

Solvent-Free Diazotization–Azidation of Aryl Amine Using a Polymer-Supported Azide Ion

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Received 18 May 2011; accepted 18 July 2011

DOI 10.1002/app.35294

Published online 26 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Crosslinked poly (4-vinylpyridine)-supported azide ion was used as an effective azidating agent for deazodination of stable arenediazonium salts under solvent-free conditions in high yields. The diazotization of aromatic amines was prepared by grinding the combination of an aromatic amine, sodium nitrite (NaNO_2), *p*-toluene sulfonic acid (*p*-TsOH), and 0.2 mL H_2O in a mortar. Grinding was continued for deazodination–azidation of the

obtained relatively stable diazonium salts, with addition of crosslinked poly (4-vinylpyridine) supported azide ion to obtain the corresponding aryl azides. The spent polymeric reagents can usually be removed and regenerated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2362–2369, 2012

Key words: grinding; diazotization; aryl amine; diazonium salt; azidation; solvent-free condition

INTRODUCTION

Aromatic diazonium salts have drawn increased importance as intermediates in many organic preparations of modern organic nanocompounds and the grafting of organic molecules onto metallic or non-metallic surfaces.^{1–4}

Despite wide applicability in the synthesis of compounds with a diazonium motif, diazonium salts have a serious drawback—their intrinsic instability and explosive nature. 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 this salts.¹

Thus, new diazonium salts that can be readily made, are stable and expulsion proof in a solid state for storage, and have high versatility in organic reactions, and are both desirable and necessary. These properties are peculiar to aryldiazonium tetrafluoroborates,⁵ hexafluorophosphates,⁵ and arenediazonium *o*-benzenedisulfonimides.⁶

Other potential diazonium salts that meet criteria are arenediazonium arylsulfonates, $\text{Ar}^1\text{N}_2^+\text{Ar}^2\text{SO}_3^-$ that 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.⁷

Aryl azides are important intermediates with a variety of applications in organic and bioorganic chem-

istry,^{8,9} with their use as photoaffinity labeling reagents for bimolecular being chiefly important.^{10,11}

Aryl azides are also useful intermediates in the synthesis of various heterocyclic compounds and transition metal complexes.^{8,12–15} A major application of these compounds is 1,3-dipolar cycloaddition to create five member heterocycles.^{12,16–19} This powerful and reliable bond-forming process has found widespread application, e.g., in combinatorial drug discovery,^{20,21} material science,^{22–24} and bioconjugation.^{17,25–27} This has stimulated a demand for readily accessible azide building blocks, and consequently, a need for reliable and efficient methods for installing this functional group.

Aryl azides are commonly prepared from the corresponding aromatic amines via their diazonium salts,^{8,28–30} which may sometimes be problematic with respect to the presence of incompatible functional groups. Aryl azides have also been prepared by reaction of arylmagnesium halides or aryllithium reagents with *p*-toluenesulfonic acid.^{31,32} More recently, Liu and Tor have applied Wong's (TfN_3) methodology toward the efficient preparation of aryl azides using a combination of aryl amine, TfN_3 , CuSO_4 , and triethylamine.³³ Also, straight coupling of aryl halides³⁴ or aryl boronic acids³⁵ with sodium azide catalyzed by copper salts has been reported. On the basis of this finding several groups subsequently developed one-pot synthetic methods for the preparation of 1-aryl-1,2,3-triazoles directly from aryl iodides, sodium azide, and terminal alkynes.^{36–38} The significance of these studies is manifested by the fact that 1,2,3-triazoles have recently found widespread use in pharmaceuticals and agrochemicals.^{39–42} Nonetheless, it is worth noting that the above methods

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usually suffer from long reaction times (overnight) even at elevated temperature (70°C) due to the slow azidation of aryl halides.^{36–38} Recently, Das et al. reported the use of *tert*-butyl nitrite (*t*-BuONO) in combination with NaN₃ in the synthesis of aromatic azides.⁴³ This procedure requires a large excess of reagents (12 equiv of *t*-BuONO, 3 equiv of NaN₃), which is undesirable considering the hazards associated with NaN₃. These compounds have also been synthesized from aromatic amines with *t*-BuONO followed by the addition of trimethylsilyl azide (TMSN₃).⁴³ Preparation of aryl azides by using stable aryl diazonium silica sulfates have also been reported by Zarei et al.⁴⁴ Furthermore, [ArN₂][BF₄] salts immobilized in [BMIM][PF₆] ionic liquid with TMSN₃ have been reported for the preparation of aryl azides.⁴⁵

However, some of these methods utilize convenient protocols with good yields, some of them suffer from disadvantages such as long reaction times, low yields and high temperatures leading to decomposition of the aryl azides, poor stability of the reagents, use of toxic solvents, and high costs.

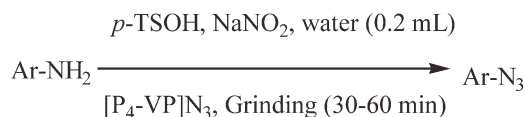
Although polymer-supported reagents especially anion exchange resins have been widely applied in organic synthesis,^{46–62} a literature search shows that there are a few reports in organic transformation based on polymer supported azide reagent. Brenelli et al. reported that Amberlite IRA 900 supported azide resin is a highly effective reagent for the conversion of α -haloketones into α -azidoketones.⁵⁹ The regioselective ring opening of polycyclic aromatic hydrocarbon epoxides by this polymer also reported by Lakshman et al.⁶⁰ Blass et al. reported a one-pot, two step preparation of functionalized 1,2,3-triazoles by Merrifield resin supported ammonium azide anion.⁶¹ The 1,3-dipolar cycloaddition by using poly (ethylene glycol)-supported azide is also reported by Molteni et al.⁶² Previously, we have also prepared crosslinked poly (4-vinylpyridine)-supported azide ion, [P₄-VP]N₃, and used for synthesis of alkyl azides from alkyl halides,⁵⁶ diazotization-azidation of amines in water⁵⁷ and [2 + 3] cycloaddition reaction of azide ion with nitriles.⁵⁸

Herein, as part of our continuing exploration on the new reactivity of [P₄-VP]N₃, we have developed the conversion of various aromatic amines to their corresponding aryl azides by grinding a combination of aryl amine, NaNO₂, *p*-TSOH, [P₄-VP]N₃ and H₂O (0.2 mL) in a mortar (Scheme 1).

EXPERIMENTAL

General

Chemicals were either prepared in our laboratory or were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), and Merck (Germany)



Scheme 1 One-pot method for diazotization-azidation of aromatic amines using [P₄-VP]N₃.

chemical companies. Poly (4-vinylpyridine) cross-linked 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, and crosslinked poly (4-vinylpyridine) supported sodium azide, [P₄-VP]N₃, were synthesized according to our reported procedures^{49–58} (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 samples 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 or DMSO-*d*₆ solutions.

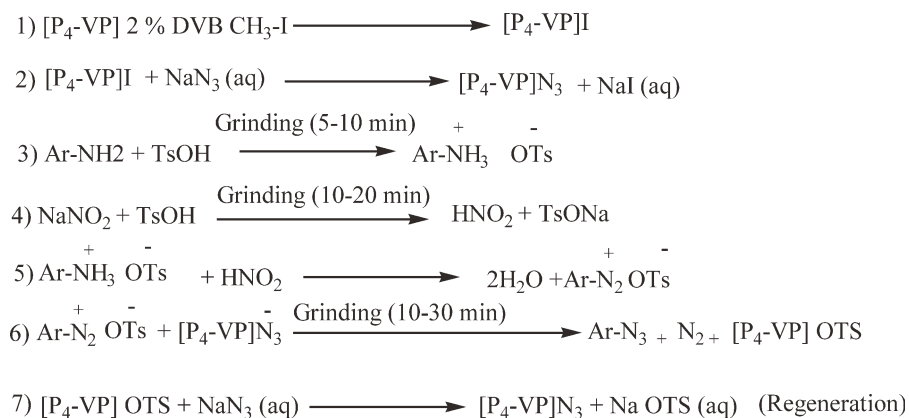
Preparation of [P₄-VP]I and [P₄-VP]N₃

Poly (4-vinylpyridine) crosslinked with 2% DVB (white powder, 100–200 mesh; 1.0 g) was added to a solution of 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 polymer, [P₄-VP]I, was filtered and was washed with acetonitrile. It was then dried under vacuum at 40°C overnight (Scheme 2, Step 1).

The obtained [P₄-VP]I was added to 40 mL of a 3M aqueous solution of sodium azide and slowly was stirred for 24 h. The prepared resin, [P₄-VP]N₃, was filtered off and was washed with distilled water (3 × 8 mL). It was then washed with diethyl ether and dried under vacuum in the presence of P₂O₅ at 40°C overnight. The activity of the polymer was determined by potentiometric titration of the filtrates with a 0.1M aqueous solution of silver nitrate and it was found to be 3.4 mmol of azide ion per gram of the polymer.

General procedure for diazotization-azidation of aromatic amines with NaNO₂/TsOH using [P₄-VP]N₃ under solvent-free conditions

In a mortar, a mixture of an aromatic amine (1 mmol), water (0.2 mL), and *p*-toluenesulfonic acid (*p*-TSOH) (6 mmol) were pulverized for appropriate



Scheme 2 Preparation of $[P_4\text{-VP}]\text{N}_3$, the plausible reaction pathway of diazotization–azidation of aromatic amines and regeneration of the polymer.

time (5–10 min) until, the ammonium 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)].

Then 345 mg (5 mmol) of sodium nitrite was added and pulverizing was continued until, the diazonium salt was formed. After completion of the reaction, 0.588 g (2 mmol) of $[P_4\text{-VP}]\text{N}_3$ was added and pulverizing the mixture was continued for appropriate time as indicated in Table I (10–30 min). The reaction progress was followed by TLC. After completion of the reaction, ethyl acetate (EtOAc, 15 mL) was added and the spent polymeric reagent was recovered by filtration, washed with 5 mL of EtOAc and regenerated by, treatment successively with 30 mL of 3M aqueous solution of sodium azide. The residue was extracted with EtOAc (3 × 5 mL) and the combined organic layer was washed with 5% aqueous solution of NaOH (12 mL) and then dried over anhydrous Na_2SO_4 . The solvent was evaporated to afford aryl azides. If further purification is needed column chromatography on silica gel, [eluent : *n*-hexane/ethyl acetate (91 : 9)] provides highly pure products.

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

4-Azidobenzonitrile.. FT-IR (neat), ν (cm^{-1}) = 2923, 2221, 2151, 2109, 1598, 1503, 1416, 1308, 1176, 1126, 833, 747; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 7.29 (2H, d, J = 8 Hz), 7.86 (2H, d, J = 8 Hz).

3-Azidobenzonitrile.. FT-IR (neat), ν (cm^{-1}) = 3069, 2229, 2196, 2198, 1577, 1485, 1473, 1433, 1321, 1301, 1277, 1173, 1183, 1112, 1099, 894, 873, 785, 750 671; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 7.39 (1H, t), 7.50 (1H, d, J = 8 Hz), 7.55 (1H, d, J = 8 Hz), 7.65 (1H, s).

2-Azidobenzonitrile.. FT-IR (neat), ν (cm^{-1}) = 3202, 2227, 2176, 2113, 1584, 1513, 1485, 1426, 1297, 1248, 1159, 1091, 832, 745; ^1H NMR (400 MHz, CDCl_3) δ

(ppm) = 7.46 (1H, t), 7.53 (1H, d, J = 8 Hz), 7.64 (1H, t), 7.69 (1H, d, J = 8.4 Hz).

1-Azido-4-nitrobenzene.. FT-IR (neat), ν (cm^{-1}) = 2923, 2121, 1605, 1512, 1489, 1445, 1420, 1368, 1328, 1286, 1177, 1130, 1118, 1105, 949, 845, 811, 746, 699, 681, 626; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 7.34 (2H, d, J = 8 Hz), 8.24 (2H, d, J = 8 Hz).

1-Azido-3-nitrobenzene.. FT-IR (neat), ν (cm^{-1}) = 3082, 2119, 2115, 1611, 1516, 1476, 1350, 1304, 1270, 1173, 1143, 1080, 903, 885, 873, 813 793, 732, 710, 665, 649; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 7.58 (1H, d, J = 8 Hz), 7.67 (1H, t), 7.83 (1H, s), 7.80 (1H, d, J = 8 Hz).

1-Azido-2-nitrobenzene.. FT-IR (neat), ν (cm^{-1}) = 2920, 2120, 2094, 1584, 1602, 1579, 1519, 1478, 1341, 1320, 1291, 1260, 1156, 1153, 1082, 951, 856, 798, 774, 739, 691, 637, 616; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 7.36 (1H, t), 7.59 (1H, d, J = 8 Hz), 7.74 (1H, t), 7.97 (1H, d, J = 8 Hz).

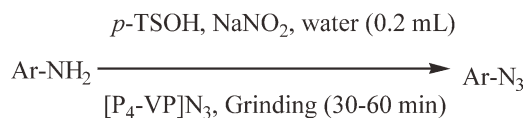
4-Azidophenyl methyl ketone.. FT-IR (neat), ν (cm^{-1}) = 2929, 2110, 2091, 1671, 1596, 1575, 1504, 1415, 1357, 1268, 1181, 1118, 1074, 1015, 957, 829, 721, 621; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 2.54 (3H, s), 7.22 (2H, d, J = 8.8 Hz), 7.97 (2H, d, J = 8.8 Hz).

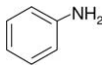
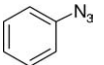

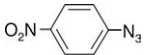

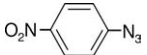

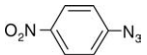

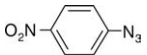

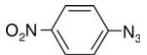
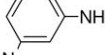
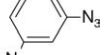
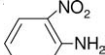
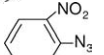


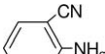
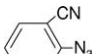
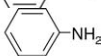
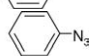
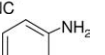
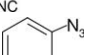
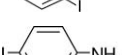
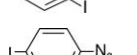
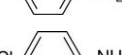

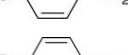

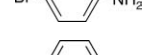
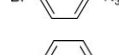
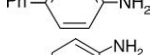

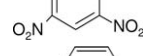
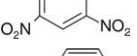
1-Azido-2-iodobenzene.. FT-IR (neat), ν (cm^{-1}) 2923, 2129, 2089, 1578, 1465, 1434, 1303, 1287, 1146, 1016, 743, 684, 633; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 6.92 (1H, t), 7.29 (1H, d, J = 7.6 Hz), 7.44 (1H, t), 7.80 (1H, d, J = 8 Hz).

1-Azido-4-iodobenzene.. FT-IR (neat), ν (cm^{-1}) = 2923, 2121, 2085 1581, 1477, 1399, 1287, 1267, 1179, 1128, 1111, 1058, 1005, 806, 684, 626; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 6.93 (2H, d, J = 7.6 Hz), 7.72 (2H, d, J = 8 Hz).

1-Azido-4-chlorobenzene.. FT-IR (neat), ν (cm^{-1}) = 2930, 2130, 2094, 1593, 1486, 1294, 1127, 1091, 1011, 824, 738, 705; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 7.18 (2H, d, J = 8.4 Hz), 7.56 (2H, d, J = 8.4 Hz).

TABLE I
Diazotization–Azidation of Aromatic Amines by NaNO₂/*p*-TsOH/[P₄-VP] N₃/H₂O^a
under Solvent-Free Conditions



Entry	Ar-NH ₂	Ar-N ₃	Diazotization/azidation Time (min)	Yield (%) ^b
1			60	0.0
2			40	72
3 ^c			40	72
4 ^c			40	72
5 ^c			43	71
6 ^c			45	71
7			55	65
8			55	75
9			40	70
10			45	60
11			55	65
12			55	60
13			55	61
14			40	62
15			55	55
16			60	0.0
17			60	8
18			40	60

^a Molar ratio of NaNO₂/*p*-TsOH/[P₄-VP]N₃/H₂O was equal to 5/6/2/0.2.

^b Yields refer to the average of three times of isolated pure products which were characterized from their spectral data and by comparison with authentic samples.

^c The Entries 3–6, refer to the use of the [P₄-VP]N₃ that is recycled first, second, third, and fourth time, respectively, under identical conditions.

1-Azido-4-bromobenzene.. FT-IR (neat), ν (cm^{-1}) = 2928, 2125, 2088, 1583, 1482, 1290, 1271, 1126, 1071, 1009, 821, 742, 694; ^1H NMR (400 MHz, DMSO- d_6) δ (ppm) = 7.21 (2H, d, $J = 8.8$ Hz), 7.57 (2H, d, $J = 8.8$ Hz).

Regeneration of $[\text{P}_4\text{-VP}]\text{N}_3$

The spent cream-colored polymer (1 g) was added to a 40 mL of a 3M aqueous solution of sodium azide, and was slowly stirred for 24 h. The mixture was filtered and washed with distilled water (3×8 mL), and 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 and it was found that, it had the same capacity as the original form (3.4 mmol of azide ion per gram of polymer). The regenerated polymer reused several times, without losing its activity. Although, the use of the $[\text{P}_4\text{-VP}]\text{N}_3$ that was recycled for fourth time, are given in Table I (Entries 3–6), but also, the regenerated polymer, $[\text{P}_4\text{-VP}]\text{N}_3$, was used for azidation of other aromatic diazonium salts for synthesis of different aryl azides.

RESULTS AND DISCUSSION

In connection with our organic program to develop environmentally being methods using polymer-supported reagents,^{49–58} herein we wish to report an extremely convenient and simple method for preparation of different aryl azides by grinding the combination of aryl amines, p -TSOH, NaNO_2 , H_2O (0.2 mL) and $[\text{P}_4\text{-VP}]\text{N}_3$ in a mortar (Scheme 1). $[\text{P}_4\text{-VP}]\text{N}_3$, is easily prepared according to our previously reported procedure^{56–58} (Scheme 2, Steps 1 and 2).

This polymeric reagent can be readily used for dediazotization-azidation of diazonium salts by grinding, which gives aryl azides. Aryl azide product is removed by adding a solvent in the mortar and dissolving the product. With filtration and evaporation of the solvent, aryl azide product is removed with good to high yields. The main advantage of this polymeric reagent over nonpolymeric reagents is its insolubility in the solvent and consequently its easier work-up by a simple filtration. The reactions can be driven to completion using excess amounts of reagent without the fear of separation of the excess of reagent from the products. We disclose a less hazardous and practical synthesis of aryl azides from their corresponding aryl amines by using a stable and nonexplosive polymeric reagent, $[\text{P}_4\text{-VP}]\text{N}_3$. Although, the toxicity of the polymer was not examined but, we observed that, the polymer is stable for long times (months) without losing its activity. On the other hand, one of the most disadvantages of the polymeric

reagents is their expensive but, in this case, appropriate chemistry is available (Scheme 2, Step 7), and the spent polymeric reagents can in principle be recycled many times (Table I, Entries 3–6).

The reactions could be carried out starting with the anilines, by generating the diazonium salts *in situ*.

Preparation of $[\text{P}_4\text{-VP}]\text{N}_3$, the plausible reaction pathway of diazotization–azidation of aromatic amine and regeneration of the polymer are given in Scheme 2.

To increase the yield of azido compounds optimization of the reaction conditions was accomplished. p -nitroaniline (1 mmol) was chosen as a model substrate and was treated with different molar ratio of NaNO_2/p -TsOH/ $[\text{P}_4\text{-VP}]\text{N}_3/\text{H}_2\text{O}$ (0.2 mL). It was observed that, the 5/6/2/0.2M ratio were the best molar ratio to achieve the highest yield of the product.

The diazotization–azidation reactions were investigated under solvent-free conditions. A good range of available aromatic amines were also subjected to diazotization–azidation by using NaNO_2/p -TsOH/ $[\text{P}_4\text{-VP}]\text{N}_3/\text{H}_2\text{O}$ (0.2 mL). This new, simple method can be successfully applied for the synthesis of a wide range of aryl azides starting from the corresponding aryl amines. Various aromatic amines, with electron-withdrawing groups as well as electron-donating groups, were transformed into aryl azides in good yields (Table I). But when aniline was subjected to this novel diazotization-azidation even after pulverizing for 60 min, no azido product was separated and a few by-products are formed that are not identified (Table I, Entry 1). This result is in agreement with previously reported diazotization-iodination of aniline,⁵⁸ and diazotization–azidation of aniline in water.⁵⁶ Also there is no reported result in some other methods for conversion of aryl amines into aryl azides, from anilines,^{33,45,63} and conversion of aryl boronic acids into aryl azides.³⁵ Also when 4-phenylaniline or 2,4-dinitroaniline were used for diazotization–azidation, the reaction rate is very slow and after 60 min, only a little amount of aryl azide is obtained. For example, when 2,4-dinitroaniline were used only 8% of corresponding aryl azide is separated and 92% of 2,4-dinitroaniline was remained intact.

We have also successfully applied this new method on a large scale. For example, up to 15 mmol of p -nitroaniline (Entry 2) could be converted into 4-nitrophenyl azide without any loss of efficiency.

The aryl azide products were characterized by FT-IR, ^1H NMR spectroscopy, and physical properties were compared to literature values, where available. In this respect, the appearance of two strong band in the region $2080\text{--}2130\text{ cm}^{-1}$ for asymmetric stretching vibration of the --N=N=N , and a weak band at

TABLE II
Comparison of Different Methods for Synthesis of Aryl Azides


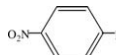

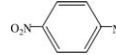

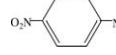
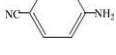
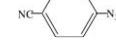
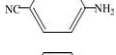
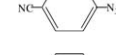

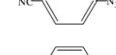

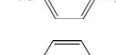

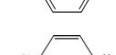
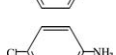
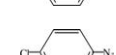
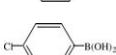
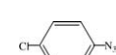
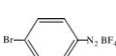
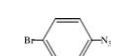
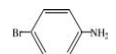
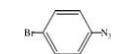

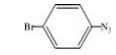
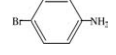
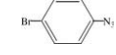
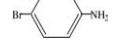
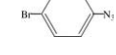
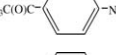
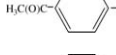
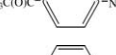
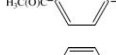
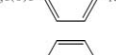
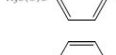
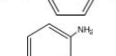
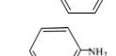
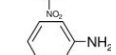
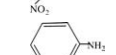








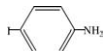

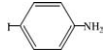

Ref.	Isolated yield (%)	Time (h)	Product	Substrate	Entry
63 ^a	83	2 h			1
56 ^b	95	30 min			2
Table I, entry 2	75	40 min			3
63 ^a	95	2 h			4
33 ^c	7	24 h			5
56 ^b	95	30 min			6
Table I, entry 9	73	40 min			7
45 ^d	99	2 h			8
56 ^b	73	40 min			9
Table I, entry 14	61	40 min			10
35 ^f	70	24 h			11
36 ^d	97	2 h			12
33 ^c	85	3 h			13
34 ^e	82	10 h			14
56 ^b	70	40 min			15
Table I, entry 15	55	55 min			16
33 ^c	15	24 h			17
63 ^a	90	2 h			18
56 ^b	80	30 min			19
Table I, entry 18	60	40 min			20
45 ^d	95	2 h			21
56 ^b	90	40 min			22
Table I, entry 11	66	55 min			23
63 ^a	76	2 h			24

TABLE II. Continued

Ref.	Isolated yield (%)	Time (h)	Product	Substrate	Entry
56 ^b	78	35 min			25
Table I, entry 13	62	55 min			26

^a In this method, the reaction was carried out in the presence of *t*-BuONO, TMSN₃ in CH₃CN at room temperature.

^b In this procedure, the reaction was carried out in the presence of NaNO₂/TsOH/[P₄-VP]N₃ in water at room temperature.

^c In this method, the reaction was carried out in the presence of TfN₃/aq.CuSO₄/Et₃N in CH₂Cl₂/MeOH at room temperature.

^d In this method, the reaction was carried out in the presence of TMSN₃, immobilized in [BMIM][PF₆] at 60–70°C under a nitrogen atmosphere.

^e In this method, the reaction was carried out in the presence of NaN₃, CuI, L-proline and NaOH in DMSO at 60°C.

^f In this method, the reaction was carried out in the presence of NaN₃, CuSO₄, in MeOH at room temperature.

1265–1290 cm⁻¹ for symmetric stretching vibration of the –N=N=N, indicate the formation of corresponding aryl azides.

In Table II, other reported methods for preparation of aryl azides are compared with this approach. As it is demonstrated, the reaction time will be developed which is shorter than previously reported methods. This can probably be attributed to the local concentration of azide ion species inside the pores.

The advantages of this method over conventional classical methods are mild reaction conditions, safe handling, rapid, mildness of polymeric reagent and very simple work-up. In addition, there is current research and general interest in heterogeneous systems because of the importance such systems have in industry and in developing technologies.⁶⁴

CONCLUSIONS

We have developed an efficient, rapid, experimentally simple method for the synthesis of aryl azides from various aniline derivatives via diazotization with sodium nitrite in the presence of *p*-toluene sulfonic acid and deazodination–azidation with a polymer supported azide ion, [P₄-VP]N₃ under solvent-free conditions. The easily accessible [P₄-VP]N₃ reacts rapidly under solvent-free conditions with various arenediazonium salts derived from anilines and related aromatic amines to provide the desired azides. The protocol is operationally simple and efficient method under solvent-free conditions, and with good to high yield in most cases.

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