An Efficient Method for Nitration of Aromatic Compounds Over Solid Acid and Polymer-Supported Sodium Nitrite

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ABSTRACT: A variety of aromatic compounds are nitrated under heterogeneous conditions using a polymer-supported hydrochloric acid, [P_4-(VP)]HCl, with a polymer-supported sodium nitrite, [P_4-VP]NO_2, or sodium nitrite in ethanol at room temperature with high yields. This methodology is useful for nitration of activated aromatic compounds. In this procedure, the work-up is very easy, and the spent polymeric reagent can be regenerated and reused. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 582–588, 2011

Key words: nitration; aromatic compound; polymeric reagent; solid acid

INTRODUCTION

Nitroaromatic compounds are important and useful intermediates for preparation of other compounds, particularly amines by reduction of nitro group.[1–5] Nitroaromatic compounds are widely studied because of their application as solvents, dyes, pharmaceuticals, perfumes, agrochemicals, explosives, and plastics in the industry.[1]

There are many useful reagents for nitration such as concentrated nitric acid,[6] mixtures of nitric acid with sulfuric acid,[7] nitric acid in acetic anhydride,[8] nitric acid and trifluoromethanesulfonic acid,[9] nitrate salts in trifluoroacetic anhydride,[10] ozone and nitrogen dioxide,[11] N_2O_5 and $Fe(acac)_3$,[12] *N*-nitropyridinium and quinolinium salts,[13] or trifluoromethanesulfonic anhydride,[14] metal nitrates in sulfuric acid,[15–17] lanthanide(III) nosylates,[18] guanidinium nitrate,[19] potassium nitrate or nitric acid and boron trifluoride monohydrate mixtures[20] and sodium nitrate/chlorotrimethyl silane and aluminum chloride mixtures.[21] Many of these reactions have been carried out in the presence of protic or Lewis acids.

However, the majority of the reported methods for nitration of aromatic compounds have disadvantages such as low regioselectivity,[12,22–24] over nitration,[23,24] competitive oxidation of substrates,[24] tedious work-up,[25–27] strong acidic media,[19,25,28,29] and safety problems (storage, handling and use of toxic transition metal cations such as Hg^{2+}, Cu^{2+}, etc.[15–17]).

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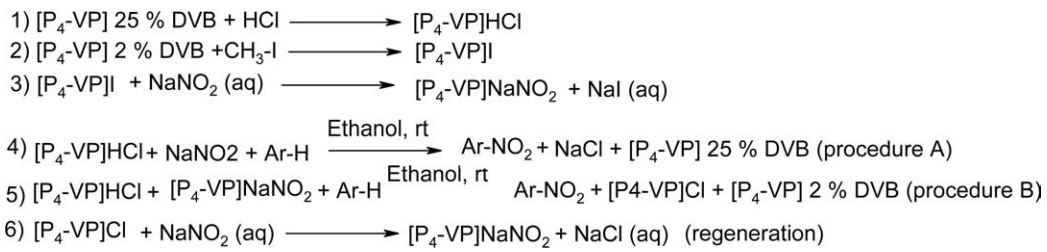
These disadvantages have encouraged the researchers for extensive efforts to use alternative reagents such as solid acids,[2,16,23,27,30–32] other sources of No_2^+ (nitronium salts,[14,22] *N*-nitropyridinum salt,[33] nitrogen oxide,[12,23] and peroxynitrite[34]), organic nitrating agents (acetyl nitrate, benzoyl nitrate, and trimethylsilyl nitrate),[35,36] etc.[18,37,38]

Although there are numerous applications of solid-supported reagents and scavengers in literature,[39–58] but to the best of our knowledge, there is only one report[53] on the nitration of aromatic compounds using polymer-supported nitrating reagents. Recently, we prepared poly(4-vinylpyridine) (VP) crosslinked with 2% divinylbenzene (DVB)-supported sodium nitrite, [P_4-VP]NO_2, and poly(4-VP) crosslinked with 25% DVB-supported hydrochloric acid, [P_4-VP]HCl, which was used for synthesis of nitroalkanes,[47] *N*-nitrosation of secondary amines,[48,49] synthesis of nitroaromatic compounds by [P_4-VP]NO_2/$KHSO_4$,[53] and synthesis of azo chromophores.[52]

Crosslinked poly(4-VP)-supported hydrochloric acid, [P_4-VP]HCl, would be a proton donor source similar to reported acidic solid supports or acidic resins such as polystyrene sulfonic acid, Nafion-H,[59] and silica sulfuric acid.[60] To run reactions in the heterogeneous conditions, this acidic resin, [P_4-VP]HCl, was used as a solid acid for generation of No_2^+ in conjunction with sodium nitrite or [P_4-VP]NO_2 in a green organic solvent (ethanol).

In continuation of our studies on application of crosslinked poly(4-VP)-supported sodium nitrite in organic synthesis,[47–49,52,53] herein we report a green, clean, and simple method for nitration of activated aromatic compounds using crosslinked poly(4-VP)-supported hydrochloric acid, [P_4-VP]HCl in the presence of [P_4-VP]NO_2 or $NaNO_2$. In this regard, a



Scheme 1 Preparation of [P_4-VP]HCl, [P_4-VP]NO_2 and nitration of aromatic compounds.

number of different reaction conditions for generation of HNO_2 with relatively strong organic acidic resins and [P_4-VP]NO_2 or $NaNO_2$ for nitration of aromatic compounds was investigated. However, in this report the study of the nitration of activated aromatic compounds in the presence of [P_4-VP]HCl/$NaNO_2$ or [P_4-VP]HCl/[P_4-VP]NO_2 is only presented.

EXPERIMENTAL

Chemicals

Chemicals were either prepared in our laboratory or were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI) and Merck (Germany) chemical companies. Poly(4-VP) crosslinked with 2% DVB, [P_4-VP] 2% DVB, and poly(4-VP) crosslinked with 25% DVB, [P_4-VP] 25% DVB, were purchased from Fluka. [P_4-VP]NO_2 and [P_4-VP]HCl were prepared according to our procedures[47–49] (Scheme 1).

The reactions were monitored by thin layer chromatography (TLC) using silica gel Polygram Sil G/UV 254 plates. All products were characterized by comparison of their Fourier transform infra red (FTIR), proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra, TLC and physical data with pure compounds. All yields refer to the isolated products. FTIR and NMR spectra were run on a Bruker, Equinox (model 55) and Bruker AC 500, Aveance DPX spectrophotometer at 500 MHz for ^{1}H and at 125 MHz for ^{13}C NMR in $CDCl_3$ solution (using tetramethylsilane as internal reference).

Preparation of [P_4-VP]HCl

Poly(4-VP) crosslinked with 25% DVB (1 g) was added to a concentrated hydrochloric acid solution (10 mL) and was slowly stirred for 24 h at room temperature. The mixture was filtered, washed with distilled water until the filtrate gave a negative test for HCl. Then it was dried in vacuum at 50°C for 5 h and 1.2 g of [P_4-VP]HCl was prepared [step (1) in Scheme 1]. The capacity of [P_4-VP]HCl was determined by titration of the filtrates with a standard solution of sodium hydroxide, and it was found to be 5 mmol g^{-1} of polymer.

Preparation of [P_4-VP]NO_2

Poly(4-VP) 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 stirred for 24 h at room temperature. The yellow quaternized polymer, [P_4-VP]I, was filtered and washed with distilled water and acetonitrile. It was then dried under vacuum in the presence of P_2O_5 at 40°C.

The obtained [P_4-VP]I was added to 40 mL of a 3*M* solution of sodium nitrite and slowly stirred for 24 h. The prepared resin, [P_4-VP]NO_2, was filtered off and was washed rapidly with distilled water until the filtrate gave a negative test for No_2^-. It was then washed with ether and dried under vacuum in the presence of P_2O_5 at 40°C (1.6 g). The activity of the polymer was determined by potentiometric titration of the filtrates with a 0.1*N* solution of silver nitrate, and it was found to be 3.7 mmol g^{-1} of the polymer.

General procedure for nitration of activated aromatic compounds using [P_4-VP]HCl/$NaNO_2$ or [P_4-VP]HCl/[P_4-VP]NO_2

[P_4-VP]HCl (1.64 g, 8.2 mmol) and sodium nitrite (207 mg, 3 mmol) or [P_4-VP]NO_2 (0.8 g, 3 mmol) were added to a solution of an activated aromatic compound (1 mmol) in ethanol (10 mL), and the mixture was slowly stirred magnetically at room temperature for appropriate time as indicated in Table II. The progress of the reaction was monitored by TLC. After completion of the reaction, the suspension was filtered, washed with ethanol (2×5 mL), and the filtrate was dried with $MgSO_4$. After filtration and evaporation of the solvent, the nitroaromatic compounds were obtained in high yields (Table II). If further purification was needed, flash chromatography on silica gel [eluent: *n*-hexane/ethyl acetate (80/20)] was used, which provides highly pure products.

Nitration of *N*,*N*-dimethylanilline using [P_4-VP]HCl/$NaNO_2$ or [P_4-VP]HCl/[P_4-VP]NO_2 (a typical procedure)

[P_4-VP]HCl (1.64 g, 8.2 mmol) and sodium nitrite (207 mg, 3 mmol) or [P_4-VP]NO_2 (0.8 g, 3 mmol),

TABLE I
Optimization of the Reaction Conditions for Nitration of Phenol (1 mmol) as a Model Substrate

Entry	Solvent	[P_4-VP]HCl/$NaNO_2$ or [P_4-VP]HCl/[P_4-VP]NO_2	Procedure A		Procedure B	
			Time (h)	Yield[a] (%)	Time (h)	Yield[a] (%)
1	*n*-Hexane	2	6	0.0	–	–
2	*n*-Hexane	2	–	–	7	0.0
3	Acetonitrile	2	9	41	–	–
4	Acetonitrile	2	–	–	10.5	35
5	1,4-Dioxane	2	6	15	–	–
6	1,4-Dioxane	2	–	–	6	12
7	CCl_4	2	7	20	–	–
8	CCl_4	2	–	–	7	18
9	$CHCl_3$	2	7	22	–	–
10	$CHCl_3$	2	–	–	10	20
11	Ethanol	2	6	50	–	–
12	Ethanol	2	–	–	7	35
13	Ethanol	5 : 2	6	57	–	–
14	Ethanol	5 : 2	–	–	7	41
15	Ethanol	7 : 3	6	61	–	–
16	Ethanol	7 : 3	–	–	7	52
17	Ethanol	8 : 3	6	65	–	–
18	Ethanol	8 : 3	–	–	7	60
19	Ethanol	8.2 : 3	6	70	–	–
20	Ethanol	8.2 : 3	–	–	7	65
21	Ethanol	8.5 : 3	6	70	–	–
22	Ethanol	8.5 : 3	–	–	7	65

[a] Yields refer to isolated total products.

were added to a solution of *N*,*N*-dimethylaniline (121 mg, 1 mmol) in ethanol (10 mL; in a round bottom flask), and the mixture was stirred magnetically at room temperature for appropriate time as indicated in Table II. The progress of the reaction was monitored by TLC. After completion of the reaction, the suspension was filtered, washed with ethanol (2×5 mL), and the filtrate was dried with $MgSO_4$. After filtration and column chromatography, 4-nitro-*N*,*N*-dimethylaniline was obtained in 74% or 79% yields (Table II).

m.p: 164–166°C (Ref. 61: 164°C); FTIR (KBr), ν (cm^{-1}): 3088 (C—H, aromatic) 2955 (C—H, CH_3), 1600, 1592, and 1484 (C=C, aromatic), 1530 (N=O, asymmetric), 1383 (N=O, symmetric), 1201 (C—O) and 1117 (C—N); ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 3.160 (6H, s, CH_3), 6.65 (2H, d, J = 9.42 Hz), 7.58 (2H, d, J = 9.42 Hz).

Regeneration of [P_4-VP]NO_2 and [P_4-VP]HCl

The spent cream-colored polymer, [P_4-VP]NO_2, (1 g) was added to 40 mL of a 3*M* solution of sodium nitrite, and was slowly stirred for 24 h and then 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. The capacity of the regenerated polymer was determined and was found that, it had the same capacity as the original form (3.7 mmol per gram of polymer). The regenerated polymer can be reused several times with little loss of activity [entries (6 and 7) in Table II].

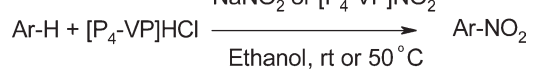
In procedure A, the spent polymer was washed with distilled water to obtain the regenerated poly(4-VP) crosslinked with 25% DVB that was easily converted to regenerated [P_4-VP]HCl in concentrated hydrochloric acid (10 mL) as previously described.

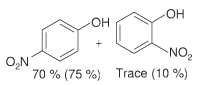
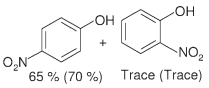
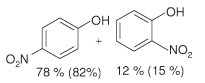
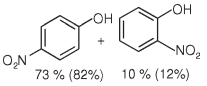
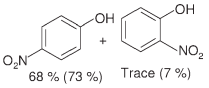
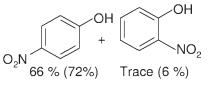
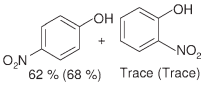
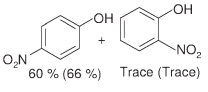
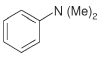
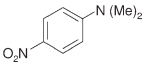
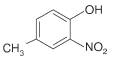
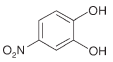
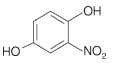
RESULTS AND DISCUSSION

[P_4-VP]HCl and [P_4-VP]NO_2 were easily prepared according to the previously reported procedures[47,48] and used as efficient, simple and general procedures for nitration of different activated aromatic compounds [steps (1–5) in Scheme 1]. A number of different reaction conditions for generation of HNO_2 were investigated, and it was observed that [P_4-VP]HCl/$NaNO_2$ [step (4) in Scheme 1, procedure A] and [P_4-VP]HCl/[P_4-VP]NO_2 [step (5) in Scheme 1, procedure B] are regioselective and chemoselective nitrating reagents for nitration of activated aromatic compounds.

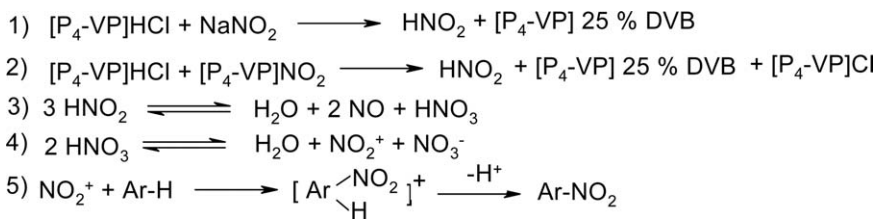
To increase the yield of nitro compounds, optimization of the reaction conditions was accomplished. Phenol (1 mmol) was chosen as a model substrate and was nitrated by [P_4-VP]HCl/$NaNO_2$ (procedure A) and [P_4-VP]HCl/[P_4-VP]NO_2 (procedure B), with a molar ratio of 2 : 2 in various available solvents.

TABLE II
Nitration of Activated Aromatic Compounds with $[P_4\text{-VP}]HCl/NaNO_2$ or $[P_4\text{-VP}]HCl/[P_4\text{-VP}]NO_2$



			Procedure A[b]		Procedure B[c]	
Entry	Substrate	Product[a]	Time (h)	Yield[d] (%)	Time (h)	Yield[d] (%)
1		 70 % (75 %) Trace (10 %)	6 (4.5)[e]	70 (85)[e]	–	–
2		 65 % (70 %) Trace (Trace)	–	–	7 (5.5)	65 (70)
3		 78 % (82%) 12 % (15 %)	9 (7.5)	88 (97)	–	–
4[f]		 73 % (82%) 10 % (12%)	–	–	10.5 (9)	85 (90)
5[f]		 68 % (73 %) Trace (7 %)	6 (4.5)	68 (80)	–	–
6[g]		 66 % (72%) Trace (6 %)	6 (4.5)	66 (78)	–	–
7[g]		 62 % (68 %) Trace (Trace)	–	–	7 (5.5)	62 (68)
8		 60 % (66 %) Trace (Trace)	–	–	7 (5.5)	60 (66)
9			4 (3.5)	74 (79)	6 (5)	70 (74)
10	Toluene	No reaction	10 (10)	0.0 (0.0)	10 (10)	0.0 (0.0)
11	*p*-Cresol		4 (3)	67 (78)	5 (4.5)	82 (84)
12	Biphenyl	No reaction	10 (10)	0.0 (0.0)	10 (10)	0.0 (0.0)
13	Catechol		1 (0.5)	89 (92)	2 (1.5)	86 (88)
14	*m*-Xylene	No reaction	10 (10)	0.0 (0.0)	10 (10)	0.0 (0.0)
15	Hydroquinone		0.33 (0.0)	97 (99)	1 (0.5)	95 (97)
16	2-Naphthol		5 (4)	95 (96)	6.5 (5.5)	90 (92)

[a] The structures were confirmed by comparison of their FTIR, ^1H and ^{13}C NMR spectra, TLC and physical data with pure compounds.
[b] Molar ratio of $[P_4\text{-VP}]HCl$: $NaNO_2$: aromatic compound is equal to 8.2 : 3 : 1, and the reaction take place in ethanol at room temperature.
[c] Molar ratio of $[P_4\text{-VP}]HCl$: $[P_4\text{-VP}]NO_2$: aromatic compound is equal to 8.2 : 3 : 1, and the reaction take place in ethanol at room temperature.
[d] Yields refer to total isolated products.
[e] Values in the parentheses refer to the reactions that take place at 50°C.
[f] The entries 4 and 5 refer to the use of $[P_4\text{-VP}]HCl$ that is reused second and third time respectively, under identical conditions.
[g] The entries 6 and 7 refer to the use of $[P_4\text{-VP}]NO_2$ that is reused second and third time respectively, under identical conditions.



Scheme 2 Plausible mechanism for nitration of aromatic compounds.

The results are summarized in Table I (entries 1–12) and show that, ethanol is the best solvent. The nitration of phenol (1 mmol; as a model substrate with different molar ratio of [P_4-VP]HCl/$NaNO_2$ (procedure A) and [P_4-VP]HCl/[P_4-VP]NO_2 (procedure B) in ethanol at room temperature were investigated, and the results are given in Table I (entries 13–22). As shown in Table I, the best molar ratio of [P_4-VP]HCl/$NaNO_2$ and [P_4-VP]HCl/[P_4-VP]NO_2 was 8.2 : 3. Then these reagents were used for nitration of aromatic compounds, and it was observed that using [P_4-VP]HCl/$NaNO_2$ and [P_4-VP]HCl/[P_4-VP]NO_2 systems are efficient reagents for the regioselective and chemoselective nitration of activated aromatic compounds. Although, some of the aromatic compounds such as phenol, substituted phenols, 2-naphthol, and *N*,*N*-dimethylaniline were nitrated with good to moderate yields under mild and heterogeneous conditions, but an attempt to nitration with toluene, biphenyl, and *m*-xylene even after 15 h, no nitro products were observed (entries 6, 8, 10 in Table II).

The nitration reactions were investigated under mild and completely heterogeneous conditions at room temperature or at 50°C (with increase in the temperature, the reaction time decreases), and the results are summarized in Table II (the values in the parentheses, refer to the reactions that take place at 50 °C). Inspection of Table II reveals that, the yields of nitration from procedure A is higher than procedure B and vice versa, the reaction time is shorter than procedure B, this can probably be attributed to the higher penetration rate of nitrite ion inside the pores, when $NaNO_2$ is used.

The plausible mechanism is given in Scheme 2; in these new systems the *in situ* generation of nitronium ion (No_2^+) mechanism may be proposed. Using acidic resin, [P_4-VP]HCl in conjunction with $NaNO_2$ or [P_4-VP]NO_2, the HNO_2 is generated [steps (1) and (2) in Scheme 2]. Dispropotionation of nitrous acid, HNO_2, is noticeable, and HNO_3 is generated [step (3) in Scheme 2].[62] Autoprotolysis is followed by rapid loss of water, which can then react with a further molecule of HNO_3 to generate nitronium ion (No_2^+) [step (4) in Scheme 2]. The nitration of aromatic compound is then followed [step (5) in Scheme 2].

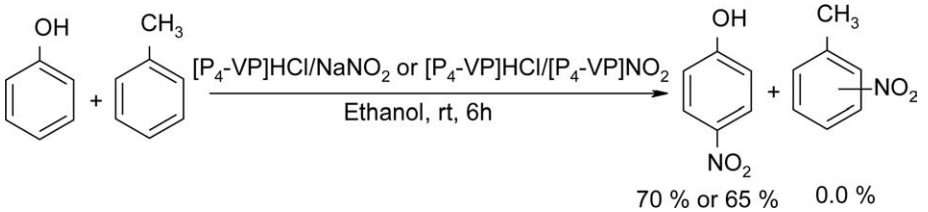
The percentages of products were obtained by GC/MASS analysis. The absence of dinitro phenols was ascertained by GC/MASS analysis of the crude reaction mixtures.

The superior regioselectivity of our method is clear and can be justified by comparison of percentages of para isomers with previously reported protocols (Table III).

To demonstrate the chemoselectivity of these methods, a competitive reaction was performed between phenol and toluene. It was observed that

TABLE III
Nitration of Phenol in Different Methods

Entry	Reagent	*o*-Nitrophenol (%)	*p*-Nitrophenol (%)	Ref.
1	$NaNO_2/KHSO_4$	63	12	63
2	$NaNO_2$/silica sulfuric acid	30	20	30
3	HNO_3/sulfated titania	68.6	2.3	64
4	HNO_3/microemulsion	50	50	10
5	Mn $(NO_3)_3{\cdot}2H_2O$	60	40	65
6	Cu $(NO_3)_2{\cdot}2H_2O$	40	60	65
7	Fe $(NO_3)_3{\cdot}9H_2O$	50	50	65
8	ZrO $(NO_3)_2{\cdot}XH_2O$	40	60	66
9	$NaNO_3$/Mg $(HSO_4)_2$	36	26	67
10	HNO_3/P_2O_5/silica gel	10	90	28
11	$NaNO_3$/silica sulfuric acid/wet SiO_2	0.0	85	60
12	[P_4-VP]HCl/$NaNO_2$	Trace	68	Entry 1, in Table I
13	[P_4-VP]HCl/[P_4-VP] NO_2	Trace	65	Entry 2, in Table I



Scheme 3 Chemoselectivity of the polymeric reagents.

nitration of phenol occurred exclusively, whereas toluene remained intact in the reaction mixture even after 7 h (Scheme 3).

The advantages of these methods over conventional classical methods are regioselectivity, chemoselectivity, simple experimental procedure, safe handling, stability, mildness of the reaction conditions, simple work-up, (if the conversion is completed and only one isomer is prepared, only filtration and evaporation of the solvent, is needed), and no oxidation product and over nitration by-products are observed.

CONCLUSION

Poly(4-VP)-supported hydrochloric acid and poly(4-VP)-supported sodium nitrite were easily prepared and have been used for the efficient and selective nitration of activated aromatic compounds by two procedures A and B. Ease of product isolation, stability, safe handling, regioselectivity, chemoselectivity, and mildness of the reaction conditions make these methods useful in the organic synthesis.

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