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Efficient and economic halogenation of aryl amines via arenediazonium tosylate salts

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ABSTRACT

Arenediazonium tosylate salts have been successfully employed as a new and efficient reagent in halogenation reactions. A novel and economic protocol has been developed for the bromination and chlorination of various anilines using arenediazonium tosylate salts. A wide variety of reaction conditions were studied in acetonitrile at either room temperature or 60 °C in the presence or absence of catalyst with good to excellent yields. A surprising result showed the formation of acetanilides as a major product of aniline and methyl-substituted aniline halogenations in high yields.

1. Introduction

Arenediazonium salts have gained attention in synthetic chemistry due to their powerful synthetic as well as industrial importance.[1–3] To broaden the scope of arenediazonium salt applications, we recently reported the synthesis of new and highly stable arenediazonium tosylate salts with various applications.[4] The close and multiple contacts between the nitrogen atom in the diazonium cation and the oxygen atoms of the tosylate anion were accountable for the unusual stability of these salts, which was supported by X-ray structure. It is well documented that arenediazonium salts[5,6] are very reactive intermediates for various organic conversions. They electrochemically reduce into radicals or cations that immediately attach covalently to carbon or other substituents. This behavior of diazonium salt was explored for the simple and efficient diazotization–iodination of aromatic amines.[7–10] The diazotization and halogenation reaction is a one-pot, two-step process that first includes the diazotization of amines with sodium nitrite or *tert*-butyl nitrite in the presence of acid and a subsequent reaction with a halogenating agent in the presence or absence of copper salt.

It is well known that aromatic halides are important building blocks in organic transformations, such as the Suzuki cross coupling and Heck-type reactions[11–17], and one of the most renowned methods for the synthesis of aryl halides by aryl amines is the traditional Sandmeyer reaction.[18–22] Subsequently, a successful method for the halogenation of aromatic amines by alkyl nitrites in the presence of anhydrous copper(II) salts via a substitutive deamination reaction was reported by Doyle et al.[23,24] Recently, a one-step method for the iodination of aromatic derivatives was reported using HI/KNO_2 in DMSO or KI/$NaNO_2$/*p*-TsOH in CH_3CN.[25] A recent publication also reports the synthesis of aryl halides using various arenediazonium salts.[26]

This manuscript is an extension of our ongoing interest on the versatility of arenediazonium tosylate salts. This report clearly demonstrates the synthesis of aryl halides that avoids the use of unstable diazonium salts. In addition, this method utilizes a complete organic medium without acids to minimize aqueous waste and to provide applicable useful, economic, and easy one-pot synthetic procedure for the synthesis of halo-benzene derivatives. The results of this study discuss the preparation of aromatic bromides and chlorides by diazotization and halogenation of aromatic amines with different halogenating reagents in the presence of *p*-TsOH in acetonitrile.

2. Results and discussion

The reaction of anilines with halogenating reagents in acetonitrile under various reaction conditions resulted in a rapid and quantitative evolution of nitrogen and the formation of aryl halides (Table 1–4). The nature of the free halide ion in solution was the main influence determining the reaction rate; use of the bromide ion reacted faster than the chloride ion, which was only converted to aryl chloride after an extended reaction period (Scheme 1).

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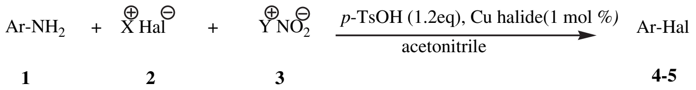


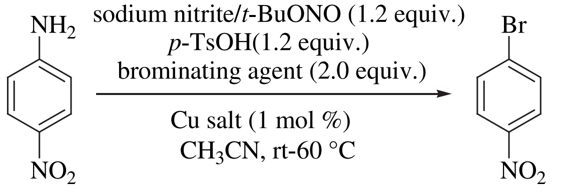
$$\mathrm{Ar\text{-}NH_2} + \overset{\oplus}{\mathrm{X}}\overset{\ominus}{\mathrm{Hal}} + \overset{\oplus}{\mathrm{Y}}\overset{\ominus}{\mathrm{NO_2}} \xrightarrow[\text{acetonitrile}]{p\text{-TsOH (1.2eq), Cu halide(1 mol \%)}} \mathrm{Ar\text{-}Hal}$$

1 **2** **3** **4-5**

Here ; **1, 4-5**: **a**, Ar = 4-$NO_2C_6H_4$; **b**, Ar = 3-$NO_2C_6H_4$; **c**, Ar = 2-NO_2-C_6H_4; **d**, Ar = 4-CNC_6H_4;
e, Ar = 2-CNC_6H_4; **f**, Ar = 4-IC_6H_4; **g**, Ar = 4-BrC_6H_4;
h, Ar = 4-ClC_6H_4; **i**, Ar = 4-$OCH_3C_6H_4$; **j**, Ar = 2-$OCH_3C_6H_4$;
k, Ar = 4-NO_2-2-$OCH_3C_6H_3$; **l**, Ar = 2-NO_2-4-$OCH_3C_6H_3$; **m**, Ar = benzothiazol
2 : sodium bromide, tertabutylammonium bromide(TBAB), benzyltriethylammonium chloride(BTAC)
3 : *t*-butyl nitrite, sodium nitrite **4** : Hal = Br **5** : Hal = Cl

Scheme 1. Diazotization–halogenation of aniline derivatives.

Table 1
Reaction conditions for diazotization–bromination of 4-nitroaniline (**1a**)



1a **4a**

Entry	Method	Catalyst	Temp	Time (h)	Yield (%)
1	1	CuBr	rt	6	62
2	1	CuBr	60 °C	3	59
3	1	CuBr	rt	6	29[a]
4	2	—	rt	6	74
5	2	CuBr	rt	2	86
6	2	$CuBr_2$	rt	2	84
7	2	CuBr	rt	6	Trace[a]
8	3	—	rt	4	78
9	3	CuBr	rt	1	81
10	3	$CuBr_2$	rt	1	86

Method 1: $NaNO_2$, *p*-TsOH, Cu salt, AcOH, NaBr in CH_3CN.
Method 2: *t*-BuONO, *p*-TsOH, Cu salt, NaBr in CH_3CN.
Method 3: *t*-BuONO, *p*-TsOH, Cu salt, TBAB in CH_3CN.
[a] In the absence of *p*-TsOH.

Table 2
Diazotization–bromination of anilines **1**

$$\underset{\mathbf{1}}{\mathrm{Ar\text{-}NH_2}} \xrightarrow[\substack{\mathrm{CuBr_2}\text{ (1 mol \%)} \\ \mathrm{CH_3CN,\ rt}}]{\substack{t\text{-BuONO (1.2 equiv.)} \\ p\text{-TsOH(1.2 equiv.)} \\ \text{TBAB (2.0equiv.)}}} \underset{\mathbf{4}}{\mathrm{Ar\text{-}Br}}$$

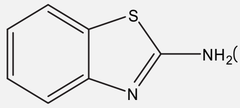
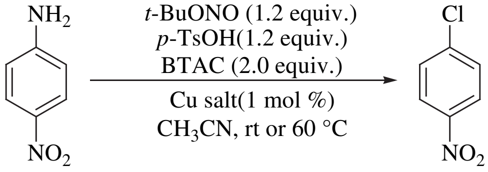
Entry	Ar	Time (h)	Yield (%)
1	3-$NO_2C_6H_4$(**1b**)	1	79(**4b**)
2	2-$NO_2C_6H_4$(**1c**)	1	76(**4c**)
3	4-CNC_6H_4(**1d**)	1	82(**4d**)
4	2-CNC_6H_4(**1e**)	1	75(**4e**)
5	4-IC_6H_4(**1f**)	1	78(**4f**)
6	4-BrC_6H_4(**1g**)	1	71(**4g**)
7	4-ClC_6H_4(**1h**)	23	58(**4h**)
8	4-$MeOC_6H_4$(**1i**)	23	77(**4i**)
9	2-$MeOC_6H_4$(**1j**)	23	74(**4j**)
10	4-NO_2-2-$MeOC_6H_3$(**1k**)	1	88(**4k**)
11	2-NO_2-4-$MeOC_6H_3$(**1l**)	1	83(**4l**)
12	 NH_2(**1m**)	3	89(**4m**)

Table 3
Reaction conditions for diazotization–chlorination of 4-nitroaniline (**1a**)



1a **5a**

Entry	Catalyst	Temp	Time (h)	Yield (%)
1	$CuCl_2$	rt	24	76
2	CuCl	rt	24	60
3	—	rt	24	39
4	—	rt	24	Trace[a]
5	CuCl	60 °C	1	60
6	$CuCl_2$	60 °C	1	71

[a] In the absence of *p*-TsOH.

Table 4
Diazotization–chlorination of anilines **1**

$$\underset{\mathbf{1}}{\mathrm{Ar\text{-}NH_2}} \xrightarrow[\substack{\mathrm{CuCl_2}\text{ (1 mol \%)} \\ \mathrm{CH_3CN,\ rt\ or\ 60\ ^\circ C}}]{\substack{t\text{-BuONO (1.2 equiv.)} \\ p\text{-TsOH(1.2 equiv.)} \\ \text{BTAC (2.0 equiv.)}}} \underset{\mathbf{5}}{\mathrm{Ar\text{-}Cl}}$$

Entry	Ar	Temp	Time (h)	Yield (%)
1	3-$NO_2C_6H_4$(**1b**)	60 °C	1	66(**5b**)
2	2-$NO_2C_6H_4$(**1c**)	rt	24	43(**5c**)
3	4-CNC_6H_4(**1d**)	rt	24	69(**5d**)
4	2-CNC_6H_4(**1e**)	rt	24	61(**5e**)
5	4-NO_2-2-$MeOC_6H_3$(**1k**)	60 °C	1	63(**5k**)
6	2-NO_2-4-$MeOC_6H_3$(**1l**)	60 °C	1	34(**5l**)

We varied several reaction parameters to optimize the reaction conditions, including the sodium nitrite or *tert*-butyl nitrite, the halogenating agent, the reaction temperature, time, catalyst, the presence or absence of catalyst, and the presence or absence of *p*-TsOH under various methods. It is known that bromination and chlorination is more challenging as compared with iodination, simply because of the lower nucleophilicity of bromide and chloride than iodide. Keeping this in mind we used acetonitrile, a polar aprotic solvent, for effective bromination and chlorination.

Reaction parameters began with the treatment of sodium nitrite and sodium bromide with aniline in the presence of *p*-TsOH using Cu halide as a catalyst in acetonitrile, and only a satisfactory yield was achieved with various substituted anilines at room temperature or 60 °C (method 1).

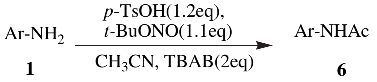
With the intension to increase the yield, we replaced the sodium nitrite with *tert*-butyl nitrite (method 2) and carried out several reactions at room temperature in the presence or absence of Cu(I) and Cu(II) halides. The observed results showed an increased yield of the desired product, and the rate of the reaction varied with aniline substitution. It was hypothesized that the halodediazoniation followed the homolytic dediazoniation pathway[27,28] and an electron transfer initiated the reaction. The electron-withdrawing substituent at the *para*-position led to a fast reaction with a high yield due to the high electrophilicity of the cation, even without using Cu as the catalyst (Table 1).

The addition of tetrabutylammonium bromide as the brominating agent (method 3) to the reaction mixture increased the formation of the desired product up to 89% yield in a shorter reaction time. Consistently high yields of the bromodediazoniation products were achieved with a variety of aniline derivatives. Method 3 proved to be equally applicable for anilines containing electron-donating as well as electron-withdrawing groups, which is not the case with method 2 (Table 1 and 2).

The comparatively low yield of chlorodediazoniation products to bromodediazoniation products can be justified by the redox potentials of both halide anions. The high redox potential of Cl^- reasonably explains its difficulty in electron transfer as compared with Br^-, which is responsible for the compared low yield. Furthermore, varying the Cu(I) and Cu(II) halides showed no significant change in yield. It is understood that the Cu(I) salt played an important role in the Sandmeyer substitution reaction. Also, the effective use of Cu(II) salt was noticed in the substitution process by its reduction to Cu(I) during the course of the reaction. We also observed that both Cu(I) and Cu(II) salts worked effectively for the generation of aryl halides. It is worth mentioning that only a catalytic amount of Cu salt worked effectively in our reaction conditions resulting in excellent yields of the desired products.

In most of the cases, it was observed that the rate of the reaction was increased at 60 °C, and moderate to high yields of the desired product were achieved in 1 h reaction time. To monitor the role of *p*-TsOH salt in the reaction, we carried out some reactions in the absence of *p*-TsOH and noticed a very poor yield, confirming the involvement of diazonium tosylate salt formation during the course of the reaction.

Finally, a very surprising result was observed with the reaction of aniline and methyl-substituted anilines (Scheme 2). The treatment of aniline or methyl-substituted aniline with *tert*-butyl nitrite and TBAB in the presence of *p*-TsOH in acetonitrile yielded the alkyl acetanilides in high yield and IR, NMR, and GC-MASS data provided the evidence for the formation of the product. Several conditions were attempted to generate the desired methyl-substituted aryl halide, but in all the process variations, we achieved acetanilides in 74–96% yield. After confirming the synthesis of 4-methylacetanilide in the 4-methylaniline reactions, we extended the study to several different methyl-substituted anilines and the results are summarized in Table 5.



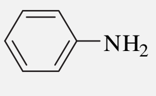
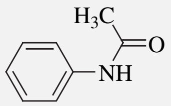
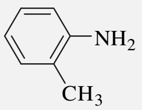
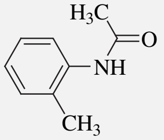
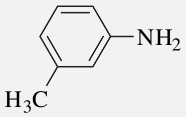
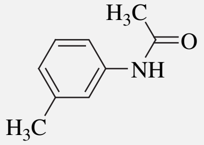
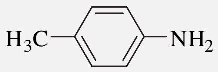
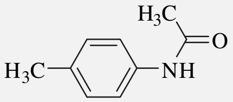
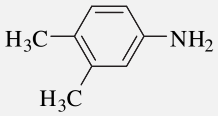
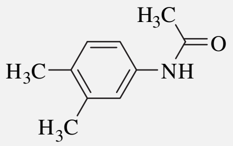
$$\underset{\mathbf{1}}{\text{Ar-NH}_2} \xrightarrow[\text{CH}_3\text{CN, TBAB(2eq)}]{p\text{-TsOH(1.2eq)},\ t\text{-BuONO(1.1eq)}} \underset{\mathbf{6}}{\text{Ar-NHAc}}$$

Here; **1**, **6**: **n**, Ar = C_6H_5; **o**, Ar=2-$CH_3C_6H_4$; **p**, Ar = 3-$CH_3C_6H_4$; **q**, Ar = 4-$CH_3C_6H_4$; **r**, Ar= 3,4-$(CH_3)_2C_6H_3$

Scheme 2. Reaction of aniline and methyl-substituted anilines.

These results were quite interesting and the synthesis of an alkylacetanilide with common anilines provides a new tool for this synthesis; however, this reaction process requires further modification and a detailed study of the reaction conditions. No clear evidence is available to explain the reaction pathway; however a plausible reaction mechanism can be suggested as follows:

Table 5
Diazotization–halogenation of aniline and methyl-substituted anilines

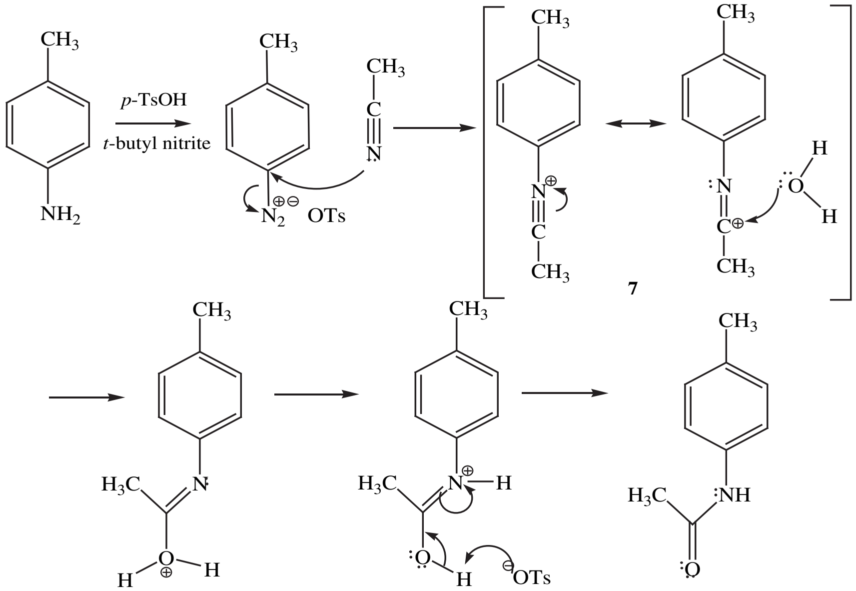
Entry	Substrate	Product **6**	Yield (%) (method 3)
1			78[b] 87[c]
2			89[a] 96[c]
3			84[a] 91[c]
4			20[a] 24[b] 74[c]
5			38[a] 45[b] 83[c]

[a] Room temperature, reaction time (6 h).
[b] Room temperature, reaction time (23 h).
[c] Reaction temperature (60 °C), reaction time (23 h).

The present reaction pathway may involve the formation of resonating structures **7** by an initial dominant attack of the tosylate salt with the acetonitrile solvent in place of the halogenating agent, which further leads to the synthesis of acetanilide in the presence of water. The formation of acetanilide was again confirmed in the absence of a brominating agent during the course of the reaction (Scheme 3).

3. Conclusion

In conclusion, this research demonstrates the synthesis of aromatic halides from various aniline derivatives via an arenediazonium tosylate salt using only catalytic amounts of Cu salt. The protocol is operationally simple, efficient, and industrially applicable; it does not require special anhydrous conditions and proceeds with good to high yield in most cases. In addition, the acetanilide synthesis is also observed with aniline and methyl-substituted anilines. We believe that this protocol is an effective compliment to the existing methods for halogenation and also establishes a wide applicability for the unusually stable arenediazonium tosylate salts. Further investigations are in progress



Scheme 3. Plausible mechanism for acetanilide synthesis.

concerning the application of arenediazonium tosylate salts as building blocks in various reactions.

4. Experimental

4.1. Materials and measurements

The melting points were uncorrected. The IR spectra were recorded on Mattson-5000(UNICAM). The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 300 MHz spectrometer. IR spectra were recorded on Varian 2000 FT-IR spectrometer and CHN analysis were carried out on varioMICRO V 1.9.4 CHN analyzer. Details for the reactions and yields of the pure isolated products are listed in Table 1–5.

4.2. Conversion of aryl amines to aryl bromides and chlorides: general procedure

4.2.1. Aryl bromides. Catalytic amounts of copper bromide (1 mol %) were added to a solution of aniline (1.0 equiv) in acetonitrile (20 ml), *p*-TsOH(1.2 equiv), sodium nitrite or *tert*-butyl nitrite (1.2 equiv), and brominating agent (2.0 equiv). The reaction mixture was stirred at the indicated reaction temperatures and times (Table 1 and 2). The evolution of N_2 was immediately observed. The solvent was removed by a rotary evaporator after completion of the reaction (confirmed by β-naphthol test and TLC). The solid was washed with water and extracted with CH_2Cl_2. The resulting solution was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The pure product was then collected by column chromatography using hexane: dichloromethane as eluting solvents. Physical and ^{1}H NMR data were identical to those of a commercially available sample of analytical purity.[29]

4.2.2. Aryl chlorides. *p*-TsOH (1.2 equiv), *tert*-butyl nitrite (2.0 equiv), benzyltriethylammoniumchloride (2.0 equiv), and catalytic amounts of copper chloride (1 mol %) were added to an acetonitrile solution (20 ml) of aniline (1.0 equiv). The reaction mixture was stirred at the indicated reaction temperatures and times (Table 3 and 4). The evolution of N_2 was immediately observed. The solvent was removed by rotary evaporator after completion of the reaction (confirmed by *β*-naphthol test and TLC). The crude residue was purified via column chromatography by using hexane/dichloromethane as the eluting solvent. Physical and ^{1}H NMR data were identical to those of a commercially available sample of analytical purity.[29]

4.2.3. Acetanilide. The reaction mixture of aniline (1.0 equiv), *p*-TsOH (1.2 equiv), *tert*-butyl nitrite (1.1 equiv), and TBAB (2.0 equiv) in acetonitrile (20 ml) was stirred at the mentioned reaction temperature and time (Table 5). The progress of reaction was monitored by TLC. After completion of reaction the solvent was evaporated by rotary evaporator. The crude solid was purified by column chromatography using hexane and dichloromethane as eluting solvents. Physical and ^{1}H NMR data were identical to those of a commercially available sample of analytical purity.[29]

*4.2.4. 2′-Methylacetanilide (**6o**).* White solid, mp: 98–100 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, 1H, J=6.0 Hz), 7.18 (t, 2H, J=8.4 Hz), 7.06 (t, 1H, J=6.0 Hz), 2.24 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 135.7, 130.6, 129.9, 126.8, 125.6, 123.8, 24.3, 17.9; IR (cm^{-1}) 3292, 3032, 2979, 1653, 1589, 1529, 1457, 756; found: C, 72.10; H,7.21; N,9.06. $C_9H_{11}NO$ requires C, 72.46; H, 7.43; N, 9.39%; MS *m*/*z* 42.9, 76.9, 105.8, 106.8, 107.8, 148.5, 149.7(M$^+$).

*4.2.5. 3′, 4′-Dimethylacetanilide (**6r**).* Ivory solid, mp: 96–98 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, 1H, J=3.0 Hz), 7.20 (dd, 1H, J=3.0, 3.1 Hz), 7.05 (d, 1H, J=8.4 Hz), 2.21 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 137.2, 135.7, 132.8, 130.0, 121.7, 117.8, 24.5, 20.0, 19.31; IR (cm^{-1}) 3289, 3125, 2967, 1664, 1610, 1539, 1444,824; found: C, 73.59; H, 7.78; N, 8.43. $C_{10}H_{13}NO$ requires C, 73.59; H, 8.03; N, 8.58%; MS *m*/*z* 42.8, 90.9, 105.8, 107.0, 119.8, 120.8, 121.8, 162.5, 163.7(M$^+$).

Acknowledgements

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Supplementary data

Supplementary data associated with this article contains NMR, IR and GC–MS spectra of 2′-methylacetanilide (**6o**) and 3′, 4′-dimethylacetanilide (**6r**), and physical and spectral data for all the known compounds. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.07.005. These data include MOL files and InChIKeys of the most important compounds described in this article.

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