] we herein report an efficient hydration of organonitriles to the corresponding amides using potassium tertiary butoxide (KO^{t}Bu) as an oxygen source (Scheme 1).

Recently, KO^{t}Bu-promoted synthesis of biaryls has been reported by the groups of Itami, Shi, Lei, and Hayashi.[16] Hartwig and co-workers reported that the nitrile group can be activated via coordination with the potassium ion.[16e] We perceived the possibility of nucleophilic addition of tertiary butoxide to the electrophilic carbon atom of the activated nitrile group. We are delighted to observe the formation of amide (**2**) in 42% yield, when KO^{t}Bu (0.5 equiv) was added to the solution of benzonitrile (**1**) in toluene at room temperature under anhydrous conditions (Table 1, entry 1). This preliminary result inspired us to investigate the reaction in detail. The yield was significantly improved by increasing the amount of base (entries 2−4). Benzamide **2** was isolated in 91% using 3 equiv of KO^{t}Bu for 5 h (entry 4). A slight improvement in yield (96%) with shorter reaction time (3 h) was observed when the reaction temperature was raised to 60

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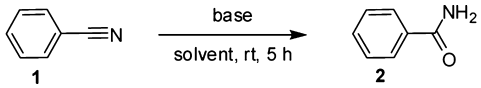
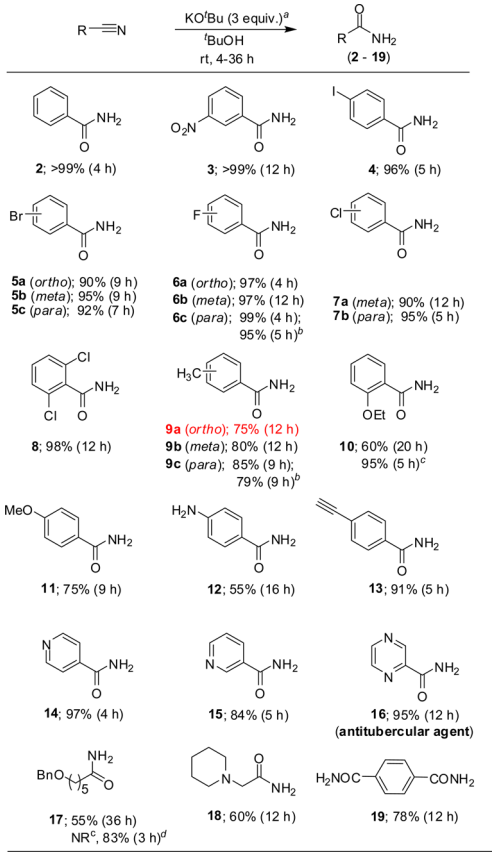
Table 1. Hydration of Benzonitrile[a]



entry[a]	base (equiv)	solvent	yield (%)
1	KO^{t}Bu (0.5)	toluene	42
2	KO^{t}Bu (1.0)	toluene	60
3	KO^{t}Bu (2.0)	toluene	80
4	**KO^{t}Bu(3.0)**	**toluene**	**91 (96)**[b]
5	KO^{t}Bu (3.0)[c]	toluene	15
6	NaO^{t}Bu (3.0)	toluene	NR
7	LiO^{t}Bu (3.0)	toluene	NR
8	K_2CO_3 (3.0)	toluene	NR[d]
9	Cs_2CO_3 (3.0)	toluene	NR[d]
10	K_3PO_4 (3.0)	toluene	NR[d]
11	KO^{t}Bu (3.0)	xylene	55
12	KO^{t}Bu (3.0)	THF	55
13	KO^{t}Bu (3.0)	dioxane	27
14	KO^{t}Bu (3.0)	DMF	NR
15	KO^{t}Bu (3.0)	DMSO	NR
16	KO^{t}Bu (3.0)	DMAc	NR
17	KO^{t}Bu (3.0)	$ClCH_2CH_2Cl$	NR
18	KO^{t}Bu (3.0)	CH_2Cl_2	traces
19	KO^{t}Bu (3.0)	$CHCl_3$	NR
20	KO^{t}Bu (3.0)	EtOH	65
21	KO^{t}Bu (3.0)	^{i}PrOH	75
22	**KO^{t}Bu (3.0)**	**^{t}BuOH**	**>99**[e]
23	KO^{t}Bu (3.0)[c]	^{t}BuOH	51

[a]All reactions were carried out under nitrogen atmosphere. [b]Performed at 60 °C for 3 h. [c]2% H_2O(v/v) was added. [d]Heating at 135 °C did not improve the result. [e]4 h.

Table 2. KO^{t}Bu-Promoted Hydration of the Nitriles



[a]See general procedure A. [b]See general procedure B. [c]5 h, 60 °C, toluene. [d]130 °C, toluene.

°C (entry 4). Only a trace amount of the product (15%) was isolated in the presence of water (entry 5). To investigate the positive counteranion effect, sodium and lithium *tert*-butoxides were used, which fail to give the desired product (entries 6 and 7). These results suggest that potassium cation plays an important role in this transformation. No reaction was observed using inorganic bases (K_2CO_3, Cs_2CO_3, K_3PO_4) containing different counteranions at room temperature or higher temperature (entries 8–10). Systematic screening of bases and temperature revealed that KO^{t}Bu is the only base, which can promote the hydration at room temperature (entries 6–10). Next, sets of representative protic solvents (EtOH, ^{i}PrOH, ^{t}BuOH) and polar solvents (DMSO, MeCN, DMF, and DMAc) were screened (Table 1). Moderate yield (55%) was obtained in aprotic solvents like THF and xylene. The reaction proceeded in toluene and ^{t}BuOH, but higher yield with shorter reaction time was obtained using ^{t}BuOH as the solvent. To avoid contamination from the glassware and reagents, hydration of benzonitrile was performed using 99.99% pure KO^{t}Bu (Sigma-Aldrich) in thoroughly clean glassware. The benzamide was obtained in similar yield in toluene and ^{t}BuOH.

With the optimized reaction conditions (1 equiv nitrile, 3 equiv KO^{t}Bu, 4 mL/mmol ^{t}BuOH) in hand, the scope of this hydration was then evaluated using different nitriles (Table 2). The yield of each of these substrates was also determined in toluene (Supporting Information, Table S1). The reactions are extremely efficient and high yielding in ^{t}BuOH, when benzonitriles are appended with electron-withdrawing group at the *ortho*- and *para*-position to give the corresponding amides **4**, **5a**, **5c**, **6a**, **6c**, and **7b**. Hydration of *meta*-substituted benzonitriles takes place in relatively slower rate (9–12 h) with comparable yields (**3**, **5b**, **6b**, **7a**). *o*-Dichlorobenzonitrile afforded the corresponding amide **8** in nearly quantitative yield after the reaction was run for 12 h. As expected, electron-rich benzonitriles afforded the corresponding amides (**9**–**12**) in realtively lower yields (55–85%) in both ^{t}BuOH and toluene.

This protocol was successfully applied for the hydration of *p*- and *m*-cyanopyridines to give the desired amides **14** and **15** in 97% and 84% yields, respectively. Antitubercular agent pyrazinamide **16** was prepared in 95% yield by hydration of the corresponding nitrile. Aliphatic nitriles were found to be less reactive compared to the aromatic nitriles. The desired amides **17** and **18** were obtained in 55% and 60% yields in ^{t}BuOH. The aliphatic amide **17** did not form in toluene at room temperature and formed in moderate yield by performing the reaction at 130 °C (Table S1, Supporting Information). We were delighted to observe the formation of the desired dicarboxamide **19** as a single product from the dicyanobenzene in 78% yield. These results indicate that the hydration methodology exhibits general substrate scope; electron-rich and electron-deficient aromatic, heteroaromatic nitriles, aliphatic nitriles, and dinitrile afforded high yields of the desired amide. The outcome of this protocol depends on both the electronic nature as well as the sterics of the substrates. It is worth mentioning that *meta*- and *ortho*-substituted halobenzonitriles reacted slowly with lower yields in toluene compared to ^{t}BuOH.

To gain mechanistic insights, radical-quenching experiments were performed in both toluene and ^{t}BuOH. Hydration of

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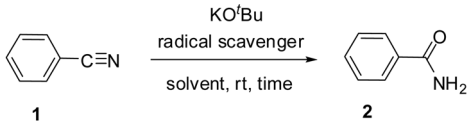
benzonitrile in the presence of radical traps 2,2,6,6-tetramethylpiperidine-1-oxyl and 1,1-diphenylethylene (DPE) proceeded with a diminished yield of the product (Scheme 2).

Scheme 2. Hydration of Nitriles in the Presence of Radical Scavengers



1 2

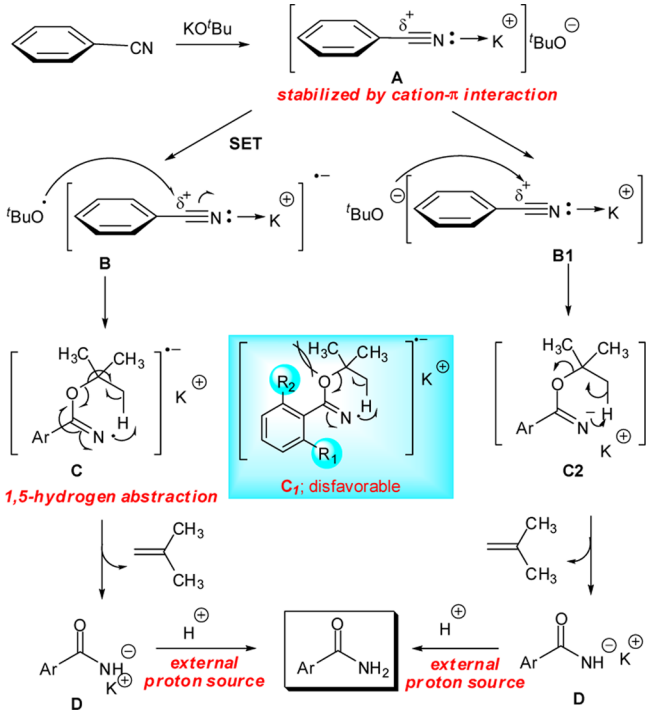
radical scavenger	Yield of 2 toluene (5 h)	Yield of 2 ^{t}BuOH (4 h)
none	91%	>99%
TEMPO (1 equiv.)	78%	82%
1,1-diphenyl ethylene (1 equiv.)	68%	70%
galvinoxyl (1 equiv.)	trace	75%
galvinoxyl (2 equiv.)	not determined	41%
galvinoxyl (3 equiv.)	not determined	trace

A complete inhibition of the reaction was observed in toluene using galvinoxyl as the radical scavenger. In ^{t}BuOH, 20−30% inhibition of product formation was observed using 1 equiv of TEMPO and DPE. By increasing the amount of galvinoxyl in ^{t}BuOH, the yield of amide **2** was decreased and the reaction was completely inhibited using 3 equiv of galvinoxyl. These experiments suggest that radical intermediates are involved during the hydration process. Electron paramagnetic resonance (EPR) studies indicated the formation of a strong EPR signal with a g value of 1.98 for the reaction mixture containing benzonitrile (0.5 mmol) and ^{t}BuOK (1.5 mmol) after stirring in toluene (3.0 mL) for 2 h, while a very weak EPR signal was detected in the absence of nitrile (Figure S1, Supporting Information).[17] This result is suggestive of an electron-transfer process between KO^{t}Bu and nitrile.

We propose that Lewis basic nitrile coordinates with the potassium cation in the presence of KO^{t}Bu to form complex **A**, which is stabilized by intermolecular cation−π as well as π−π* stacking interactions (Scheme 3).[18] On the basis of the EPR evidence, a single electron transfer (SET) may occur between the cationic complex **A** and tertiary butoxide anion to generate the radical ion pair **B**. Next, the *tert*-butoxy radical adds to the electrophilic carbon atom of the nitrile to form the iminyl radical intermediate **C**. The lower reactivity of aliphatic nitriles compared to the aromatic nitriles (Table 2) suggests that cation−π interaction plays a key role in aromatic nitriles. The intermediate **C** subsequently gives potassium amidate **D** via 1,5-hydrogen abstraction followed by elimination of 2-methylpropene. The formation of 2-methylpropene from the reaction mixture was detected by GC−MS analysis (Figure S2, Supporting Information). Finally, protonation of **D** affords the desired amide.

In case of *ortho*-substituted aryl nitriles, the formation of intermediate **C1** is unfavorable due to the steric interaction between the *ortho*-substituents and the 6-membered cyclic intermediate. This explains why the hydration of *ortho*-substituted aryl nitriles does not proceed at room temperature in toluene and occurs at 60 °C to give moderate yields of the desired products. The improved reactivity in ^{t}BuOH compared to toluene could be due to the strong hydrogen-bonding ability

Scheme 3. Proposed Mechanism



of ^{t}BuOH with the heteroatom present in the aryl moiety (see the Supporting Information for further explanation, Figure S3). However, we cannot rule out the possibility of a nucleophilic addition of *tert*-butoxy anion to the electrophilic carbon atom of the nitrile (as shown in **B1**) to generate the iminyl anion intermediate **C2**. Subsequent deprotonation of **C2** followed by elimination of 2-methylpropene may lead to the formation of the amidate **D**.

In conclusion, we have developed an efficient potassium *tert*-butoxide-mediated hydration of organonitriles to prepare the corresponding amides in excellent yields under mild reaction conditions. The method has a broad scope. No overhydrolysis with high selectivity was observed for the double hydration of dicyanobenzene. This protocol does not need any metal catalyst or any special experimental setup and is easily scalable to bulk scale synthesis.

EXPERIMENTAL SECTION

General Information. All starting materials were obtained from commercial suppliers and used as received. Products were purified by flash chromatography on silica gel (100−200 mesh, Merck). Unless otherwise stated, yields refer to analytical pure samples. NMR spectra were recorded in DMSO-d_6. ^{1}H NMR spectra were recorded at 500 and 400 MHz instruments at 278 K. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on either 100 or 125 MHz with complete proton decoupling. Chemical shifts (δ) are reported in ppm. Infrared (FTIR) spectra were recorded with the KBr disk and KBr plate techniques for solid and liquid samples, ν_{max} (cm^{-1}).

General Procedure A (GP-A): Hydration of *m*-Nitrobenzonitrile. A flame-dried flask fitted with magnetic stir bar was charged with *m*-nitrobenzonitrile (148 mg, 1.0 mmol, 1.0 equiv) and KO^{t}Bu (336 mg, 3.0 mmol, 3.0 equiv), and dry *tert*-butyl alcohol (4 mL/mmol) was added. The reaction mixture was stirred at room temperature for 12 h under nitrogen atmosphere, and progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was

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treated with water (10 mL). The solid amide product was filtered, washed with water, and dried under vacuum to provide the corresponding amide **3** in 99% (164 mg, 0.99 mmol) as a light yellow solid.

General Procedure B (GP-B): Hydration of Benzonitrile. A flame-dried flask fitted with a magnetic stir bar was charged with benzonitrile (103 mg, 1.0 mmol, 1.0 equiv) and KO^{t}Bu (336 mg, 3.0 mmol, 3.0 equiv), and dry toluene (4 mL/mmol) was added. The reaction mixture was stirred at room temperature for 5 h under nitrogen atmosphere, and progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was treated with water (10 mL). The solid amide product was filtered, washed with water, and dried under vacuum to provide the corresponding amide **2** in 91% (110 mg, 0.91 mmol) as a white solid.

In most cases (except **17**), the solid amide products were filtered, washed with water, and dried under vacuum to afford **2**−**19** in high yields and purities. The ^{1}H and ^{13}C NMR spectroscopic data of the amides **2**,[18] **3**,[9d] **4**,[6] **5a**,[18] **5b**,[18] **5c**,[18,9d] **6a**,[19] **6b**,[20] **6c**,[11] **7a**,[11] **7b**,[19,9d] **9a**,[18,21] **9b**,[19,21] **9c**,[19,21] **10**,[22] **11**,[19,9d] **12**,[6b] **13**,[23] **14**,[19,6b] **15**,[9d,21] **16**,[9d] **18**,[24] and **19**[19,6] matched with those reported in the literature (see the Supporting Information).

■ ASSOCIATED CONTENT

Supporting Information

EPR, GC−MS, ^{1}H NMR, and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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