LETTER

Water extract of pomegranate ash–I$_2$ as sustainable system for external oxidant/metal/catalyst-free oxidative iodination of (hetero)arenes

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ABSTRACT

Utilization of waste-derived materials for industrially pertinent chemical transformations is highly challenging and offers sustainable solution to waste management. Despite several difficulties in the manufacture of aryl iodides (AIs), which are the fundamental substrates in organic synthesis, we report here, an added oxidant/metal/catalyst/additive and problematic solvent-free versatile and straightforward protocol for the synthesis of AIs using molecular iodine (I$_2$) in water extract of pomegranate ash (WEPA). These transformations were performed at room temperature (rt) and the reactions takes place in 5–20 min to give 83–99% yields of AIs. WEPA was characterized by using XPS, EDX, XRF, XRD, and FTIR analysis and a plausible mechanism has been established based on these analyses along with some control experiments. Further, the products were purified by recrystallization technique. This work with intrinsic sustainability, high substrate feasibility, utilization of biorenewable catalystytic media, ease of execution and separation of products, and added oxidant/catalyst/metal and additive-free conditions may become one among the forefront sustainable procedures in making AIs. The use of waste-derived WEPA as catalystytic media for this iodination is the novelty of this method and may be used these AIs for further in-process transformations (e.g. cross-couplings, nucleophilic reactions, etc.) to access fine chemicals.

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1. Introduction

The population of the world was predicted as 9.7 and 11.0 billion people by 2050 and 2100 from present 7.7 billion \(1,2\). The growing population owing to the utilization of food, energy, feed, fiber, etc. can create enormous amounts of waste. According to the World Bank report \(~\sim 2017\) metric tons of waste have been produced globally in 2018 and may reach \(~\sim 2586\) and \(~\sim 3401\) metric tons by 2030 and 2050 \(2,3\). The content of organic matter of this waste is 40–50% and its disposal in landfill has several environmental problems like liberation of greenhouse gases (GHGs), emanation of odor, contamination of surface as well as ground water, transmissions via vector such as birds, mammals and insects \(2,4\). Hence, there is a large demand in the conversion of these wastes by physical or chemical means into useful products including biofuels, animal feed and feedstocks of biochemical and chemical relevance \(2,4,5\). Furthermore, the diminishing delivery associated with the increasing demand for fossil-based depleting substances impetus in pursuit for biorenewable sources of chemical substances \(6–10\). In this connection the utilization of waste-derived products as useful feedstocks, auxiliaries and solvents is the challenging, sustainable, highly economic, and convenient processes in chemical synthesis.

Recently, the extracts of ashes of biorenewable wastes are considered as emerging green media/catalysts in the evolution of significant synthetic transformations such as Suzuki–Miyaura, Ullmann, Sonogashira, Henry, Dakin, Knoevenagel, and Michael addition reactions \(2\). These extracts are also explored in the construction of biselenols, coumarins, C–P bonds, allylsulfides, organic disulfides, and peptide bonds \(2\). The ashes of biorenewable wastes are also reported as sustainable catalysts in the production of biodiesel \(2,11\) and chiral tert-butylsulfinyl-laldimines \(12\). The sturdy attributes of these media/catalysts include the strategic ejection of commercial and depleting resources-based bases and solvents, effective utilization of waste as biorenewable resources, and sustainable media – catalyst system. The choice of the water as a solvent is a strategic method to minimize the use of volatile organic compounds (VOCs), which are the major culprits of environmental pollution and volatile solvents occupy about 85% of chemicals utilized by the pharma industry can merely be recovered at the rate, 50–80% \(13\).

Nature, especially marine organism has evidenced a tremendous number of organic iodine compounds \(14,15\). Most of these natural iodides and their synthetic analogues were turned out to be biologically indispensable \(15,16\). Medicinal applications of radioiodinated organic compounds are also familiar in radio imaging towards the assessment and treatment of diseases like thyroid disorders \(17\), cancers, and neurological defects \(18\). Additionally, organic halides are the highly reactive and fundamental substrates in numerous organic transformations including C–C and C–heteroatom couplings, organometallations, hypervalent iodine syntheses, and free-radical initiations \(19,20\). Despite the most reactivity of organic iodides, particularly, aryl iodides (AIs) (caused by the easily frangible C–I bond over C–Br and C–Cl bonds of aryl bromides and chlorides), the commercially less availability and relatively high cost of AIs restricted their widespread aptness in chemical synthesis \(19,21\). The commercial scarcity of AIs is due to the limited methods and reagents that exist for their preparation than aryl bromides and aryl chlorides, perhaps, making the C–I bond is complicated than C–Br and C–Cl. Molecular iodine \(22,23\), N-iodosuccinimide (NIS) \(24\), ICI \(25\), dichloroiodates \(26\), KI \(27\), and polyhalogenated reagents \(28,29\) are frequently used for AIs synthesis. Although the substitution reactions of aryl diazonium salts, aryloboronic acids, and aryl bromides are the other infrequently used methods to access AIs, these require metals or harsh conditions \(24\) are less atom economic in the green chemistry standpoint.

Besides several environmental benefits, iodine is the simplest, inexpensive, and readily available reagent, but the general low reactivity of I\(_2\) in aromatic electrophilic substitutions is very unfortunate and hence, the use of an oxidant is obligatory \(30\). In this vein, I\(_2\)–H\(_3\)P\(_2\)Mo\(_{10}\)O\(_{40}\)–O\(_2\)–CH\(_2\)CN \(31\), I\(_2\)–poly-vinylpyrrolidone supported H\(_2\)O\(_2\)–H\(_3\)PW\(_{12}\)O\(_{40}\)–DCM \(32\), I\(_2\)–Fe(NO\(_3\))\(_3\)–1.5 N\(_2\)O\(_4\)–charcoal–DCM \(33\), I\(_2\)–NO\(_2\)–CH\(_3\)CN \(22\), I\(_2\)–H\(_2\)O\(_2\)–H\(_2\)O \(34\), I\(_2\)–Al\(_2\)O\(_3\)–benzene \(35\), I\(_2\)–AgSO\(_4\)–EtOH \(36\), I\(_2\)–Ph(OCCF\(_3\))\(_2\)–pyridine–DCM \(37\), I\(_2\)–SiO\(_2\)–Fe(NO\(_3\))\(_3\)–H\(_2\)O–DCM \(38\), I\(_2\)–(Bu\(_4\)N)\(_2\)SO\(_4\)–CH\(_2\)CN \(39\), I\(_2\)–(NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) \(40\), I\(_2\)–Pb(OAc)\(_4\)–AcOH–Ac\(_2\)O \(41\), I\(_2\)–NaNO\(_2\)–HCl–trifluoroethanol \(42\), IBX–I\(_2\)–TFA–DMSO/TFA/CH\(_3\)CN/AcOH \(43\), I\(_2\)–AgOTf/AcOH/AcOAc \(44\), I\(_2\)–NaNO\(_2\)–air–silica-supported H\(_2\)SO\(_4\)–CH\(_2\)CN \(45\), and (PhiO)\(_n\)–NH\(_4\)–K\(_2\)PO\(_4\)–MeOH \(23\) systems are noticed as synthetically useful for AIs access. Some of the recent methods in aryl iodonations using I\(_2\) as a source of iodine are shown in Scheme 1. In addition to the obligations of oxidant and (or) catalyst the reported procedures necessitate hazardous/problematic solvents, additives, high temperature, or large reaction times, and thus it is necessary to develop new protocols to access the AIs at mild and environment friendly conditions. Moreover, the iodonation with molecular iodine reveals the natural process of making organic iodides \(46\).
Therefore, we directed to develop an economical and green protocol for easy synthesis of AIs and found WEPA is advantageous as bioresource-based catalyst and media in this pursuit. In continuation to our research on WEPA (12,47–52), we disclose here an added catalyst, oxidant, volatile/hazardous solvent, metal and additive-free, versatile protocol for the preparation of AIs in WEPA. Furthermore, in pursuance of the green chemistry philosophy, the use of aqueous media and renewable substances greatly reduce the ecological impacts caused by the application of problematic solvents and depleting materials (usually VOCs) (12,52–54). The application of biorenewable and waste-derived WEPA for a very quick synthesis of (hetero)aryl iodides by avoiding non-renewable resources-based oxidants, catalysts, promoters, and solvents is the novelty and the innovative development of this work.

2. Materials and methods

2.1. General information

Aryl/heteroaryl substrates used in the current conversion are obtained from AVRA synthesis, Alfa Aesar, Sigma-Aldrich, Spectrochem, and Sd-fine were employed as they obtained. Silica gel-based thin layer chromatography (TLC) (Merck) was used to predict the reaction progress using UV light visualization. The (hetero)aryl iodides are settled their structures using $^1$H & $^{13}$C NMR and MS spectral data. $^1$H & $^{13}$C NMR spectra were obtained using Bruker Avance (Billerica, MA, USA) 400/100 MHz spectrometer. X-ray fluorescence (XRF) analysis was performed using wavelength-dispersive XRF spectrometry (Philips PW-2440 Magix-Pro® model, Eindhoven, The Netherlands). Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) data were obtained using JEOL JST-IT-500 (Tokyo, Japan) instrument. FTIR of WEPA has been measured using Bruker (Billerica, MA, USA) ALPHA-II ECO-ATR model compact FTIR spectrometer. The X-ray diffraction (XRD) patterns were recorded using Rigaku MiniFlex600 (Tokyo, Japan) instrument. The X-ray photoelectron spectra (XPS) were recorded using Thermo Scientific (USA) ESCALB 250 model instrument with the monochromatic Al Kα X-ray source.

2.2. Preparation of WEPA

WEPA was made adopting our recent publications (12,47–49). Pomegranate peels were obtained from a fresh pomegranates collection. Washed the peels with distilled water and dried under shade was made into small pieces. The pieces of peels were made to ash and 10 g of ash was macerated in 100 mL distilled water, stirred at rt for 2 h has been filtered to give a light pale yellow colored extract called WEPA. WEPA was characterized for the available chemical constituents using its XPS, EDX, XRF, XRD, and FTIR data (Figure 1) (please see the discussion in Section 3.1).

2.3. General procedure for the synthesis of AIs

WEPA (1.5 mL), I$_2$ (1.05 mmol), and EtOH (0.2 mL) in a reaction flask were allowed to stir at rt for 5 min. Added all at once the aryl/heteroaryl substrate (1) (1 mmol) to a mixture containing 0.3 mL EtOH and 1.0 mL of WEPA and the resultant mixture was subjected for stirring at rt for appropriate time as indicated by TLC. Added 10 mL cold water and the precipitate obtained has been separated by filtration was washed using
cold water. Pure products are obtained via recrystallization using water–ethanol mixture. The structures of products are detected using $^1$H & $^{13}$C NMR and Mass spectral data and the copies of $^1$H & $^{13}$C NMR spectra have been provided in supplementary material.

2.3.1. 4-Iodoaniline (2ab) (24)
Dark brown liquid; Yield: 95%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.40 (d, $J$ = 8.8 Hz, 2H), 6.47 (d, $J$ = 8.8 Hz, 2H), 3.02 (brs, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.0, 137.9, 117.3, 79.4 ppm; MS (EI): 220 (M + 1).

2.3.2. 4-Bromo-2-iodoaniline (2ag) (55)
Pale red solid; Yield: 99%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.66 (d, $J$ = 2.3 Hz, 1H), 7.14 (dd, $J$ = 2.3, 8.6 Hz, 1H), 6.54 (d, $J$ = 8.6 Hz, 1H), 4.03 (brs, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.9, 140.3, 132.0, 115.5, 109.8, 84.0 ppm; MS (EI): 298 (M + 1).

2.3.3. 2-Chloro-4-iodoaniline (2ah) (24)
Colorless solid; Yield: 95%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (d, $J$ = 2.0 Hz, 1H), 7.21 (dd, $J$ = 2.0, 8.6 Hz, 1H), 6.42 (d, $J$ = 8.6 Hz, 1H), 3.96 (s, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.6, 137.1, 136.3, 120.2, 117.4, 77.9 ppm; MS (EI): 254 (M + 1).

2.3.4. 4-Amino-3-iodobiphenyl (2ak) (55)
Pale yellow solid; Yield: 91%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.89 (d, $J$ = 1.8 Hz, 1H), 7.49 (d, $J$ = 7.8 Hz, 2H), 7.43-7.25 (m, 3H), 7.31-7.23 (m, 1H), 6.80 (d, $J$ = 8.3 Hz, 1H), 4.14 (brs, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.0, 139.6, 137.3, 133.2, 128.7, 128.1, 126.7, 126.4, 114.7, 84.5 ppm; MS (EI): 296 (M + 1).

2.3.5. 4-Fluoro-2-iodoaniline (2an) (56)
Brown solid; Yield: 94%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31 (d, $J$ = 2.9, 8.1 Hz, 1H), 6.86-6.79 (m, 1H), 6.57 (dd, $J$ = 4.9, 8.9 Hz, 1H), 3.87 (brs, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.7 (d, $J$ = 240.2 Hz), 143.1 (d, $J$ = 1.3 Hz), 124.5 (d, $J$ = 24.6 Hz), 115.8 (d, $J$ = 22.0 Hz), 114.4 (d, $J$ = 7.3 Hz), 82.6 (d, $J$ = 8.4 Hz) ppm; MS (EI): 238 (M + 1).

2.3.6. 4-Iodoanisole (2ap) (24)
Colorless solid; Yield: 98%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55 (d, $J$ = 8.2 Hz, 2H), 6.68 (d, $J$ = 8.2 Hz, 2H), 3.78 (s, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.4, 138.1, 116.3, 82.6, 55.3 ppm; MS (EI): 235 (M + 1).

2.3.7. 4-Iodophenol (2ar) (24)
Colorless semi solid; Yield: 94%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.51 (d, $J$ = 8.9 Hz, 2H), 6.62 (d, $J$ = 8.9 Hz, 2H), 4.99 (brs, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.2, 138.4, 117.8, 82.7 ppm; MS (EI): 221 (M + 1).

2.3.8. 1-Iodo-2-naphthol (2at) (57)
Pale brown solid; Yield: 99%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J$ = 8.4 Hz, 1H), 7.78-7.71 (m, 2H), 7.55 (t, $J$ = 7.9 Hz, 1H), 7.40-7.36 (m, 3H), 7.18 (d, $J$ = 7.8 Hz, 1H), 7.06 (d, $J$ = 7.4 Hz, 1H), 6.93 (d, $J$ = 7.4 Hz, 1H), 6.80 (d, $J$ = 7.2 Hz, 1H), 6.40 (d, $J$ = 7.2 Hz, 1H), 6.20 (d, $J$ = 7.0 Hz, 1H), 6.00 (d, $J$ = 7.0 Hz, 1H), 5.80 (d, $J$ = 7.0 Hz, 1H), 5.60 (d, $J$ = 7.0 Hz, 1H), 5.40 (d, $J$ = 7.0 Hz, 1H), 5.20 (d, $J$ = 7.0 Hz, 1H), 5.00 (d, $J$ = 7.0 Hz, 1H), 4.80 (d, $J$ = 7.0 Hz, 1H), 4.60 (d, $J$ = 7.0 Hz, 1H), 4.40 (d, $J$ = 7.0 Hz, 1H), 4.20 (d, $J$ = 7.0 Hz, 1H), 4.00 (d, $J$ = 7.0 Hz, 1H), 3.80 (d, $J$ = 7.0 Hz, 1H), 3.60 (d, $J$ = 7.0 Hz, 1H), 3.40 (d, $J$ = 7.0 Hz, 1H), 3.20 (d, $J$ = 7.0 Hz, 1H), 3.00 (d, $J$ = 7.0 Hz, 1H), 2.80 (d, $J$ = 7.0 Hz, 1H), 2.60 (d, $J$ = 7.0 Hz, 1H), 2.40 (d, $J$ = 7.0 Hz, 1H), 2.20 (d, $J$ = 7.0 Hz, 1H), 2.00 (d, $J$ = 7.0 Hz, 1H), 1.80 (d, $J$ = 7.0 Hz, 1H), 1.60 (d, $J$ = 7.0 Hz, 1H), 1.40 (d, $J$ = 7.0 Hz, 1H), 1.20 (d, $J$ = 7.0 Hz, 1H), 1.00 (d, $J$ = 7.0 Hz, 1H), 0.80 (d, $J$ = 7.0 Hz, 1H), 0.60 (d, $J$ = 7.0 Hz, 1H), 0.40 (d, $J$ = 7.0 Hz, 1H), 0.20 (d, $J$ = 7.0 Hz, 1H), 0.00 (d, $J$ = 7.0 Hz, 1H).
8.3 Hz, 1H), 7.38 (t, J = 8.3 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 6.79 (brs, 1H) ppm; MS (EI): 271 (M + 1).

2.3.9. 2-Bromo-4-iodophenol (2a) (58)
Pale yellow solid; Yield: 98%; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.68 (d, J = 2.0 Hz, 1H), 7.42 (dd, J = 2.0, 8.6 Hz, 1H), 6.71 (d, J = 8.6 Hz, 1H), 5.52 (brs, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 152.3, 139.6, 138.0, 118.1, 111.3, 82.0 ppm; MS (EI): 299 (M + 1).

2.3.10. 2-Hydroxy-5-iodoacetophenone (2b) (59)
Pale yellow solid; Yield: 90%; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.91 (d, J = 2.3 Hz, 1H), 7.71 (dd, J = 2.3, 8.9 Hz, 1H), 6.78 (d, J = 8.9 Hz, 1H), 2.62 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 203.4, 162.0, 144.7, 139.0, 121.8, 120.9, 79.6, 26.7 ppm; MS (EI): 263 (M + 1).

2.3.11. 5-Iodoacetovanillone (2ax) (60)
Colorless solid; Yield: 93%; $^1$H NMR (400 MHz, CDCl$_3$): δ 9.77 (s, 1H), 7.66 (d, J = 1.7 Hz, 1H), 7.38 (d, J = 1.7 Hz, 1H), 6.68 (brs, 1H), 3.98 (s, 3H); 2.54 (s, 3H) ppm; MS (EI): 293 (M + 1).

2.3.12. 5-Iodovanillin (2av) (61)
Colorless solid; Yield: 96%; $^1$H NMR (400 MHz, CDCl$_3$): δ 10.49 (brs, 1H), 7.60 (s, 2H) ppm; 13C NMR (100 MHz, CDCl$_3$): δ 189.5, 151.4, 146.5, 136.2, 131.0, 108.6, 80.4, 56.5 ppm; MS (EI): 279 (M + 1).

2.3.13. 2,4-Dihydroxy-3-iodoacetophenone (2az) (62)
Yellow solid; Yield: 93%; $^1$H NMR (400 MHz, CDCl$_3$): δ 13.76 (brs, 1H), 7.66 (d, J = 8.7 Hz, 1H), 6.62 (d, J = 8.7 Hz, 1H), 6.18 (brs, 1H), 2.61 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 202.3, 163.5, 161.7, 132.6, 114.0, 106.8, 26.0 ppm; MS (EI): 279 (M + 1).

2.3.14. 4-Iodopyrazole (2ba) (63)
Colorless solid; Yield: 95%; $^1$H NMR (400 MHz, CDCl$_3$): δ 10.49 (brs, 1H), 7.60 (s, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.8, 56.5 ppm; MS (EI): 195 (M + 1).

2.3.15. 2-Amino-5-iodopyridine (2bb) (64)
Pale yellow solid; Yield: 96%; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.22 (d, J = 1.7 Hz, 1H), 7.63 (dd, J = 1.7, 8.7 Hz, 1H), 6.36 (d, J = 8.7 Hz, 1H), 4.52 (brs, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 157.2, 153.6, 145.4, 110.9, 77.8 ppm; MS (EI): 221 (M + 1).

2.3.16. 2-Amino-5-bromo-3-iodopyridine (2bd) (65)
Pale yellow solid; Yield: 94%; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.05 (d, J = 2.0 Hz, 1H), 7.95 (d, J = 2.0 Hz, 1H), 5.07 (brs, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.4, 148.4, 148.1, 107.2, 77.6 ppm; MS (EI): 299 (M + 1).

3. Results and discussion
3.1. Characterization of WEPA
The XPS (48) (see supplementary material) and EDX analysis (Figure 1(d)) indicates the presence of large quantities of K and O in WEPA. XRF analysis of dried WEPA showed (Table 1) the major constituents as K$_2$O (66.513%), Cl (19.393%), SO$_3$ (3.892%), Na$_2$O (2.197%), MgO (1.895%), SiO$_2$ (1.926%), and CaO (2.112%) along with other minor metallic and non-metallic components and the quantities of constituents are found to be similar with our recent XRF analysis (Table 1) (12,51) provides crucial information on the qualities of the chemical constituents of WEPA. The XRF data resembles the XPS data of WEPA for the elements present in it (48). Further, the EDX data of freshly prepared WEPA (Figure 1(d)) was also found to show good agreement with our reported EDX data at different time periods (12,48,49) and this can indicate the chemical constituents (about both the quantity and quality) are constant in WEPA. The SEM images (Figure 1(a–c)) of pale yellow powder received after evaporation of WEPA have been showing a uniform, smooth, and well-defined plate-like morphology of its surface (12,66,67).

The XRD analysis (Figure 2) indicates the presence of K, O, Mg, Cl, Ca, and C in WEPA. The appearance of peaks in XRD at 2θ = 25.69°, 28.39°, 30.21°, 32.21°, 36.41°, 40.55°, and 50.21° signifies the presence of K$_2$O (11,68,69). Two peaks at 2θ = 37.79° and 66.41° indicate

| Entry | Compound | Current | Reported (12,51) | Unit |
|-------|----------|---------|-----------------|------|
| 1     | K$_2$O   | 66.513  | 64.309          | %    |
| 2     | Cl       | 19.393  | 23.504          | %    |
| 3     | SiO$_2$  | 1.926   | 1.577           | %    |
| 4     | MgO      | 1.895   | 1.599           | %    |
| 5     | Na$_2$O  | 2.197   | 2.629           | %    |
| 6     | Fe$_2$O$_3$ | 0.152  | 936 (ppm)      | %    |
| 7     | ZnO      | 71.8    | 35.3 (Zn)      | ppm  |
| 8     | CaO      | 2.112   | 1.545           | %    |
| 9     | SrO      | 0.132   | –               | %    |
| 10    | SO$_3$   | 3.892   | 4.331           | %    |
| 11    | P$_2$O$_5$ | 576.4  | 571.7          | ppm  |
| 12    | Al$_2$O$_3$ | 0.236  | 0.131          | %    |
| 13    | Cu       | 193.6   | 70.8            | ppm  |
| 14    | Br       | 0.136   | 0.179           | %    |
| 15    | Cr$_2$O$_3$ | 11.4    | –              | %    |
| 16    | MnO      | 51.2    | –               | ppm  |
| 17    | TiO$_2$  | 19.2    | 38.4            | ppm  |
| 18    | Y        | 6.5     | 5.9             | ppm  |
| 19    | Rb       | –       | 251.3           | ppm  |
| 20    | Bi       | –       | 38.4            | ppm  |
| 21    | Ni       | –       | 65.1            | ppm  |

These data are based on semi-quantitative analysis.
CaO (11,70). XRD peaks at 42.95° and 73.65° represents MgO (71) and two peaks at 2θ = 12.77° and 46.05° correspond to Na2O (72,73). The peaks at 28.39° and 39.11° represents KCl (74) and two peaks at 2θ = 29.69° and 34.19° represents K2CO3 (68) in WEPA.

The peaks at 1616, 1450, and 1365 cm⁻¹ in the FTIR spectrum of WEPA (Figure 3) represents C = O groups (11,75). The peaks at 1130, 1060, and 817 cm⁻¹ represent the K–O bond (11,55). The peaks at 1573, 701, and 609 cm⁻¹ indicate Ca–O bond asymmetric and symmetric stretching (11,75). The absorption at 879 cm⁻¹ corresponds to Mg–O–Mg (11,75). The shoulder peaks around 2200 cm⁻¹ represent adsorbed CO2 on metal ions surface (11,75). The FTIR and XRD analysis of WEPA used for this investigation also resembles the XRF, EDX, and XPS analysis and also with the reported
EDX, XRD, and FTIR data (12,48,49). Hence, the comparable results at different time intervals using a variety of analytical methods may reveal the presence of chemical constituents is constant in WEPA and are indicated by its XRF data. Further, the titration of WEPA with oxalic acid was indicated the ∼0.09 N base is present in WEPA.

3.2. Investigation of WEPA for iodination of (hetero)arenes

We started the present quest using 2-bromoaniline (1aa) (1 mmol), WEPA (1.5 mL), and 0.55 mmol of I₂, and was identified the creation of 2% of 2-bromo-4-iodoaniline (2aa) in 20 min at rt (Table 2, entry 1). The increase of I₂ to 1.05 mmol significantly increased the yield of 2aa to 61% and further increase of I₂ to 1.55 mmol showed no improvement (Table 2, entries, 2 & 3). The increase of the amount of WEPA to 2.0, 2.5, and 3.0 mL has produced the yields of 2aa as 67%, 75%, and 76% in 20, 10, and 10 min using 1.05 mmol of I₂ (Table 2, entries, 4–6). These results indicated that this iodination requires 1.05 mmol of I₂ and 2.5 mL WEPA. At this stage the 0.5 mL addition of ethanol resulted in nearly quantitative yields (99%) of 2aa (Table 2, entry 7), it may be because of sufficient solubility of both the 1aa and I₂. Further, no sole effect of EtOH was concluded by reacting 1aa and I₂ in 3 mL ethanol (Table 2, entry 8).

With these optimized reaction criteria, we explored the potency of this method to a wide array of substrates and exemplified the results in Table 3. Anilines, phenols, and aryl methyl ethers with an array of functional groups were made into iodoaromatics under present conditions (Table 3, products, 2ab–2ao). Trace amounts of regioisomers were found in case of aniline (1ab) and 1-naphthylamine (1al). The I₂–(Bu₄N)₂S₂O₈–CH₃CN system (39) was required large reaction time (24 h) to produce 4-N,N-dimethylamono-1-iodobenzene (2ac) in 88% from N,N-dimethylamonobenzene, however, this method produces 96% of 2ac from the same substrate in just 10 min (Table 3).

Aryl methyl ethers such as anisole (1ap) and 6-bromo-2-methoxynaphthalene (1aq) have also given excellent yields (98% and 83%) of their iodinated analogues, 2ap and 2aq in 15 min. No trace of regioisomers was identified in these cases.

Phenols with electron releasing (bromo), neutral (hydrogen), and electron-withdrawing (benzo, acetyl, and formyl) groups were readily converted to iodinated products in 5–20 min in 92–99% yields (Table 3, products, 2ar–2az). Formation of negligible amounts of iso-meric iodides was observed with phenol (1ar) and 1-naphthol (1as). The formation of 92% of 4-iodophenol (2ar) from 1ar using I₂–(Bu₄N)₂S₂O₈–CH₃CN system (39) required 30 h, while the present methods are very advantageous to deliver the 94% of 2ar in 5 min. The substrates with mono electron-withdrawing group substituents, such as chlorobenzene, benzaldehyde, aceto-phenone, and nitrobenzene did not deliver iodination products under these mild conditions.

Finally, the heteroaromatics such as pyrazole (1ba), 2-aminopyridine (1bb), 2-amino-3-bromopyridine (1bc), 2-amino-5-bromopyridine (1bd), and 4-N,N-dimethylami-nopyridine (1be) were also found to form the monoiodilated products (2ba–2be) with high rates (5–10 min) in excellent yields (94–99%) under current conditions.

In most of these reactions, the mono-iodination products are formed with high position selectivity and

Table 2. Optimization of reaction conditions.

| Entry | Amount of I₂ (mmol) | WEPA (mL) | EtOH (mL) | Time | Isolated Yield (%) |
|-------|---------------------|-----------|-----------|------|--------------------|
| 1     | 0.55                | 1.5       | –         | 20 min | 29                 |
| 2     | 1.05                | 1.5       | –         | 20 min | 61                 |
| 3     | 1.05                | 2.0       | –         | 20 min | 61                 |
| 4     | 1.05                | 1.5       | –         | 20 min | 67                 |
| 5     | 1.05                | 2.5       | –         | 10 min | 75                 |
| 6     | 1.05                | 3.0       | –         | 10 min | 76                 |
| 7     | 1.05                | 2.5       | 0.5       | 5 min  | 99                 |
| 8     | 1.05                | 3.0       | 2.5       | 24 h   | trace              |

*Reaction conditions: 1aa (1 mmol) at rt in open-air.*
hence WEPA catalyzed oxidative iodination of (hetero)-arenes are significantly regioselective. However, no selectivity over mono-iodination has resulted with I₂/H₂O₂ (34) and the formation of large quantities of regioisomers on certain substrates was reported with I₂/Al₂O₃ (35) and I₂/(NH₄)₂Ce(NO₃)₆ (40). Furthermore, the iodo(hetero)arenes are separated by simple crystallization technique by eliminating the routine extraction and column chromatography thereby avoiding the use of organic solvents (as extracting and eluting solvents) and other chemical substances. From the global sustainability point-of-view, the development of nature mimicking/nature derived systems for conducting the reactions at ambient conditions by avoiding/reducing the use of volatile organics is highly useful (2,12,76–80). Hence, this protocol is highly beneficial for the synthesis (hetero)aryl iodides, since, it uses naturally derived material as catalyst and works at depleting source-based oxidant/solvent/additive-free ambient conditions.

3.3. Mechanistic features

Based on the XPS, EDX, FTIR, XRD, and XRF investigations, the dried WEPA consists of high amounts of K₂O (∼66.5%) and KCl (∼19%) (Section 2.1). It is also known that the K₂O is highly reactive with water to produce KOH (12,51,56). Based on these facts the WEPA contains KOH and KCl in large (relative) quantities. Towards understanding the influence of these substances on the present conversion as well as the mechanism of present C–H iodination, some

| Table 3. Iodination of aromatics or heteroaromatics using I₂ in WEPA. |
| --- |
| Iodination of aromatics or heteroaromatics using I₂ in WEPA. |
| **Condition** | **Product** | **Time** | **Yield** |
| --- | --- | --- | --- |
| 1 (1 mmol), I₂ (1.05 mmol), WEPA (2.5 mL) and EtOH (0.5 mL) at rt in open-air. | 2ab | 5 min | 95% |
| 2ac | 10 min | 96% |
| 2ad | 10 min | 98% |
| 2ae | 10 min | 99% |
| 2af | 15 min | 92% |
| 2ag | 10 min | 99% |
| 2ah | 10 min | 95% |
| 2ai | 10 min | 96% |
| 2aj | 5 min | 98% |
| 2al | 10 min | 99% |
| 2ak | 15 min | 91% |
| 2am | 15 min | 91% |
| 2an | 15 min | 94% |
| 2ao | 15 min | 93% |
| 2ap | 15 min | 98% |
| 2aq | 15 min | 94% |
| 2ar | 5 min | 94% |
| 2as | 5 min | 93% |
| 2at | 5 min | 93% |
| 2au | 10 min | 98% |
| 2av | 20 min | 90% |
| 2aw | 15 min | 92% |
| 2ax | 15 min | 93% |
| 2ay | 15 min | 96% |
| 2az | 10 min | 93% |
| 2ba | 5 min | 95% |
| 2bb | 10 min | 96% |
| 2bc | 10 min | 95% |
| 2bd | 10 min | 94% |
| 2be | 5 min | 99% |

*Reaction conditions: 1 (1 mmol), I₂ (1.05 mmol), WEPA (2.5 mL) and EtOH (0.5 mL) at rt in open-air.

*Isolated yield.
controlled experiments have been conducted (Scheme 2). Initially, the reaction of 2-bromoaniline (1aa) with I₂ in the presence of K₂O in a 2.5 mL and 0.5 mL mixture of water and EtOH was produced the desired product, 2-bromo-4-iodoaniline (2aa) with 73% yield in 10 min. Further, 1aa on reacting with I₂ using KOH in water and ethanol mixture (2.5 mL & 0.5 mL) was also provided 2aa in 76% yield in 10 min. Surprisingly, the addition of KCl has improved the yields in both the cases to >95% in 10 min and it is well documented that the enhancement of the catalytic activity of bases in the presence of KCl (55,57,58). This study supports the involvement of K₂O (as KOH) and KCl of WEPA in the C–H iodination of (hetero)arenes and it may provide a large breadth of research directed to study most of the K₂O or KOH influenced reactions by the addition of KCl.

From these evidences and some reported iodinations using base I₂/AI₂O₃ (35) or (and) I₂/NaOH (39) the possible iodination pathway of aromatics or heteroaromatics using I₂ in WEPA has been sketched in Scheme 3. The oxides (M₂O₆; mostly K₂O and some other minor oxides) of WEPA or base of WEPA (M⁺ B⁻) react with MI. Then, the I⁺ species participates in nuclear electrophilic substitution of aromatics or heteroaromatics (59)

### Table 4. Comparison of reported iodinations of aromatics/heteroaromatics using I₂ as iodine source.

| Entry | Catalyst | Oxidant/additive | Solvent | Temp. (°C) | Time (h) | Yields (%) | Remarks |
|-------|----------|------------------|---------|------------|----------|------------|---------|
| 1     | NO₂ (22) | –                | CH₃CN   | 40–120     | 10       | 28–95      | Organic solvent, large reaction times and non-renewable catalyst are necessary. |
| 2     | H₂PV₃Mo₁₀O₄₆ – O₂ (31) | – | CH₃CN   | 80–130     | 8–36     | 11–quant | Metal based catalyst, oxidant and organic solvent are reported. Volatile organic solvent and additional catalyst/oxidant are required. |
| 3     | H₃PV₃Mo₁₀-polyvinylpyrrolidone supported H₂O₂ (32) | – | DCM     | Reflux     | 3–24     | 15–95     | Dry volatile organic solvent, external catalyst/additive are required. No control on mono iodination (only multiple iodination products) and H₂O₂ as oxidant are reported. |
| 4     | Fe(NO₃)₃·1.5 N₂O₄–charcol (33) | – | Dry DCM | Rt         | 2–24     | 31–96     | Dry volatile organic solvent, external catalyst/additive are required. Requires dry Al₂O₃ in large quantity and large reaction time. |
| 5     | (Bu₄N)₂S₂O₈ (34) | – | H₂O     | 50         | 24       | Nil–95    | Requirement of non-renewable catalyst and suffers with low substrate scope/low product yields in some cases. Requires non-renewable catalytic system, large reaction times and volatile solvent. This method necessitates volatile solvent, large reaction times and depleting material as catalyst. Large quantity (0.5 eq.) of depleting material based catalyst, volatile organic solvent and large reaction times are obligatory. Requires depleting materials based catalyst/oxidant. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 6     | Al₂O₃ (35) | – | C₆H₆     | Rt         | 100      | 20        | Nil-quant. | Requires dry Al₂O₃ in large quantity and large reaction time. |
| 7     | Ag₂SO₄ (36) | – | EtOH    | Rt         | 0.5–3.5  | 46–91     | Requirement of non-renewable catalyst and suffers with low substrate scope/low product yields in some cases. Requires non-renewable catalytic system, large reaction times and volatile solvent. This method necessitates volatile solvent, large reaction times and depleting material as catalyst. Large quantity (0.5 eq.) of depleting material based catalyst, volatile organic solvent and large reaction times are obligatory. Requires depleting materials based catalyst/oxidant. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 8     | Phl(OCCOCF₃)₂–pyridine (37) | – | DCM     | Rt         | 2–36     | 56–96     | Requires non-renewable catalytic system, large reaction times and volatile solvent. This method necessitates volatile solvent, large reaction times and depleting material as catalyst. Large quantity (0.5 eq.) of depleting material based catalyst, volatile organic solvent and large reaction times are obligatory. Requires depleting materials based catalyst/oxidant. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 9     | SiO₂–Fe(NO₃)₃·9H₂O₂ (38) | – | DCM     | 20         | 2–28     | 47–95     | Requires non-renewable catalytic system, large reaction times and volatile solvent. This method necessitates volatile solvent, large reaction times and depleting material as catalyst. Large quantity (0.5 eq.) of depleting material based catalyst, volatile organic solvent and large reaction times are obligatory. Requires depleting materials based catalyst/oxidant. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 10    | (Bu₄N)₅S₂O₈ (39) | – | CH₃CN   | 20–60     | 0.7–30   | 87–95     | Requires non-renewable catalyst and suffers with low substrate scope/low product yields in some cases. Requires non-renewable catalytic system, large reaction times and volatile solvent. This method necessitates volatile solvent, large reaction times and depleting material as catalyst. Large quantity (0.5 eq.) of depleting material based catalyst, volatile organic solvent and large reaction times are obligatory. Requires depleting materials based catalyst/oxidant. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 11    | (NH₄)₂Ce(NO₃)₆ (40) | – | AcOH    | Rt         | 3–6      | 70–95     | Requires non-renewable catalyst, volatile organic solvent and large reaction times. <1% conversion using aniline. Requires non-renewable catalyst, volatile organic solvent and large reaction times. < 1% conversion using aniline. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 12    | PbI(OAc)₃–AcOH·AcO (41) | – | AcOH    | Rt         | Unclear  | 24–94     | Requires non-renewable catalyst, volatile organic solvent and large reaction times. <1% conversion using aniline. Requires non-renewable catalyst, volatile organic solvent and large reaction times. < 1% conversion using aniline. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 13    | NaNO₂–HCl (42) | – | Trifluoroethanol | Rt | 1–72     | <1–98     | The use of problematic solvent and non-renewable catalyst/oxidant are obligatory. Requires non-renewable catalyst, volatile organic solvent and large reaction times. <1% conversion using aniline. Requires non-renewable catalyst, volatile organic solvent and large reaction times. < 1% conversion using aniline. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 14    | IBX (43) | – | DMSO/TFA/CH₃CN/AcOH | Rt/ reflux | 1.25–5.0 | 64–97     | The use of problematic solvent and non-renewable catalyst/oxidant are obligatory. Requires non-renewable catalyst, volatile organic solvent and large reaction times. <1% conversion using aniline. Requires non-renewable catalyst, volatile organic solvent and large reaction times. < 1% conversion using aniline. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 15    | AgOTf/AgoAc/AgOMs (44) | – | CH₃CN/DCM | Rt | 1–24     | <1–95     | Requires non-renewable catalyst, volatile organic solvent and large reaction times. < 1% conversion using aniline. Requires non-renewable catalyst, volatile organic solvent and large reaction times. <1% conversion using aniline. Requires problematic catalyst and Ac₂O and suffers with low product yields. Use of non-conventional solvent, external catalyst/additive and large reaction times are necessary. |
| 16    | NaNO₂ (45) | – | CH₃CN | 22         | 1–24     | 85–98     | Large reaction times, volatile organic solvent and added catalyst/additive/oxidant are required. Large reaction times, volatile organic solvent and added catalyst/additive/oxidant are required. Large reaction times, volatile organic solvent and added catalyst/additive/oxidant are required. Large reaction times, volatile organic solvent and added catalyst/additive/oxidant are required. Large reaction times, volatile organic solvent and added catalyst/additive/oxidant are required. |
| 17    | WEPA | – | WEPA-EtOH (5:1) | Rt | 0.08–0.33 | 83–99     | Renewable and waste based catalyst/media, added catalyst/additives free ambient condition and quick reactions with large substrate scope and high yields of iodo(hetero)arenes. |
substance system of WEPA is assumed to be accountable for the activation of aromatic/heteroaromatic systems towards their participation in substitution, thus making the iodination very rapid.

3.4. Comparison of reported methods with the present protocol

Table 4 presents a comparison of various C–H iodination protocols with the present method and it clearly displays several advantages of the present protocol over the reported methods.

4. Conclusions

In summary, WEPA has been demonstrated as a biorenewable waste-derived media for the nuclear iodination of aromatics/heteroaromatics using I₂ under added metal and external oxidant/additive/catalyst-free ambient conditions. The present method shows remarkable assets as significant regioselectivity (preferential formation of mono-iodination products over the other possibilities), wide substrate viability, quick reaction times (5–20 min), ease of operation, internal sustainability, evading chemical waste caused by the use of added substances and up to 99% yields of iodinated products. The nature and position of substituents showed less influence on the present iodination process. A plausible mechanism has been illustrated using some control experiments along with XPS, EDX, XRF, XRD, and FTIR studies. The (hetero)aryl iodides are purified using crystallization technique by avoiding the work-up and column chromatography. Since these reactions are operated using safer catalytic media of bioresource at ambient conditions employing challenging iodination reagent (such as I₂) at very mild conditions, this protocol establishes a novel room for the aryl iodination. The synthesized (hetero)aryl iodides may also be investigated for further in-process transformations including C–C homo/cross-couplings, C–hetero atom couplings, nucleophilic reactions, organometallations, etc. Hopefully, the remarkable attributes of the present method with a systematic study of WEPA to be a biorenewable materials for significant chemical transformation such as the synthesis of (hetero)aryl iodides can gain the attention of the scientific community for further investigations of this green technique in synthetic organic chemistry, energy, and materials related applications.

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