

Diazotization–Azidation of Amines in Water by Using Crosslinked Poly(4-vinylpyridine)-Supported Azide Ion

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ABSTRACT: The use of polymeric reagents simplifies routine azidation of diazonium salts, because it eliminates the traditional purification. An efficient, simple, and effective method for the preparation of aryl azides is described. The synthesis of aromatic azides from the corresponding amines is accomplished under mild conditions with sodium nitrite in the presence of *p*-toluenesulfonic acid or concentrated H₂SO₄ at low temperature (0–5°C to room temperature). The obtained relatively stable diazonium

salts, followed by treatment with a polymer-supported azide ion in water at room temperature to produce the corresponding aryl azides. The spent polymeric reagents can be regenerated and reused for several times without losing their activity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 788–795, 2012

Key words: diazotization; azidation; aryl amine; diazonium salt

INTRODUCTION

In 1963, Merrifield¹ introduced a modified technique that overcame the problems associated with classical multistep synthesis in solution. This technique has been used in the production of large amount of products. However, recently the chemistry of functional polymers has received great attention and became a practical method for the efficient preparation of novel chemical libraries.^{2–16}

Aromatic diazonium salts have gained attention in synthetic chemistry due to their powerful synthetic and industrial importance. 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 these salts.¹⁷

Aromatic azides are versatile intermediates with a diverse range of applications in organic and bioorganic chemistry,^{18,19} with their use as photoaffinity labeling reagents for biomolecules being particularly important.^{20–22}

Recently, organic azides have been somewhat popularized due to their pivotal role in the emerging

field of “click chemistry,”^{23–26} and in particular, since the discovery of the Cu(I)-catalyzed (stepwise) Huisgen²⁷ cycloaddition between organic azides and terminal alkynes.^{28,29} This powerful and reliable bond-forming process has found to have widespread applications, for example, in combinatorial drug discovery^{30,31} and material science.^{32–34}

The preparation of alkyl azides is relatively straightforward^{18,19,35,36} and can be achieved by simple substitution using azide ion and various electrophiles, or by reaction of the corresponding aliphatic amine with triflyl azide (TfN₃).^{37–39} A recent modification of the latter method, popularized by Wong,⁴⁰ has found to have numerous applications,^{41,42} due to the high yields and relatively mild conditions of the adapted procedure. However, the synthesis of aryl azides relies on a more limited selection of transformations.¹⁸ They are commonly prepared from the corresponding amines via their diazonium salts,^{43,44} which may sometimes be problematic with respect to the presence of incompatible functional groups.

Alternative methods have been investigated, for example, reactions of organometallic aryls (derived from the corresponding aryl halide) with *p*-tosyl azide.^{45,46} More recently, Liu and Tor have applied Wong’s (TfN₃) methodology toward the efficient preparation of aryl azides.⁴⁷ Although powerful, this procedure presents some drawbacks. First, toxic and potentially explosive NaN₃, and the highly reactive Tf₂O are used in excess. Second, TfN₃ has been reported to be explosive when not in solvent, thus presentive further potential hazards.⁴⁸ Recently, Das et al. reported the use of *tert*-butyl nitrite (*t*-BuONO) in combination with NaN₃ in the synthesis of

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aromatic azides.⁴⁹ 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. Direct coupling of aryl halides⁵⁰ or aryl boronic acids⁵¹ with sodium azide catalyzed by copper salts has been reported. These compounds have also been synthesized from aromatic amines with *t*-BuONO followed by the addition of trimethylsilyl azide (TMSN₃).⁴⁹ Preparation of aryl azides by using stable aryl diazonium silica sulfates have also been reported by Zarei et al.⁵² Furthermore, [ArN₂][BF₄] salts immobilized in [BMIM][PF₆] ionic liquid with TMSN₃ have been reported for the preparation of aryl azides.⁵³

Although 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.

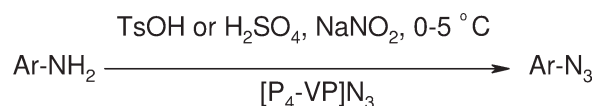
Although polymer-supported reagents especially anion exchange resins have been widely applied in organic synthesis,^{1–16} but a literature search shows that there are a few reports in organic transformation based on polymer supported azide reagent. Brenelli et al. reported that Amberlite IRA 900 supported azide resin is a highly effective reagent for the conversion of α -haloketones into α -azidoketones.⁵⁴ The regioselective ring opening of polycyclic aromatic hydrocarbon epoxides by this polymer also reported by Lakshman et al.⁵⁵ Blass et al.⁵⁶ reported a one-pot, two step preparation of functionalized 1,2,3-triazoles by Merrifield resin supported ammonium azide anion. 1,3-Dipolar cycloaddition by using poly (ethylene glycol)-supported azide also reported by Molteni et al.⁵⁷ Previously, we have also prepared crosslinked poly (4-vinylpyridine) supported azide ion, [P₄-VP]N₃, and have used for synthesis of alkyl azides with alkyl halides.³⁵

In continuation of our studies on the development of application of [P₄-VP]N₃ in organic synthesis, herein we wish to report an improved, fast, and general convenient procedure for the synthesis of aryl azides via diazotization–azidation of aryl amines, in the presence of *p*-toluenesulfonic acid (TsOH) or H₂SO₄ using [P₄-VP]N₃ under heterogeneous conditions (Scheme 1).

EXPERIMENTAL

General

Chemicals were either prepared in our laboratory or were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), and Merck (Germany) Chemical companies. Poly (4-vinylpyridine) crosslinked with 2% divinyl benzene (DVB), [P₄-VP] 2%



Scheme 1 One-pot method for diazotization–azidation of aromatic amines.

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^{10–12,35} (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, FTIR, 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. FTIR 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.

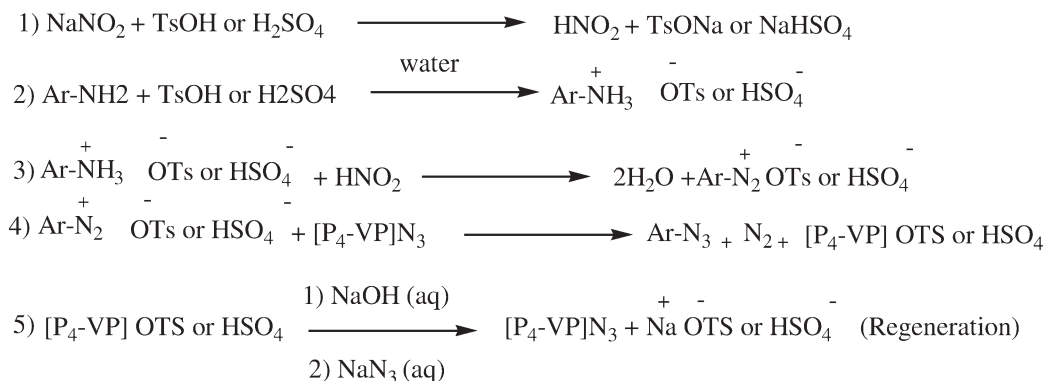
Preparation of [P₄-VP]I and [P₄-VP]N₃

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 distilled water and acetonitrile. It was then dried under vacuum in the presence of P₂O₅ 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 rapidly 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 0.1N 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 or H₂SO₄ by using [P₄-VP]N₃ in water at 0–5°C to room temperature

An aryl amine (1 mmol) was added to a solution of H₂SO₄ or TsOH (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



Scheme 2 Preparation of $[\text{P}_4\text{-VP}]\text{N}_3$, mechanism of diazotization–azidation of aromatic amines and regeneration of polymer.

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, 0.276 g (4 mmol) of NaNO_2 was added, and stirring was continued until the diazonium salt was formed. After completion of the reaction, 0.58 g (2 mmol) of $[\text{P}_4\text{-VP}]\text{N}_3$ was added (the salient of nitrogen gas is observed), and the mixture was slowly stirred magnetically at room temperature for appropriate time as indicated in Table I (30–100 min). The mixture was filtered and was washed with distilled water (3×8 mL) and ethyl acetate (EtOAc; 15 mL). The residue was extracted with EtOAc (3×10 mL) and the combined organic layer was washed with 5% NaOH solution (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.

FTIR and $^1\text{H-NMR}$ Spectral data of some selected prepared aryl azides are given bellow:

1-Azido-4-nitrobenzene

FTIR, ν (cm^{-1}) = 3081, 2150, 2100, 1611, 1585, 1516, 1476, 1350, 1304, 1270, 1142, 1080, 902, 873, 813, 793, 732, 711, 696, 650; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.34 (d, 2H, $J = 8$ Hz), 8.28 (d, 2H, $J = 8$ Hz).

1-Azido-3-nitrobenzene

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.26 (d, 1H), 7.34 (d, 1H); 7.54 (t, 1H), 7.98 (s, 1H).

1-Azido-2-nitrobenzene

FTIR, ν (cm^{-1}) = 3072, 2120, 2090, 1601, 1581, 1522, 1478, 1341, 1289, 1168, 1081, 1014, 856, 775, 739, 701, 639; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 7.30 (t, 2H), 7.61(d, 1H), 7.91 (d, 1H).

4-Azidophenyl methyl ketone

FTIR (neat), ν (cm^{-1}) = 3092, 2120, 2091, 1678, 1594, 1574, 1502, 1413, 1358, 1264, 1177, 1130, 957, 831, 720, 624; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 2.57 (s, 3H), 7.06 (d, 2H), 7.95 (d, 2H).

1-Azido-2-iodobenzene

FTIR (neat): ν (cm^{-1}) 3070, 2125, 2088, 1578, 1465, 1434, 1303, 1287, 1147, 1016, 744, 686, 633; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 6.87 (d, 1H), 7.15 (d, 1H), 7.39 (t, 1H), 7.79 (t, 1H).



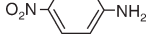







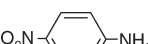

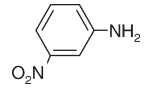
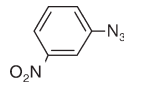


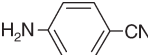
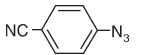



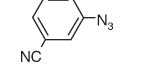


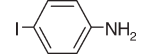
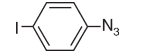
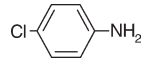
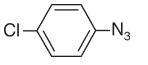
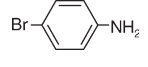
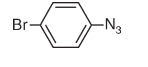

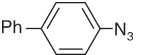
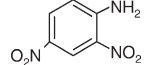
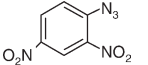
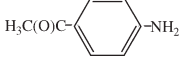
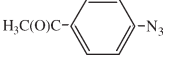
1-Azido-4-iodobenzene

FTIR (neat): ν (cm^{-1}) = 3092, 2120, 2086, 1618, 1587, 1478, 1287, 1267, 1187, 1128, 1058, 1005, 811, 683, 632; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 6.79 (d, 2H), 7.80 (d, 2H).

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

To an aqueous solution of NaOH (10 mL, 0.10N) was added the spent cream-colored polymer (1 g) and was slowly stirred for 2 h. Then, the suspension was filtered and was washed with water. Then, the polymer 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 was washed several times with distilled water and dried under vacuum in the presence of P_2O_5 at 40°C overnight (Scheme 2, step 5). The capacity of the regenerated polymer was determined and 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 can be 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 preparation of other aryl azides.

TABLE I
Diazotization-Azidation of Aromatic Amines by NaNO₂/TsOH or H₂SO₄/[P₄-VP]N₃ at 0°C to Room Temperature

$\text{Ar-NH}_2 \xrightarrow[\text{[P}_4\text{-VP]N}_3]{\text{TsOH or H}_2\text{SO}_4, \text{NaNO}_2, 0-5^\circ\text{C}} \text{Ar-N}_3$				
Entry	Ar-NH ₂	Ar-N ₃	Diazotization/Azidation Time (min)	Yield (%) ^a
1			100 (100) ^b	0.0 (0.0) ^b
2			30 (40)	95 (72)
3 ^c			30 (40)	95 (72)
4 ^c			30 (40)	95 (72)
5 ^c			32 (43)	95 (72)
6 ^c			35 (45)	95 (72)
7			40 (55)	90 (75)
8			50 (60)	86 (65)
9			30 (40)	95 (70)
10			35 (45)	88 (60)
11			40 (55)	83 (65)
12			40 (55)	73 (60)
13			35 (40)	78 (60)
14			40 (55)	73 (58)
15			40 (55)	70 (55)
16			240 (240)	trace (0.0)
17			240 (240)	10 (0.0)
18			30 (40)	80 (60)

^a Yield refers to isolated pure products, which were characterized from their spectral data and by comparison with authentic samples.

^b Values in the parentheses correspond to the reaction that took place in the presence of H₂SO₄.

^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.

TABLE II
Comparison of Different Methods for Synthesis of Aryl Azides


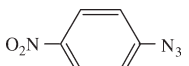



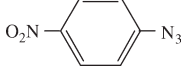
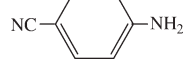
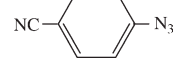

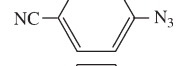

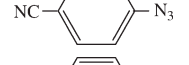

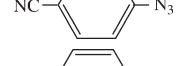
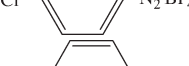
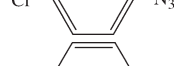
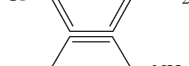
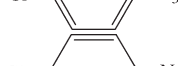
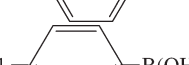
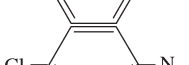
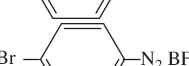

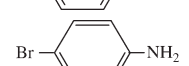





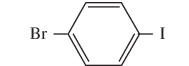

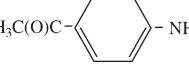
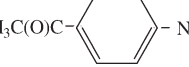
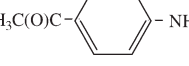
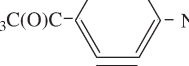
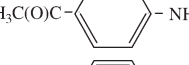
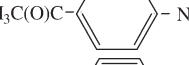
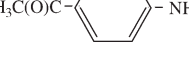
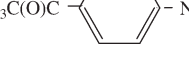


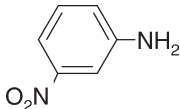
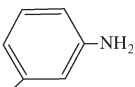
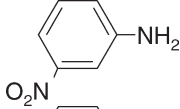
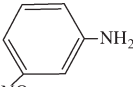
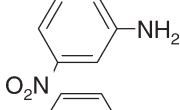
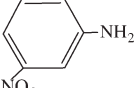
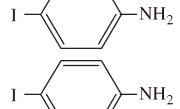
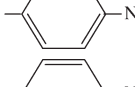
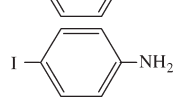
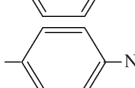
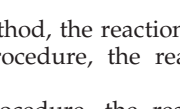
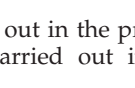
Entry	Product	Substrate	Time (h)	Isolated yield (%)	Ref.
1			2 h	83	58 ^a
2			30 min	95	Table I, entry 2 ^b
3			40 min	72	Table I, entry 2 ^c
4			2 h	95	58 ^a
5			24 h	7	47 ^d
6			30 min	95	Table I, entry 9 ^b
7			40 min	70	Table I, entry 9 ^c
8			2 h	99	53 ^e
9			40 min	73	Table I, entry 14 ^b
10			55 min	58	Table I, entry 14 ^c
11			24 h	70	51 ^f
12			2 h	97	53 ^e
13			3 h	85	47 ^d
14			10 h	82	50 ^g
15			40 min	70	Table I, entry 15 ^b
16			55 min	55	Table I, entry 15 ^c
17			24 h	15	47 ^d
18			2 h	90	58 ^a
19			30 min	80	Table I, entry 18 ^b
20			40 min	60	Table I, entry 18 ^c

TABLE II. (Continued)

Entry	Product	Substrate	Time (h)	Isolated yield (%)	Ref.
21			2 h	95	53 ^e
22			40 min	90	Table I, entry 7 ^b
23			55 min	75	Table I, entry 7 ^c
24			2 h	76	58 ^a
25			35 min	78	Table I, entry 13 ^b
26			40 min	60	Table I, entry 13 ^c

^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 procedure, the reaction was carried out in the presence of NaNO₂/H₂SO₄/[P₄-VP]N₃ in water at room temperature.

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

^e 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.

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

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

RESULTS AND DISCUSSION

Crosslinked poly (4-vinylPyridine) supported sodium azide, [P₄-VP]N₃, was easily prepared according to our previously reported procedure³⁵ and used as an efficient procedure for azidation of stable diazonium salts of aromatic amines (Scheme 1). 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 for azidation of generating the diazonium salts *in situ*, which gives aryl azides on dediazotiation. This polymeric reagent is used in single step reaction; its main advantage over nonpolymeric reagents is its insolubility in the reaction medium 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, [P₄-VP]N₃. Although the toxicity of the polymer was not examined, 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 5), 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*.

The plausible mechanism of diazotization–azidation of aromatic amine is 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 NaNO₂/TsOH or H₂SO₄/[P₄-VP]N₃. It was observed that the 4/2/2 molar ratio and water as solvent were the best.

The diazotization–azidation reactions were investigated under mild and completely heterogeneous conditions at room temperature. A good range of available aromatic amines were also subjected to diazotization–azidation by using NaNO₂/TsOH/[P₄-VP]N₃ or NaNO₂/H₂SO₄/[P₄-VP]N₃ in water at 0°C

to room temperature. 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 100 min, no azido product was separated and a few byproducts are formed that are not identified (Table I, entry 1). This result is in agreement with previously reported diazotization–iodination of aniline.⁵⁸ Also there is no reported result in some other methods for conversion of aryl amines into aryl azides, from anilines,^{47,53,59} and conversion of aryl boronic acids into aryl azides.⁵¹ Also when 4-phenylaniline or 2,4-dinitroaniline were used for diazotization–azidation, the reaction rate is very slow and after 4 h, only a little amount of aryl azide is obtained. For example, when 2,4-dinitroaniline were used only 10% of corresponding aryl azide is separated and 90% of 2,4-dinitroaniline was remained intact.

Inspection of Table I reveal that when TsOH is used, the reaction times are shorter and the isolated yields are higher than diazotization–azidation in the presence of H₂SO₄. This can probably be attributed to that; diazonium salt of TsOH is more stable⁶⁰ than diazonium salt of sulfuric acid.

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 FTIR, ¹H- and ¹³C-NMR spectroscopy, and physical properties were compared with literature values, where available. In this respect, the appearance of two strong band in the region 2080–2130 cm⁻¹ for asymmetric stretching vibration of the –N=N=N, and a weak band at 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 our procedure. 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.⁶¹

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 TsOH or sulfuric acid and azidation with a polymer supported azide ion, [P₄-VP]N₃. The easily accessible [P₄-VP]N₃ reacts rapidly under mild conditions with various anilines and related aromatic amines to provide the desired azides. The protocol is operationally simple and efficient method under heterogeneous conditions, and at room temperature with good to high yield in most cases.

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