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Letter

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Copper-Catalyzed Direct Nitration on Aryl C−H Bonds by Concomitant Azidation−Oxidation with TMS Azide and TBHP under Aerobic Conditions

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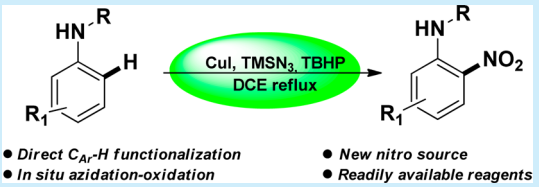
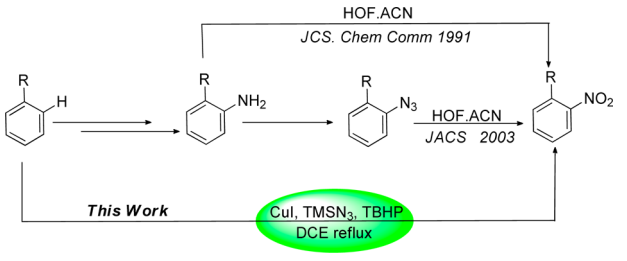
Supporting Information

ABSTRACT: An unprecedented copper-catalyzed in situ azidation−oxidation for the nitration of anilides and sulfonamides has been developed by direct C_{Ar}−H functionalization. This novel and efficient nitration protocol is achieved employing $TMSN_3$ and TBHP without the exclusion of air or moisture. The synthetic applications of the 2-nitroanilides have been explored.



Organic azides are energy-rich molecules that are widely employed in organic synthesis as valuable intermediates and building blocks owing to their utility for the synthesis of nitrogen-containing heterocycles, peptide chemistry, materials science, polymer chemistry, and drug discovery.[1] Despite their importance, the chemistry of azides is underexplored and is limited to their reduction to amines[2a−d] and 1,3 cycloaddition reactions.[2e−i] In contrast, the oxidation of azides is not so common,[3a−c] and the azide oxidations to nitro compounds reported by Corey and co-workers[3d] involving phosphinimine formation and application of Rozen's[3e−g] method which employs an efficient oxygen transfer reagent, the HOF·CH_3CN complex, are associated with limitations. Corey's method is limited to aliphatic substrates that are tolerant of ozone at −78 °C. Though Rozen's method is the first ever reported oxidative approach to nitro compounds from aryl azides, the use of a corrosive fluorine reagent is a limitation and is not practical, since these azides are usually obtained from the corresponding aromatic amines, which are themselves excellent substrates for oxidation by HOF·CH_3CN to the nitro derivatives (Scheme 1). The direct azidation of aryl C−H bonds is a fascinating and challenging transformation in organic chemistry. The C_{Ar}−H nitration by direct in situ azidation−oxidation would represent a powerful strategy and hitherto unknown chemistry. In this letter we report on the discovery of a new nitration strategy[4] that employs the readily available precursors azidotrimethylsilane ($TMSN_3$) and *tert*-butyl hydroperoxide (TBHP) to accomplish the concomitant azidation−oxidation of anilides and sulfonamides in the presence of a copper catalyst, in a new example of direct C−H functionalization (Scheme 1).

Scheme 1. Azidation−Oxidation on Aryl Ring



We have been engaged in C−C, C−O, and C−N bond forming reactions through C−H functionalizations, and recently we reported an iron-mediated direct mono C_{Ar}−H nitration reaction under aerobic oxidation conditions.[5] In continuation of our efforts, we attempted the direct azidation of anilides in the presence of $TMSN_3$ and TBHP using CuI as catalyst in DCE solvent at room temperature, but the reaction was found to be sluggish. After the reaction mixture was heated at reflux for 15 h, to our surprise, instead of the expected azidoanilide, the nitro variant was obtained in <5% yield. The salient features of this new chemistry include the following: (1) novel in situ azide oxidation employing a simple reagent, TBHP; (2) compatibility with air or moisture; (3) the ability to convert a latent amino group into Cl, Br, I, CN, OH, or H substituents; (4) a controlled mononitration; (5) the avoidance of corrosive materials such as F_2 or O_3 and mineral acids; and (6) the nitro products are useful precursors for the preparation of nitro-anilines, *o*-phenylenediamines, sulfonamides, benzimidazoles, and Baran hydroamination products.

N-(*p*-Tolyl)benzamide **1b** was chosen as a model substrate to test the efficacy of the nitration reaction in open air with various nitrogen sources, oxidants, catalysts, and solvents (Table 1).[6] The reaction was initially performed at room temperature with 1 equiv of $TMSN_3$, 2 equiv of TBHP (5.5 M in decane), and CuI (0.2 equiv) in DCE solvent, but produced no desired product (Table 1, entry 1). However, on increasing the quantities of $TMSN_3$ and *t*-BuO_2H (Table 1, entries 2−5) and heating the reaction mixture to 83 °C, product **2b** was formed in <5% yield and starting material **1b** was recovered. To

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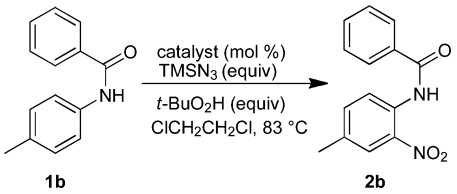
Table 1. Optimization Studies for the Copper Catalyzed Azidation−Oxidation of Anilides Leading to Nitration Products[a]



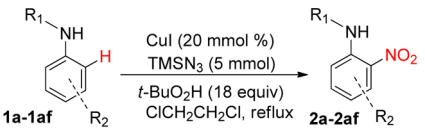
1b 2b

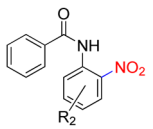
entry	catalyst	$TMSN_3$ (equiv)	t-BuO_2H (equiv)	temp (°C)	yield (%)[b]
1	CuI	1 equiv	2 equiv	rt	0
2	CuI	1 equiv	2 equiv	83	0
3	CuI	2 equiv	2 equiv	83	0
4	CuI	4 equiv	2 equiv	83	0
5	CuI	4 equiv	4 equiv	83	<5
6	CuI	5 equiv	8 equiv	83	<15
7	CuI	5 equiv	10 equiv	83	30
8	CuI	5 equiv	15 equiv	83	62
9	CuI	5 equiv	18 equiv	83	73
10	CuI	5 equiv	20 equiv	83	71
11	CuI	6 equiv	18 equiv	83	70
12	CuI	6 equiv	20 equiv	83	71
13[c]	CuI	5 equiv	18 equiv	83	33
14[d]	CuI	5 equiv	18 equiv	83	55
15[e]	CuI	5 equiv	18 equiv	83	43
16	–	5 equiv	18 equiv	83	0
17	$CuBr_2$	5 equiv	18 equiv	83	58
18	$Cu(OAc)_2$	5 equiv	18 equiv	83	63
19	$Cu(OTf)_2$	5 equiv	18 equiv	83	57
20	$CuCl_2$	5 equiv	18 equiv	83	55
21	CuBr	5 equiv	18 equiv	83	38
22	$FeCl_3$	5 equiv	18 equiv	83	20
23	$FeBr_3$	5 equiv	18 equiv	83	16
24	$Pd(OAc)_2$	5 equiv	18 equiv	83	0

[a]The reaction was performed with **1b** (1 mmol), catalyst (20 mmol %), $TMSN_3$, and TBHP (5.5 M in decane) in $ClCH_2CH_2Cl$ (3 mL); the reaction mixture was refluxed for 18 h in an open air atmosphere unless otherwise noted. [b]Isolated yields. [c]aq. TBHP (70% in H_2O). [d]Oxygen [e]Nitrogen atmosphere.

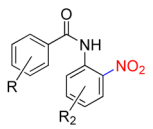
our delight, the further increase (5 equiv of $TMSN_3$ and 18 equiv of TBHP) led to improved yields of the nitration product to 73% (entries 6−9). Further increases did not improve the outcome of the reaction (entries 10−12). With aq. TBHP the yield of the desired product dropped to 33% (entry 13), while the reaction under oxygen and an inert atmosphere lowered the yields to 55%, 43% (entries 14−15). In the absence of catalyst the reaction did not proceed (entry 16). The reaction efficiency was lowered with other copper and iron catalysts and detrimental with a Pd catalyst (entries 17−24). A 20 mol % CuI catalyst loading proved to be optimum; a lower (10%) loading of catalyst decreased the yields, while a higher (30%) loading did not improve the efficiency of the reaction.[6] When $TMSN_3$ was replaced with either NaN_3 or TsN_3, the reaction did not proceed.[6] Other nitrogen sources were also ineffective for the nitration reaction.[6] Oxidants other than TBHP failed to produce the desired result.[6] Among the solvents tested, 1,2-dichloroethane proved to be the best.[6] The maximum yield of 73% for the nitration product **2b** could be obtained at reflux temperature.[6] The effect of external additives was screened, and the results were best in the absence of any additive.[6] With the optimized conditions in hand, the substrate scope of the reaction was investigated (Scheme 2). Good yields of the mono

Scheme 2. Substrate Scope for the Copper-Catalyzed Azidation−Oxidation of Anilides and Sulfonamides Leading to Nitration Products[a]

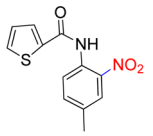




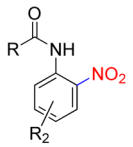
2a R_2 = H, 53% (**a'** 8%), 20 h
2b R_2 = 4-Me, 73%, 18 h
2c R_2 = 4-Et 67%, 20 h
2d R_2 = 5-Me, 56% (**d'** 12%), 19 h
2e R_2 = 3-OMe, 68% (**e'** 17%), 18 h
2f R_2 = 2-Me, 0% (**f'** 10%), 20 h
2g R_2 = 4-F, 55% 20 h
2h R_2 = 4-Br, 51% 22 h
2i R_2 = 4-I, 48% 24 h
2j R_2 = 4-CF_3, 43% 24 h
2k R_2 = 4,5-dimethyl, 82% 18 h

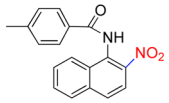


2l R = 4-Me, R_2 = 3,4,5-trimethoxy, 86% 18 h
2m R = 4-Me, R_2 = 4-Me, 84%, 18 h
2n R = 4-OMe, R_2 = H, 64%,(n' 10%) 20 h
2o R = 4-Me, R_2 = 4-*n*-butyl, 75%, 20 h
2p R = 4-Me, R_2 = 4-*t*-butyl, 72%, 20 h
2q R = 4-Me, R_2 = 4-*c*-hexyl, 70%, 20 h
2r R = 4-F, R_2 = 4-OMe, 73%, 18 h
2s R = 4-Cl, R_2 = 4-Me, 65%, 19 h
2t R = 2-I, R_2 = 4-OMe, 63%, 18 h
2u R = 2,4,6-trichloro, R_2 = Me, 63%,19 h
2v R = 4-CF_3, R_2 = Me, 64%, 20 h
2w R = 4-NO_2, R_2 = Me, 61%, 20 h



2x, 50%, 18 h





2y, trace, 30 h

2z, R = Me, R_2 = H, 53% (**z'** 6%) 20 h
2aa, R = Et, R_2 = 4-Me, 63%, 20 h
2ab, R = Vinyl, R_2 = 4-Me, 58%, 20 h

2ac R_2 = H, 53% (**ac'** 12%), 5 h
2ad R_2 = 4-Me, 64%, 3 h
2ae R_2 = 4-Cl, 60%, 6 h
2af R_2 = 3-CF_3 55% (**af'** 8%), 6 h

[a]Reaction conditions: All the reactions were performed with **1** (1 mmol), catalyst (20 mmol %), $TMSN_3$ (5 mmol), and t-BuO_2H (5.5 M in decane) (18 equiv) in $ClCH_2CH_2Cl$ (3 mL) at reflux; isolated yields.

nitration products were often achieved when electron-donating moieties including methyl, ethyl groups were present on the *para*-position of the aromatic ring (Scheme 2, **2b**, **2c**). Substrates with an electron-donating group at the *meta*-position gave good results, forming a mono *ortho*-nitrated product, alongside a minor *para*-nitration product (Scheme 2, **2d**, **2e**). The steric crowding in the substrate **1f** inhibited *ortho*-nitration and led to the exclusive *para*-nitration product instead (Scheme

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2, **2f**). The nitration reaction tolerated halogen substituents at the *para*-position and afforded moderate yields of the products (Scheme 2, **2g**–**2i**). A 4-trifluoromethyl-substituted anilide also underwent smooth nitration giving a moderate yield of **2j**. Substrates bearing 3,4-dimethyl and 3,4,5-trimethoxy groups delivered the desired product in 82% and 86% yields respectively (Scheme 2, **2k**, **2l**). Substrates with different carboxamides (aryl, alkyl, and vinyl) showed similar reactivity, and the yields were moderate to good (Scheme 2, **2m**–**2z**). Moderate to good yields of the nitration products were obtained with 4-fluoro-, 4-chloro-, 2-iodo-, and 2,4,6-trichloro-substituted benzamides (Scheme 2, **2r**–**2u**). Substrates with strong electron-withdrawing groups such as 4-trifluoromethyl or 4-nitro benzamides also showed reasonably good reactivity toward this nitration reaction (Scheme 2, **2v**, **2w**). Further, a heteroaryl substrate also underwent smooth nitration in moderate yield (**2x**). *N*-Naphthyl anilide produced only a trace amount of the nitro product, presumably because of the steric crowding arising from the adjacent aryl ring (**2y**). Alkyl and vinyl carboxamides also underwent azidation–oxidation reactions under the standard reaction conditions (Scheme 2, **2z**–**2ab**). Aromatic sulfonamides underwent direct oxidative nitration reaction under the standard reaction conditions and afforded the desired products (Scheme 2, **2ac**–**2af**). The scope of the nitration reaction is similar to that for anilides. Halogen substitution or an electron-withdrawing trifluoromethyl group on the aniline partner was also tolerated for the sulfonamide nitrations (Scheme 2, **2ae**–**2af**). The reaction of tosylamines was faster when compared with that of anilides.

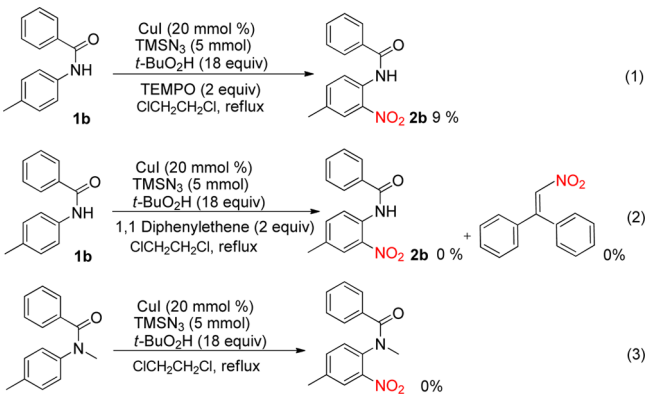
This C_{Ar}–H nitration reaction is efficient for different electron-donating and -withdrawing groups on either of the aryls (aniline or carboxamide/tosyl rings). The *ortho*-selectivity is observed for the azidation–oxidation reactions, as the azide radical prefers to attack at the *ortho*-position of the anilide or sulfonamide.[5d] Though a *para*-nitration product was formed in minor quantities in some cases (a′, d′, e′, f′, ac′, and af′), this could be easily separated by SiO_2 column chromatography. Further, the synthetic value of the aromatic nitration reaction is demonstrated from the tolerance of halogens on either of the rings which have been shown to be leaving groups in a variety of transition metal catalyzed cross-coupling reactions, demonstrating that these halogens could be used as handles for further functional group transformations. It is noteworthy to mention that nitration selectively occurred on the aniline ring while no nitration occurred on the carboxamide/tosyl ring.

This high level of chemoselectivity was further demonstrated from competition studies between *N*-(*p*-tolyl)benzamide **1b** and the electron-rich phenol and anisole.[6] Thus, phenol and anisole were found to be resistant to nitration while **1b** underwent smooth nitration in good yield. When a mixture of **1b** and phenylacetylene was subjected to our standard reaction conditions, the *ortho*-nitrated product (**2b**) was obtained in 70% yield and no triazole product formation was observed.[6] Unlike other $TMSN_3$ promoted CuAAC reactions,[2f] free azide appears to be unavailable to phenylacetylene for 1,2,3-triazole formation under the reaction conditions.

The substrates 4-methyl aniline, 4-methyl-*N*,*N*-dimethylaniline, and *N*-benzylamide were found to be resistant to the azidation–oxidation reaction.[6] Heteroaryl substrates such as *N*-(*p*-tolyl)picolinamide, *N*-(4-fluorophenyl) picolinamide, and *N*-(pyridin-3-yl)benzamide also failed to afford the nitration products under our standard reaction conditions.[6] Our efforts to perform the oxidation of 4-tolyl azide, benzyl azide, and *n*-hexylazide under our standard reaction conditions also met with failure.[6]

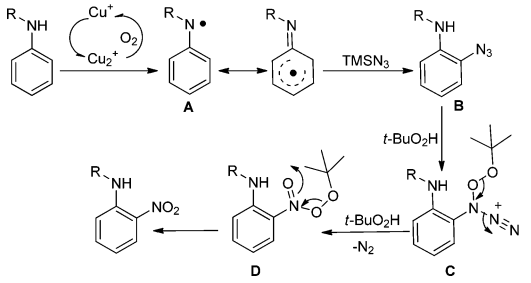
To understand the mechanism, **1b** was subjected to the standard reaction conditions in the presence of the radical scavenger TEMPO, which led to a diminished yield (9%) of the product **2b** (Scheme 3, eq 1) demonstrating that a radical

Scheme 3. Mechanistic Insights



species may be involved in the reaction process. When 1,1-diphenylethylene was employed as a radical acceptor, formation of neither **2b** nor a radical intercepted product was detected indicating that a nitro radical is not involved in the reaction pathway (Scheme 3, eq 2). These experiments demonstrate that the azidation–oxidation reaction may proceed by a radical mechanism. Furthermore, no nitration occurred when *N*-methyl-*N*-(*p*-tolyl) benzamide was subjected to nitration under the standard reaction conditions, indicating that the proton on nitrogen is essential for the reaction to proceed (Scheme 3, eq 3). Although the reaction mechanism is not clear yet, from the above observations and prior literature,[7,3a] a plausible mechanism has been proposed. It is assumed that the initial oxidation by CuI occurs through single electron transfer (SET) to an anilide and results in the formation of an anilide radical **A** (Scheme 4). The azide radical generated in situ from $TMSN_3$

Scheme 4. Proposed Mechanism



combines with **A** to form intermediate **B**. Successive peroxidation on the incipient azide[7b] associated with extrusion of molecular nitrogen and *t*-BuOH (**C**, **D**) affords the nitro product.

Our copper-catalyzed azidation–oxidation protocol has been successfully applied for potentially useful organic transformations (Scheme 5).[8] Synthetically important secondary amines were obtained from the reaction of **1b** and olefins under Baran hydroamination conditions.[8e]

One-step iron-catalyzed sulfonamidation of **1b** from sodium arylsulfinates under mild conditions was carried out to afford

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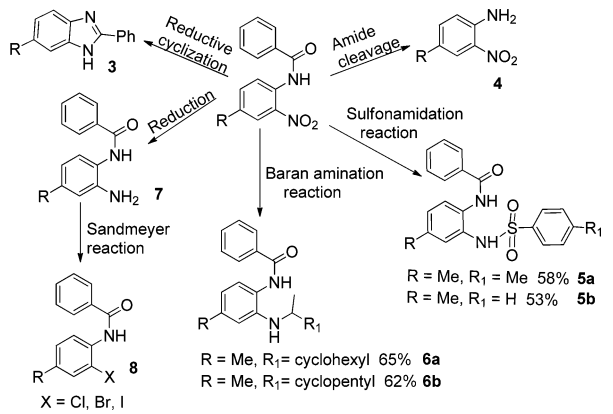
Scheme 5. Synthetic Applications



the differently protected *o*-phenylenediamine. *o*-Nitroanilides are known to be potential precursors for reductive cyclization to obtain 2-substituted benzimidazoles. 2-Amino-anilides can also be accessed from the reduction of the nitro compounds and later easily decorated with halogens by the Sandmayer reaction.

In conclusion we have reported the discovery of a new nitration protocol from a hitherto unreported concomitant azidation−oxidation reaction that delivers a variety of nitro-substituted anilides and sulfonamides. The copper-catalyzed mononitration reaction involves a novel and efficient C−N bond forming reaction via direct C_{Ar}−H functionalization. For the first time, a nitro group has been installed in one step directly onto an aryl carbon by in situ oxidation of an incipient arylazide. An inexpensive copper catalyst and readily available reagents effect the C_{Ar}−H nitration without the exclusion of air or moisture, which highlights the operational simplicity of the reaction. Further mechanistic investigations are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01489.

^{1}H and ^{13}C NMR spectra of all new compounds and the experimental procedures (PDF)

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Notes

The authors declare no competing financial interest.

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(6) All optimization tables, competition studies, and substrates resistant to nitrations are placed in the Supporting Information (SI).

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