

Iodination of Stable Aromatic Diazonium Salt Using Crosslinked Poly (4-vinylpyridine)-Supported Iodide

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ABSTRACT: An efficient and simple method for the iodination of stable arenediazonium salts has been developed by using a polymer-supported iodide. The arenediazonium chlorides, $\text{Ar-N}_2^+\text{Cl}^-$, were obtained by the reaction between primary aryl amine and sodium nitrite in the presence of concentrated hydrochloric acid (HCl) at low temperature (0–5°C). By ion exchange reaction between $\text{Ar-N}_2^+\text{Cl}^-$ with NaBF_4 , the stable arenediazonium tetrafluoroborates, $\text{Ar-N}_2^+\text{BF}_4^-$, were prepared. $\text{Ar-N}_2^+\text{BF}_4^-$,

were then converted to aryl iodides by crosslinked poly (4-vinylpyridine)-supported iodide, $[\text{P}_4\text{-VP}]\text{I}$, in acetonitrile at room temperature. The spent polymeric reagent was regenerated and reused for several times without losing its activity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2807–2813, 2012

Key words: diazotization; aryl iodide; aryl amine; diazonium salt; polymer supported iodide

INTRODUCTION

Aromatic diazonium salts are important intermediates in many organic reactions.^{1–4} They are building blocks in classical organic synthesis such as, in the preparation of modern organic nanocompounds and in the grafting of organic molecules onto metallic or nonmetallic surfaces.^{1–6}

Despite wide interest in the synthesis of compounds with a diazonium motif, diazonium salts have a serious drawback due to their intrinsic instability and explosive nature. Thus, because of this instability, subsequent reactions with diazonium salts must be carried out in the same medium in which they were produced. This restricts many chemists from approaching potentially important transformations of these salts.¹ Thus, new diazonium salts that are readily made, are stable and explosion proof in the solid state for storage, and have high versatility in organic reactions, and are desirable and necessary. These properties are peculiar to aryl diazonium tetrafluoroborates,² hexafluorophosphates,^{3–7} and arenediazonium *o*-benzenedisulfonimides.^{8,9}

Other potential diazonium salts that meet criteria are arenediazonium arylsulfonates, $\text{Ar}^1\text{N}_2^+\text{Ar}^2\text{SO}_3^-$ that are used only for the production of azo dye stuffs and analytical purposes. About half a century

has passed since some of their characteristics were reported.^{10–12} Aromatic iodo compounds are important intermediates for the synthesis of various pharmaceutical and bioactive compounds.^{13–23} They are also useful in metal-catalyzed cross coupling reactions, such as Heck, Stille, and Negishi reactions which are utilized in C–C and C–N bond formation.^{13–19} However, direct iodination of aromatic compounds is difficult due to the low electrophilicity of molecular iodine and the possibility of formation of a mixture of regioisomers.

One of the most commonly method that used for preparation of aromatic iodide was the substitution of the diazonium group by iodine, the so-called Sandmeyer reaction.^{1–4} The process of diazotization is usually carried out with sodium nitrite at low temperature in aqueous hydrochloric or sulfuric acid,^{15–18,20–29} and then aromatic diazonium salts are reacted with KI in a subsequent reaction (iodination) usually in the presence of copper salts.^{1–3}

Alternative procedures involve more expensive alkyl nitrites as diazotizing agents in the presence of diiodomethane or other sources of iodine.^{30,31}

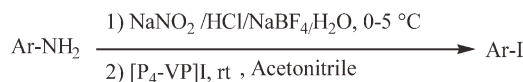
Recently the chemistry of functional polymers has received great attention and became a practical method for the efficient preparation of novel chemical libraries.^{32–56} These polymeric reagents are generally used in single-step reactions; the main advantage of polymeric reagent over nonpolymeric reagents is their insolubility in the reaction medium and consequently their easier work-up by a simple filtration. The reactions often can be driven to completion using excess amounts of reagents without

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the fear of separation of the excessive reagents from the products. The used polymeric reagents usually can be quantitatively removed and regenerated. These reagents usually can be prepared from commercial anion exchange resins or polymers such as crosslinked poly (4-vinylpyridine) as supports.

Although polymer-supported reagents especially anion exchange resins have been widely applied in organic synthesis,^{32–56} but based on our knowledge, there are a few reports in the literature for preparation of aryl iodides by using a polymeric reagent.^{54–56} Filimonov et al. reported⁵⁵ unusually stable arenediazonium tosylates and used Amberlyst A-26 NO₂⁻ form (Resin-NO₂⁻) for diazotization–iodination of aromatic amines. With using polymeric quaternary ammonium nitrite, the reaction time is very long (in some cases, many hours). Zarei et al.⁵⁶ reported one-pot method for the diazotization–iodination of aryl amines via stable arenediazonium silica sulfates under solvent-free conditions. Previously we have also prepared crosslinked poly (4-vinylpyridine) supported iodide ion, [P₄-VP]I, but used for synthesis of various polymeric reagents and used in organic transformations such as; polymer-supported thiocyanate ion,⁴⁴ polymer-supported carboxylate,⁴⁵ polymer-supported ferrate ion,⁴⁶ polymer-supported azide ion^{47–49} and polymer-supported nitrite ion, [P₄-VP]NO₂.^{41–43,48–51} Recently, we reported, diazotization–iodination of aromatic amines with [P₄-VP] NO₂/H₂SO₄/KI in water at 0.0–60°C, under heterogeneous conditions but, for removing the aryl iodide products requires the addition of aqueous Na₂SO₃ (10%), and also some of the reactions were took place at 60°C.⁵³ On the other hand, most of the reported methods for synthesis of aryl iodides suffer from at least one of the following limitation: (1) low reaction yield; (2) long reaction time; (3) need for a phase transfer catalyst; (4) need for a copper salt catalyst; (5) formation of by-products; and (6) difficult or multi step work-up. However, use of [P₄-VP]I, overcomes most of the above-mentioned limitation.

Although, [P₄-VP]I, was recently prepared and is well known but, was used for preparation of other functionalized polymers.^{41–53} Also a literature search shows that; there is no any report in the literature for the synthesis of aryl iodides based on polymer-supported iodide. Hence, herein, we wish to report an effective and facile diazotization–iodination of primary aromatic amines. Diazotization of aniline derivatives were took place by using NaNO₂/HCl system at 0–25°C and the obtained arenediazonium chlorides, Ar-N₂⁺Cl⁻, were stabilized by anion exchange reaction with NaBF₄. Then the stable arenediazonium tetrafluoroborates, Ar-N₂⁺BF₄⁻, were converted to aryl iodides by using [P₄-VP]I in acetonitrile at room temperature.



Scheme 1 Diazotization–iodination of aromatic amines.

EXPERIMENTAL

General

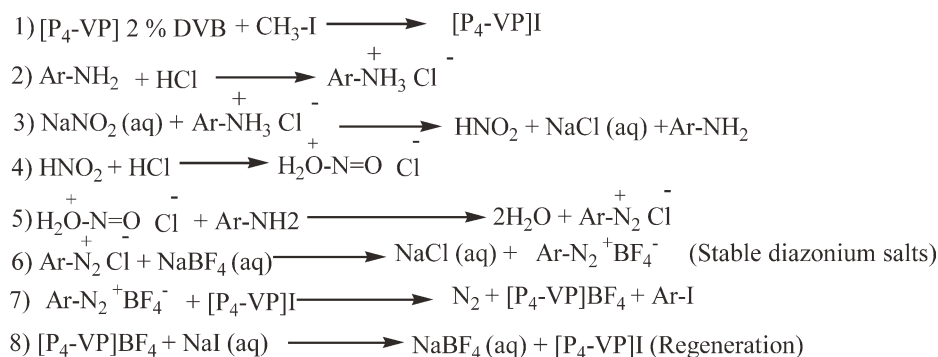
Chemicals were either prepared in our laboratory or were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), and Merck chemical companies. Poly (4-vinylpyridine) crosslinked with 2% divinyl benzene (DVB), [P₄-VP] 2% DVB, was purchased from Fluka (Buchs, Switzerland). Crosslinked poly (*N*-methyl-4-vinylpyridinium) iodide, [P₄-VP]I, was synthesized according to the previously reported procedures^{41–43} (Scheme 1). Progress of the reaction was followed by thin layer chromatography (TLC) using silica gel Poly Gram SIL G/UV 254 plates. All products were characterized by comparison of their melting point, FT-IR, and ¹H NMR spectral data, with those of known compounds and all yields refer to the isolated pure products. Melting points were determined with a Buchi melting point B-540 B.V. CHI apparatus. FT-IR spectra were obtained by using a Bruker, Equinox (model 55) and NMR spectra were recorded on a Bruker AC 400, Avance DPX spectrophotometer at 400 MHz in CDCl₃ solutions.

Preparation of [P₄-VP]I

Poly (4-vinylpyridine) crosslinked with 2% DVB (white powder, 100–200 mesh; 1.0 g) was treated with methyl iodide (20 mmol, 3.24 g) in acetonitrile (10 mL) and the mixture was slowly stirred for 24 h at room temperature. The yellow quaternized prepared polymer, [P₄-VP]I, was filtered and washed with acetonitrile. It was then dried under vacuum in the presence of P₂O₅ at 40°C overnight. 2.23 g of [P₄-VP]I was obtained (Scheme 2, Step 1). The capacity of the polymer was determined by gravimetric method and it was found to be 4 mmol of iodide ion per gram of the polymer.

General procedure for diazotization–iodination of aromatic amines with [P₄-VP] I in water at room temperature under heterogeneous conditions

One mmol of an aryl amine, was added to a solution of concentrated HCl (2 mmol) in water (5 mL), and the mixture was slowly stirred magnetically at 0–5°C for appropriate time (10–20 min), until the ammonium salt was obtained and the aromatic amine was disappeared. The progress of the reaction was monitored by TLC [eluent: *n*-hexane/ethyl acetate (80 : 20)]. Then 138 mg of NaNO₂ (2 mmol) was added

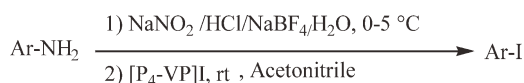


Scheme 2 Preparation of $[P_4\text{-VP}]\text{I}$, reaction pathway of diazotization–iodination of aromatic amines and regeneration of the polymer.

and stirring was continued until, the diazonium salt was formed and the aromatic amine was disappeared. The progress of the reaction was monitored by TLC [eluent: *n*-hexane/ethyl acetate (80/20)]. After completion of the diazotization, the cooled aqueous solution of NaBF_4 (1.5 mmol) was added and the mixture was slowly stirred at 10–15°C for 10–20 min and the stable arenediazonium tetrafluoroborate was precipitated. The mixture was filtered and

washed with about 30 mL of ice-water, 15 mL of methanol and 30 mL of diethyl ether. The yellow solid was allowed to dry overnight. The dried stable arenediazonium tetrafluoroborate, was dissolved in acetonitrile (5 mL) and 0.750 g of $[P_4\text{-VP}]\text{I}$ (3 mmol of I^-) was added and the mixture was slowly stirred magnetically at room temperature for appropriate time as indicated in Table I (90–240 min). After completion of the reaction (TLC), the spent polymer was

TABLE I
Diazotization of Aromatic Amines by $\text{NaNO}_2/\text{HCl}/\text{NaBF}_4$ in Water at 0–5°C and Iodination with $[P_4\text{-VP}]\text{I}$ in Acetonitrile at Room Temperature.



Entry	Ar-NH ₂	Ar-I	Diazotization/ iodination time (min)	Isolated yield (%)	M.P/ Lit ⁵⁷ (°C)
1	Ph-NH ₂	Ph-I	10/100	Trace	–
2	4-NO ₂ C ₆ H ₄ NH ₂	4-NO ₂ C ₆ H ₄ I	10/120	90	173/172–174
3	4-NO ₂ C ₆ H ₄ NH ₂	4-NO ₂ C ₆ H ₄ I	10/120	90 ^a	173/172–174
4	4-NO ₂ C ₆ H ₄ NH ₂	4-NO ₂ C ₆ H ₄ I	10/122	90 ^a	173/172–174
5	4-NO ₂ C ₆ H ₄ NH ₂	4-NO ₂ C ₆ H ₄ I	10/125	89 ^a	173/172–174
6	4-NO ₂ C ₆ H ₄ NH ₂	4-NO ₂ C ₆ H ₄ I	10/125	89 ^a	173/172–174
7	3-NO ₂ C ₆ H ₄ NH ₂	3-NO ₂ C ₆ H ₄ I	15/130	89	Oil/Oil
8	2-NO ₂ C ₆ H ₄ NH ₂	2-NO ₂ C ₆ H ₄ I	20/170	85	50/49–51
9	4-NCC ₆ H ₄ NH ₂	4-NCC ₆ H ₄ I	10/90	93	125/124–128
10	4-IC ₆ H ₄ NH ₂	4-IC ₆ H ₄ I	10/100	91	127/130
11	2-IC ₆ H ₄ NH ₂	2-IC ₆ H ₄ I	20/150	89	Oil/Oil
12	4-BrC ₆ H ₄ NH ₂	4-BrC ₆ H ₄ I	15/110	92	88/89–91
13	4-ClC ₆ H ₄ NH ₂	4-ClC ₆ H ₄ I	15/175	74	54/52–56
14	4-MeC ₆ H ₄ NH ₂	4-MeC ₆ H ₄ I	15/200	80	30/33–35
15	2-BrC ₆ H ₄ NH ₂	2-BrC ₆ H ₄ I	20/160	75	Oil/Oil
16	4-HOCC ₆ H ₄ NH ₂	4-HOCC ₆ H ₄ I	10/90	91	270/270–273
17	2-HOCC ₆ H ₄ NH ₂	2-HOCC ₆ H ₄ I	15/170	81	161/160–162
17	4-MeOC ₆ H ₄ NH ₂	4-MeOC ₆ H ₄ I	10/120	82	49/50–53
18	4-MeCOC ₆ H ₄ NH ₂	4-MeCOC ₆ H ₄ I	10/100	91	83/82–84
19	1-Naphthyl amine	1-Iodonaphthalene	20/220	81	Oil/Oil
20	2,4 (NO ₂) ₂ C ₆ H ₃ NH ₂	2,4-(NO ₂) ₂ C ₆ H ₃ I	20/240	56	–

^a The Entries 3–6, refer to the use of the $[P_4\text{-VP}]\text{I}$ that is recycled first, second, third and fourth time, respectively, under identical conditions.

filtered and washed with acetonitrile (3×5 mL). The aryl iodide product was obtained by filtering and evaporating of the solvent.

When further purification was needed crystallization in ethanol or column chromatography on silica gel [eluent : acetone-petroleum ether (10 : 90)] was applied and highly pure product was obtained. When the product was liquid, the reaction mixture was extracted with diethyl ether (3×8 mL) and, after drying of the organic layer (with MgSO_4) and evaporating the solvent, a highly pure product was obtained (Table I, Entries 7, 11, 15, 19).

FT-IR and ^1H NMR spectral data of some selected prepared aryl iodides are given below:

p-bromiodobenzene. FT-IR (neat), ν (cm^{-1}) = 3072, 1885, 1619, 1466, 1375, 1256, 1095, 1063, 994, and 799; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.24 (d, 2H, J = 8.4 Hz) and 7.55 (d, 2H, J = 8.4 Hz).

p-iodophenyl methyl ketone. FT-IR (neat), ν (cm^{-1}) = 3003, 1671, 1581, 1422, 1390, 1358, 1302, 1262, 1180, 1100, 1076, 1004, 958, 817, 741, 708, and 625; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 2.64 (s, 3H), 7.66 (d, 2H, J = 8.8 Hz) and 7.83 (d, 2H, J = 8.4 Hz).

m-iodonitrobenzene. FT-IR (neat) ν (cm^{-1}) = 3100, 3072, 2925, 2864, 1595, 1516, 1377, 1300, 1273, 1181, 1160, 1120, 1106, 1095, 1066, 993, 988, 930, 863, 807, 799, 729, 714, 663, and 642; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.27 (t, 1H), 7.98 (d, 1H, J = 7.6 Hz), 8.15 (d, 1H, J = 8 Hz), and 8.47 (s, 1H).

p-iodoanisole. FT-IR (neat) ν (cm^{-1}) = 3007, 2968, 2839, 1585, 1568, 1484, 1454, 1285, 1243, 1176, 1062, 998, 955, 830, 808, 875, and 627; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 3.78 (s, 3H, OCH_3), 6.68 (d, 2H, J = 8.4 Hz) and 7.56 (d, 2H, J = 8.4 Hz).

p-iodonitrobenzene. FT-IR (neat) ν (cm^{-1}) = 3092, 1593, 1569, 1504, 1469, 1391, 1337, 1308, 1178, 1105, 1051, 1008, 835, 733, and 674; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.92 (d, 2H, J = 8.4 Hz) and 7.95 (d, 2H, J = 8.4 Hz).

2,4-dinitroiodobenzene. FT-IR (neat) ν (cm^{-1}) = 3098, 2186, 2157, 1583, 1522, 1460, 1343, 1251, 1152, 1094, 1068, 1023, 993, 908, 832, 801, 756, 729, 655, 619, and 607; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 8.12 (1H, d, J = 6.8 Hz), 8.301 (1H, d, J = 8.4 Hz) and 8.69 (1H, s).

p-iodobenzonitrile. FT-IR (neat) ν (cm^{-1}) = 3078, 2226, 1909, 1646, 1577, 1474, 1391, 1274, 1111, 1055, 1010, 961, 816, 765, 700, 647; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.38 (2H, d, J = 8 Hz) and 7.86 (2H, d, J = 8 Hz).

p-chloriodobenzene. FT-IR (neat) ν (cm^{-1}) = 3074, 2954, 2924, 2474, 1886, 1470, 1410, 1384, 1378, 1339, 1259, 1216, 1176, 1106, 1091, 1082, 1064, 1006, 994, 962, 810, and 721; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.09 (2H, d, 8.4 Hz) and 7.61 (2H, d, 8.4 Hz).

o-bromiodobenzene. FT-IR (neat) ν (cm^{-1}) = 3075, 3055, 2983, 2560, 2524, 1951, 1828, 1792, 1687, 1600,

1552, 1460, 1439, 1428, 1422, 1402, 1371, 1342, 1253, 1151, 1124, 1105, 1094, 1037, 1031, 1002, 973, 941, 855, 744, and 688; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 7.00 (1H, t), 7.21 (1H, t), 7.63 (1H, d, 7.2 Hz) and 7.87 (1H, d, 7.2 Hz).

Regeneration of $[\text{P}_4\text{-VP}]\text{I}$

The spent cream-colored polymer (1 g) was added to an aqueous solution of sodium iodide, and was slowly stirred for 24 h. The mixture was filtered, washed several times with distilled water (3×5 mL), and was dried under vacuum in the presence of P_2O_5 at 40°C overnight (Scheme 2, Step 7). The capacity of the regenerated polymer was determined by potentiometric titration of the remained iodide ion in the filtrates and it was found that, it had the same capacity as the original form (4 mmol of iodide ion per gram of polymer). The regenerated polymer was reused several cycles, without losing its activity (Table I, Entries 3–6). The data of recyclability study of regenerated polymeric reagents (Table I, Entries 3–6) are shown in Figure 1.

RESULTS AND DISCUSSION

Crosslinked poly (4-vinylpyridine)-supported methyl iodide was prepared according to our previous procedure^{41–43} (Scheme 2, Step 1) and used as an effective polymeric reagent for iodination of stable arenediazonium tetrafluoroborates under mild and heterogeneous conditions (Scheme 2, Step 7). Arenediazonium chloride, $\text{Ar-N}_2^+\text{Cl}^-$ was prepared by the reaction of an aryl amine with sodium nitrite in the presence of concentrated HCl. By an exchange reaction between $\text{Ar-N}_2^+\text{Cl}^-$ and NaBF_4 , the stable arenediazonium tetrafluoroborates, were obtained and consequently dediazonation–iodination were occurred by using $[\text{P}_4\text{-VP}]\text{I}$. It is important to note that, this polymeric reagent is stable and can be stored for long time (months), without losing its activity and can be readily used in synthesis of aryl iodides via diazotization–iodination of primary aromatic amines (Scheme 1). This polymeric reagent is recently prepared and used for preparation of other functionalized polymers such as, polymer-supported thiocyanate,⁴⁴ polymer-supported carboxylate,⁴⁵ polymer-supported potassium ferrate,⁴⁶ polymer-supported azide ion,^{47–49} polymer-supported nitrite ion.^{41–43,50–53} However, $[\text{P}_4\text{-VP}]\text{I}$, is well known and, based on our knowledge, there is no any report in the literature for the synthesis of aryl iodides based on polymer-supported iodide hence, in this work, the characterization of the polymer is not given and preparation of aryl iodides from primary aromatic amines is described (Scheme 1).

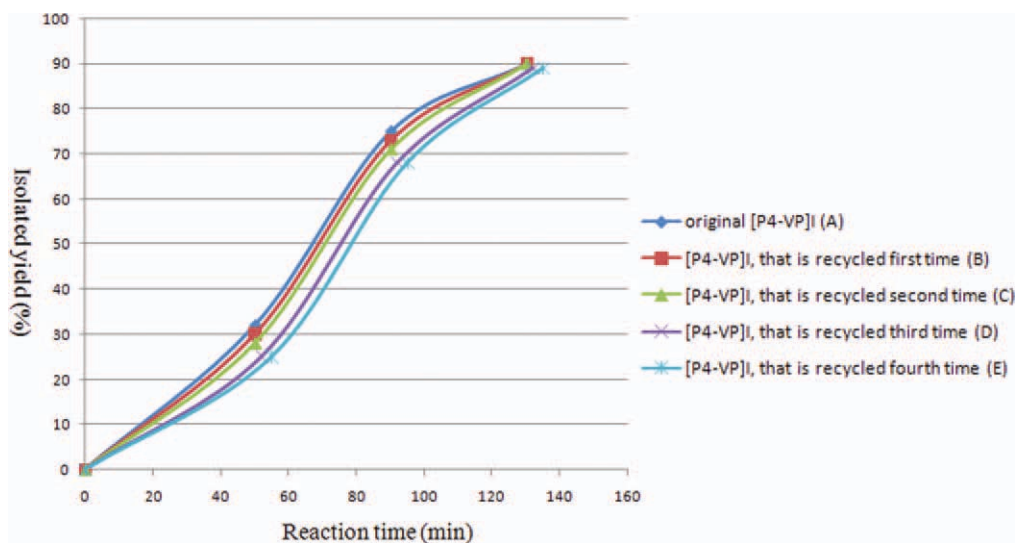


Figure 1 Isolated yield of *p*-iodo nitrobenzene as a function of time, using original [P₄-VP]I (A), [P₄-VP]I that is recycled first time (B), [P₄-VP]I that is recycled second time (C), [P₄-VP]I that is recycled third time (D), and [P₄-VP]I that is recycled first time (E) under identical conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To increase the yield of iodo compounds, optimization of the reaction conditions was accomplished. The 4-nitroaniline (1 mmol; Table I, Entry 2) was chosen as a model substrate and was converted to 4-nitrophenyl diazonium tetrafluoroborate according to the previously reported method in the literature,⁵⁸ using NaNO₂ (2 mmol)/HCl (2 mmol)/NaBF₄ (1.5 mmol) in water at 0–5°C. For optimization of the reaction conditions, dediazotization–iodination of 4-nitrophenyl diazonium tetrafluoroborate was performed with different molar ratio of 4-NO₂-C₆H₄-N₂⁺BF₄⁻/[P₄-VP]I and in different solvents and the results are summarized in Table II. It was observed that, the molar ratio of 1/3 and an aprotic solvent (acetonitrile) at room temperature was the best and gave the highest yield of the product (Table II).

We then applied the optimized conditions to the conversion of different primary aromatic amines into the corresponding aryl iodides and the results are shown in Table I. A good range of available aromatic amines were also subjected to diazotization–iodination using NaNO₂/HCl/NaBF₄ system in water at 0–25°C and then, the obtained Ar-N₂⁺BF₄⁻ converted into aryl iodides using [P₄-VP]I in an aprotic solvent (acetonitrile) at room temperature. Some of the aromatic amines such as substituted anilines with electron withdrawing groups and electron donating groups were diazotized and subsequently were iodinated with good to moderate yields. However with aniline even after 300 min, only a trace of iodo product was separated and a few by-products were formed that were not identified (Table I, Entry 1). This was in agreement with our previously reported method for diazotization–iodination of aromatic amines in water⁵³ using a polymer supported

nitrite ion. On the other hand, there is no report on the diazotization–iodination of aniline with other methods reported for halogenation of arenediazonium salts such as; arenediazonium tosylates with nucleophilic reagents,⁵⁵ halogenation of aryl amines via arenediazonium tosylate salts,⁵⁵ a simple and efficient procedure for diazotization–iodination of aromatic amines in aqueous pastes by the action of sodium nitrite and sodium hydrogen sulfate,⁵⁹ and iodination of aryl amines in a water-paste via stable aryl diazonium tosylates.²⁹ The iodination of 2,4-dinitroaniline also provided only moderate yield (56%) of the corresponding iodo derivative. Thus this result is in agreement with the previously reported methods.^{29,59}

TABLE II
Optimization of the Reaction Conditions for Dediazotization–Iodination of *p*-Nitrobenzene Diazonium Tetrafluoroborate (Obtained from 1 mmol of *p*-Nitroaniline) Using [P₄-VP]I^a

Entry	Solvent	[P ₄ -VP]I (mmol of I ⁻)	Isolated yield (%)
1	H ₂ O	1	0.0 ^b
2	Ethanol	1	0.0 ^b
3	Acetone	1	45
4	Acetonitrile	1	65
5	Acetonitrile	1.5	76
6	Acetonitrile	2	85
7	Acetonitrile	3	90
8	Acetonitrile	3.5	90

^a The reactions were performed at room temperature for 100 min.

^b Decomposition of diazonium salt took place and by-products were observed before, the [P₄-VP]I was added and no iodo compound was detected.

TABLE III
Comparison of Different Methods for Synthesis of Various Aryl Iodides via
Diazotization–Iodination of Aromatic Amines

Ref.	Isolated yield (%)	Product	Substrate	Entry
60 ^a	81	4-NO ₂ C ₆ H ₄ I	4-NO ₂ C ₆ H ₄ NH ₂	1
29 ^b	72	4-NO ₂ C ₆ H ₄ I	4-NO ₂ C ₆ H ₄ NH ₂	2
53 ^c	79	4-NO ₂ C ₆ H ₄ I	4-NO ₂ C ₆ H ₄ NH ₂	3
56 ^d	68	4-NO ₂ C ₆ H ₄ I	4-NO ₂ C ₆ H ₄ NH ₂	4
Table II, entry 2	90	4-NO ₂ C ₆ H ₄ I	4-NO ₂ C ₆ H ₄ NH ₂	5
60 ^a	71	2-NO ₂ C ₆ H ₄ I	2-NO ₂ C ₆ H ₄ NH ₂	6
29 ^b	72	2-NO ₂ C ₆ H ₄ I	2-NO ₂ C ₆ H ₄ NH ₂	7
53 ^c	74	2-NO ₂ C ₆ H ₄ I	2-NO ₂ C ₆ H ₄ NH ₂	8
56 ^d	68	2-NO ₂ C ₆ H ₄ I	2-NO ₂ C ₆ H ₄ NH ₂	9
Table II, entry 8	85	2-NO ₂ C ₆ H ₄ I	2-NO ₂ C ₆ H ₄ NH ₂	10
60 ^a	75	4-MeCOC ₆ H ₄ I	4-MeCOC ₆ H ₄ NH ₂	11
29 ^b	75	4-MeCOC ₆ H ₄ I	4-MeCOC ₆ H ₄ NH ₂	12
53 ^c	84	4-MeCOC ₆ H ₄ I	4-MeCOC ₆ H ₄ NH ₂	13
56 ^d	75	4-MeCOC ₆ H ₄ I	4-MeCOC ₆ H ₄ NH ₂	14
Table II, entry 18	91	4-MeCOC ₆ H ₄ I	4-MeCOC ₆ H ₄ NH ₂	15
60 ^a	50	1,4-I ₂ C ₆ H ₄	4-IC ₆ H ₄ NH ₂	16
29 ^b	87	1,4-I ₂ C ₆ H ₄	4-IC ₆ H ₄ NH ₂	17
53 ^c	88	1,4-I ₂ C ₆ H ₄	4-IC ₆ H ₄ NH ₂	18
56 ^d	52	1,4-I ₂ C ₆ H ₄	4-IC ₆ H ₄ NH ₂	19
Table II, entry 10	91	1,4-I ₂ C ₆ H ₄	4-IC ₆ H ₄ NH ₂	20
60 ^a	90	1,2-I ₂ C ₆ H ₄	2-IC ₆ H ₄ NH ₂	21
29 ^b	79	1,2-I ₂ C ₆ H ₄	2-IC ₆ H ₄ NH ₂	22
53 ^c	80	1,2-I ₂ C ₆ H ₄	2-IC ₆ H ₄ NH ₂	23
56 ^d	67	1,2-I ₂ C ₆ H ₄	2-IC ₆ H ₄ NH ₂	24
Table II, entry 11	89	1,2-I ₂ C ₆ H ₄	2-IC ₆ H ₄ NH ₂	25
60 ^a	61	4-MeOC ₆ H ₄ I	4-MeOC ₆ H ₄ NH ₂	26
29 ^b	70	4-MeOC ₆ H ₄ I	4-MeOC ₆ H ₄ NH ₂	27
53 ^c	78	4-MeOC ₆ H ₄ I	4-MeOC ₆ H ₄ NH ₂	28
56 ^d	61	4-MeOC ₆ H ₄ I	4-MeOC ₆ H ₄ NH ₂	29
54 ^e	80	4-MeOC ₆ H ₄ I	4-MeOC ₆ H ₄ NH ₂	30
Table II, entry 17	82	4-MeOC ₆ H ₄ I	4-MeOC ₆ H ₄ NH ₂	31
60 ^a	56	4-CNC ₆ H ₄ I	4-CNC ₆ H ₄ NH ₂	32
29 ^b	79	4-CNC ₆ H ₄ I	4-CNC ₆ H ₄ NH ₂	33
53 ^c	89	4-CNC ₆ H ₄ I	4-CNC ₆ H ₄ NH ₂	34
56 ^d	75	4-CNC ₆ H ₄ I	4-CNC ₆ H ₄ NH ₂	35
54 ^e	64	4-CNC ₆ H ₄ I	4-CNC ₆ H ₄ NH ₂	36
Table II, entry 9	93	4-CNC ₆ H ₄ I	4-CNC ₆ H ₄ NH ₂	37

^a In this procedure, the reactions were carried out in the presence of NaNO₂/sulfo-nated-resin/KI at room temperature.

^b In this procedure, the reactions were carried out in the presence of NaNO₂/*p*-TsOH in water-paste form and KI.

^c In this procedure, the reactions were carried out in the presence of [P₄-VP]NO₂/H₂SO₄/KI in water at 0–60°C.

^d In this procedure, the reactions were carried out in the presence of NaHSO₄/NaNO₂/KI in aqueous paste at 18–20°C.

^e In this procedure, the reactions were carried out in the presence of Resin-NO₂/TsOH in AcOH at room temperature and then KI/H₂O at room temperature.

This method was also successfully applied on a large scale. For example, up to 15 mmol of *p*-nitroaniline (Entry 2) could be converted into 4-iodonitrobenzene without any loss of efficiency.

Preparation of [P₄-VP]I, the reaction pathway of diazotization–iodination of aromatic amines and regeneration of the polymer are given in Scheme 2.

In this study, we observed that, the reaction times of the present method were shorter than other reported methods^{29,53,60,61} and the isolated yields of aryl iodide than other reported methods.^{29,55,59,62}

products were higher. This can probably be attributed to the local concentration of iodide ion species inside the pores.

In Table III, the yields of aryl iodide products are compared with other reported methods for synthesis of aryl iodides. As shown in Table III, the isolated yields of the products were higher than previously reported methods. This can probably be attributed to the stability of aryldiazonium salts (Ar-N₂⁺BF₄⁻).

The advantages of this method over conventional methods^{59,63} are: mild reaction conditions, mildness

of polymeric reagent, ready availability, fast reaction rates, and very simple work-up. In addition, there is current research and general interest in heterogeneous systems because of these systems are very important in industry and in developing technologies.⁵⁷

CONCLUSIONS

This research demonstrates the use of [P₄-VP]I in the synthesis of aromatic iodides from iodination of stable aryldiazonium tetrafluoroborate that was derived from various primary aromatic amines. The protocol is operationally simple, efficient under heterogeneous conditions, free-catalyst (Cu salt) and industrially applicable at room temperature in a green solvent (H₂O) with good to high yields in most cases.

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