Added catalyst-free, versatile and environment beneficial bromination of (hetero)aromatics using NBS in WEPA

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Abstract

The aromatic or heteroaromatic bromides are the quite common substrates in several organic transformations. The synthesis of arylbromides is challenging and required expensive catalytic systems or problematic organic solvents. This article unveils an environment beneficial, versatile and facile procedure for the synthesis of aryl/heteroaryl bromides using *N*-bromosuccinimide in water extract of pomegranate ash. The preparation of bromoarenes or bromoheteroarenes was accomplished under atmospheric conditions in the absence of added catalyst, promoter, problematic solvent and additives. The products were formed with greater rates in very high to quantitative yields using biowaste derived media shows the environmental benefits like utilization of waste, safer media, rich chemical economy, economic feasibility and dwindling the chemical waste, has eventual scope towards further explorations.

Graphic abstract

Keywords Water extract of pomegranate ash · *N*-Bromosuccinimide · Sustainable media · Nuclear bromination · Bromo(hetero)arenes · Economical process

1 Introduction

The nuclear bromination of aromatic or heteroaromatic compounds is the frequently used transformation in making highly reactive aryl/heteroaryl bromides. These bromides are the principal substrates in the synthesis

of biaryls, aryl amines, organometallics, cinnamate esters, functional materials and diverse biologically effective organics [1–7]. By virtue of this essentiality a sizeable efforts have been appeared in the literature for the preparation of aryl bromides and heteroaryl bromides. In this context, Das et al. [8–10] explored NBS/

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-019-1274-x>) contains supplementary material, which is available to authorized users.

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SN Applied Sciences (2019) 1:1281 | <https://doi.org/10.1007/s42452-019-1274-x>

Received: 20 July 2019 / Accepted: 12 September 2019 / Published online: 25 September 2019

sulfonic-acid-functionalized silica, NBS/NH₄OAc and NBS/PEG-400 systems for the nuclear brominations. Further, NH₄Br/oxone [11], CuBr₂/oxone [12], HBr/H₂O₂/AcOH [13], CaBr₂/Br₂ [14], NBS/*p*TSA [15], Br₂/lithium tetramethylpiperidide (LiTMP) [16], NH₄Br/H₂O₂/AcOH [17] and Br₂/LDH-WO₄/H₂O₂ [18] are the significant methods for this purpose. However, majority of these procedures require added catalysts, oxidants, non-conventional solvents, reagents or large reaction times were occasionally operated at harsh conditions. Most recently, NBS/PhSSPh (or PhSSiMe₃) [19], NBS/indoles [20], NBS/hexafluoroisopropanol [21], NBS/I₂ [22], NaBr/H₂O₂/AcOH [23] and 1,2-ethanedithiolbis(triphenylphosphonium)-ditribromide [24] were found attractive. Nevertheless, these also suffer with the necessity of catalysts, expensive solvents, oxidants or large reaction times. Therefore, it is extremely desirable to establish the operationally simple, cost-effective and substantially benign protocols for the synthesis of aryl/heteroaryl bromides.

NBS is the best reagent among all the conventional reagents that are employed for nuclear brominations, because, it makes easy the electrophilic substitutions under mild conditions, readily available, inexpensive and ease of handling [25]. Moreover, NBS has been explored as catalyst in several prevalent organic transformations [25].

Recently the agro-waste extracts (AWEs) are found as alternative and renewable media for the several significant organic reactions offers tremendous environmental benefits like sustainability, safeness, ease of preparation and choice of avoiding the volatile organic solvents, bases, ligands, and so on [5, 6, 26–29]. In this context, the ligand and (or) added base free Suzuki–Miyaura [6, 28], Sonogashira [28], Henry [2, 28], Ullmann [5] and Michael [30] reactions were developed in which the use of the AWEs found crucial. Further, the efficient protocols for the synthesis of 3-carboxycoumarins [31], bisenols [32], disulfides [29], phenols (from arylboronic acids) [26] and allylthioethers [33] were also appeared using AWEs, which act as sole catalysts as well as media. Furthermore, green chemistry reveals that the use of aqueous (or non toxic) media is the superior technique in decreasing the ecological pollution [34]. In pharmaceutical industry the organic solvents cover ~85% of the chemicals that are used can be recycled hardly at 50–80% rate [35] which generates enormous amount of environmental waste.

The economic and environmental impacts of the AWEs prompted us to investigate on these media in developing new synthetic methodologies. Thus, in continuation of our recent investigations on WEPA [5, 6, 36], we report here a green protocol for the bromination of arenes or heteroarenes using NBS in WEPA at room temperature (rt) under added catalyst and volatile solvent free aerobic conditions.

This protocol implies the future scope of bio-waste derived extract, WEPA in organic synthesis.

2 Experimental

2.1 General information

The aromatic and heteroaromatic compounds, NBS, solvents and other materials used in the present investigation were procured from Merck, Spectrochem, Sigma-Aldrich and Alfa-Aesar. The reaction progress was ensured by thin layer chromatography (TLC). The NBS was recrystallized in water prior to its use. Silica gel (60–120 mesh—Merck) packed glass columns were employed for the separation of brominated products using a mixture of EtOAc and hexanes. ¹³C & (or) ¹H NMR spectra were recorded using Bruker Avance 100/400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. Coupling constant (*J*) was represented in Hz and the chemical shifts (δ) in ppm with the signal pattern: s, singlet; m = multiplet; d, doublet; t, triplet; q = quartet; dd, doublet of doublet; and brs, broad singlet.

2.2 Experimental procedures

Preparation of WEPA [5, 6, 36] The small pieces of fairly dried pomegranate peels were burned to ash. 10 g of ash was suspended in 100 mL of distilled water. The resultant suspension was subjected for stirring at 80 °C for 1 h. Finally pale yellow extract (WEPA) was obtained by cooling and filtering the resultant mixture.

General experimental procedure Dissolved aryl or heteroaryl compound (**1**) (1 mmol) in a 3 mL mixture of WEPA and EtOH (5:1). 1.02 mmol of recrystallized NBS was then added and allowed the resultant mixture for stirring at rt. The bromination process was ensured by thin layer chromatography and after bromination (Table 2) the EtOH was evaporated in vacuo. Added 10 mL of EtOAc and 10 mL of distilled water to the resultant mixture, transferred to a separatory funnel and separated the organic (EtOAc) portion. Further extraction of aqueous layer was performed with EtOAc (2 × 7 mL) and all the EtOAc extracts were combined. Dried the combined EtOAc portions using anhydrous MgSO₄ and purified the products using column chromatography. The structures of all the aryl/heteroaryl bromides (**2**) were ascertained from their ¹³C NMR & (or) ¹H NMR and mass spectral data and these resembles the reported data. The characterization data and copies of ¹H & ¹³C NMR spectra of the products were provided at online supporting information.

3 Results and discussion

In the initial screening towards the optimization of the reaction conditions, we used to react 4-methylphenol (**1aa**) (1 mmol) with 0.5 mmol of NBS in 1.5 mL of WEPA at rt and observed the formation of 2-bromo-4-methylphenol (**2aa**) in 18% yield in 15 min (Table 1, entry 1). Further increase of media, (WEPA) to 2.0, 2.5 and 3.0 mL, formed the product, **2aa** in 25%, 39% and 39% yields in 15 min (Table 1, entries 2–4) indicates the requirement 2.5 mL of WEPA for this bromination. The addition of 0.5 mL of ethanol at this stage enhanced the yield of **2aa** to 48% in just 5 min (Table 1, entry 5). However the formation of < 2% of **2aa** along with 4% of 2,6-dibromo-4-methylphenol (**3**) was observed using ethanol as sole solvent (Table 1, entry 6) indicates ethanol helps only to dissolve the substances. The formation of quantitative yield of **2aa** was observed when the amount of NBS was enhanced to 1.02 mmol using a mixture of 2.5 mL of WEPA and 0.5 mL of ethanol (Table 1, entry 7). The reaction was then conducted at 0 °C, 50 °C and 80 °C using 1 mmol of **1aa**, 1.02 mmol of NBS, 2.5 mL of WEPA and 0.5 mL of ethanol, and identified the formation of quantitative yield of **2aa** (Table 1, entries 8–10) indicates these conditions are not showed any influence on the WEPA catalyzed bromination of **1aa**. We also investigated the influence of the excess amount of NBS on the

current reaction. In this connection we used 1.5 mmol and 2.02 mmol of NBS and found the formation of 2,6-dibromo-4-methylphenol (**3**) in 47% and 97% along with 51% and 0% of **2aa** (Table 1, entries 11 & 12), which indicates the requirement of 1.02 mmol of NBS for the selective monobromination of aromatic systems under the present experimental conditions. The optimized conditions were then exercised on a variety of aromatics or heteroaromatics and the results are listed in Table 2.

Phenols and anilines with electron-donating methyl, bromo, iodo and phenyl groups were made easily into their moniodo derivatives with high regioselectivity in 1–5 min with 96% to quantitative yields (Table 2, entries 2–8). Unsubstituted phenol (**1ai**) and aniline (**1aj**) were also found to be very quick in brominations under WEPA catalysis to give 91% and 93% yields of 4-bromophenol (**2ah**) and 4-bromoaniline (**2ai**) (Table 2, entries 9 & 10), however, minor amounts of positional isomers were observed in these two cases. *N,N*-Dimethyl (**1ak**), *N,N*-diethyl (**1al**) and *N*-acetyl (**1am**) anilines forms only *para* brominated products **2aj–2al** in 1–10 min (Table 2, entries 11–13). 2-Naphthol (**1an**), 2-naphthylamine (**1ao**) and 1-naphthylamine (**1ap**) gave the monobrominated products (**2am–2ao**) in 2 min with 92–quantitative yields (Table 2, entries 14–16) and minor amount of regio isomer was found with **1ap**.

Table 1 Optimization of reaction conditions

Entry	NBS (mmol)	Medium (mL)	Temperature (°C)	Time (min)	Isolated yield 1aa:3 (%)
1	0.50	WEPA (1.5)	Rt	15	18:0
2	0.50	WEPA (2.0)	Rt	15	25:0
3	0.50	WEPA (2.5)	Rt	15	39:0
4	0.50	WEPA (3.0)	Rt	15	39:0
5	0.50	WEPA (2.5) + EtOH (0.5)	Rt	5	48:0
6	0.50	EtOH (3.0)	Rt	60	< 2:4
7	1.02	WEPA (2.5) + EtOH (0.5)	Rt	1	Quantitative:0
8	1.02	WEPA (2.5) + EtOH (0.5)	0	5	Quantitative:0
9	1.02	WEPA (2.5) + EtOH (0.5)	50	1	Quantitative:0
10	1.02	WEPA (2.5) + EtOH (0.5)	80	1	Quantitative:0
11	1.50	WEPA (2.5) + EtOH (0.5)	Rt	1	51:47
12	2.02	WEPA (2.5) + EtOH (0.5)	Rt	1	0:97

Table 2 Bromination of (hetero)aromatics using NBS in WEPA

Entry	Substrate (1)	Time (min)	Product (2)	Isolated yield (%)
1	4-Methylphenol (1aa)	1	2aa	Quantitative
2	2-Methylphenol (1ab)	1	2ab	97
3	4-Methylaniline (1ac)	1	2ac	Quantitative
4	2-Methylaniline (1ad)	1	2ad	98
5	4-Bromoaniline (1ae)	1	2ae	97
6	2-Bromoaniline (1af)	1	2ae	Quantitative
7	4-Iodophenol (1ag)	1	2af	Quantitative
8	4-Aminobiphenyl (1ah)	5	2ag	96
9	Phenol (1ai)	1	2ah	91
10	Aniline (1aj)	1	2ai	93
11	<i>N,N</i> -Dimethylaniline (1ak)	1	2aj	Quantitative
12	<i>N,N</i> -Diethylaniline (1al)	1	2ak	Quantitative
13	Acetanilide (1am)	10	2al	92
14	2-Naphthol (1an)	2	2am	Quantitative
15	2-Naphthylamine (1ao)	2	2an	Quantitative
16	1-Naphthylamine (1ap)	2	2ao	92
17	Salicylaldehyde (1aq)	15	2ap	95
18	Vanillin (1ar)	5	2aq	97
19	2-Hydroxyacetophenone (1as)	15	2ar	92
20	2-Aminobenzoic acid (1at)	15	2as	93
21	2-Chloroaniline (1au)	10	2at	98
22	4-Aminoacetophenone (1av)	15	2au	95
23	4-Chloroaniline (1aw)	15	2av	96

Table 2 (continued)

Entry	Substrate (1)	Time (min)	Product (2)	Isolated yield (%)
24	4-Fluoroaniline (1ax)	5	2aw	96
25	4- <i>N,N</i> -Dimethylbenzaldehyde (1ay)	15	2ax	97
26	2-Aminopyridine (1az)	1	2ay	96
27	4- <i>N,N</i> -Dimethylaminopyridine (1ba)	1	2az	Quantitative
28	2-Amino-4-hydroxy-6-methylpyrimidine (1bb)	10	2ba	93

Reaction conditions **1** (1 mmol), NBS (1.02 mmol), WEPA (2.5 mL) and EtOH (0.5 mL) at rt in open air

Phenols with electron-withdrawing, formyl and acetyl groups (**1aq–1as**) and anilines with carboxyl, chloro, acetyl and fluoro groups (**1at–1aw**) formed excellent yields (92–97%) of monobrominated products (**2ap–2aw**) with high regioselectivity in 5–15 min (Table 2, entries 17–24). 4-*N,N*-Dimethylbenzaldehyde (**1ay**) was also produced 97% of 3-bromo-4-*N,N*-dimethylbenzaldehyde (**2ax**) in 15 min (Table 2, entry 25).

The heterocyclic arenes such as 2-aminopyridine (**1bz**), 4-*N,N*-dimethylaminopyridine (**1ba**) and 2-amino-4-hydroxy-6-methylpyrimidine (**1bb**) were also observed as good substrates to form 93% to quantitative yields in 1–10 min under WEPA catalytic mediations (Table 2, entries 26–28).

A high chemoselectivity i.e., the selectivity of aromatic groups over α -position of α -methyl carbonyls (**1am**, **1as** & **1av**) and benzylic methyl groups (**1aa–1ad**) was observed under the current development. Further, the high regioselectivity (i.e., the selectivity over the possible reactive sites) was the noteworthy future of this protocol. Moreover, the base sensitive amide (**1am**) and methyl keto (**1as** & **1av**) groups were also observed to be unaffected using these experimental conditions is an added advantage.

The process of WEPA accelerated bromination of aromatics/heteroaromatics is not fully understood at this point, but, it may be related to the electrophilic brominative cyclization of alkynoic acids in the presence of NBS and K_2CO_3 [37]. The species, M^+B^- of WEPA generates the electrophilic bromine intermediate, Br^+B^- which involves in substitution of heteroaromatic/aromatic systems (**1**) to give heteroaryl/aryl bromides (**2**) (Scheme 1). Further activation of aromatics/heteroaromatics is also possible in basic media WEPA by the polarization of heteroatom(oxygen or nitrogen)–hydrogen bonds. The high reactivity of aromatics/heteroaromatics towards bromination in WEPA leads further scope of investigations.

Scheme 1 Plausible pathway of bromination in NBS/WEPA system

4 Conclusions

In summary, a versatile, novel and highly economical protocol has been put forward for the monobromination of aromatics/heteroaromatics using WEPA as a catalytic media. The reactions can be implemented at ambient aerobic conditions using biowaste derived WEPA. The functional groups including hydroxy, amino, benzylic-methyl, formyl, methyl keto, carboxyl, amide and *N,N*-dialkyl got tolerated under WEPA promoted brominations of aromatics and heteroaromatics. A very high to quantitative yields of brominated products, utilization of agro-waste extract as catalytic media, actual usage of renewable resources, rich position, monobromination and chemoselectivity, high scope of reactants and easy operation of the reactions are the outstanding features of this finding. These findings open further scope of high-quality research using agro-waste derived catalytic media.

Acknowledgements Authors are grateful to SERB, New Delhi for the financial support (No. SB/FT/CS-009/2014). JL thanks DST, New Delhi for INSPIRE fellowship (No. IF150772) and BRN thanks CSIR, New Delhi for JRF (No. 09/1076(0003)/2018-EMR-I).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

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