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Melamine-$(H_2SO_4)_3$ and PVP-$(H_2SO_4)_n$ as solid acids: Synthesis and application in the first mono- and di-nitration of bisphenol A and other phenols

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Abstract

Melamine and poly vinylpyrrolidone (PVP) reacted with neat sulfuric acid readily to form two new organic solid acids namely melamine-$(H_2SO_4)_3$ and PVP-$(H_2SO_4)_n$. These solid acids were used for the first nitration of bisphenol A as well as other phenols in the presence of NH_4NO_3. Mono- and di-nitro bisphenol A have been characterized with IR and ^1H NMR techniques.

Keywords: Bisphenol A; Melamine-$(H_2SO_4)_3$; Nitration; PVP-$(H_2SO_4)_n$; Phenols

In several industrially important processes such as nitration, nitrosation, *etc*., a large amount of sulfuric acid is required because the water by-product slows the reaction down by diluting the acid. At the end of these processes, a large amount of ‘‘spent acid’’ is obtained which, in batch reactions, is usually neutralized and disposed of, while, in continuous processes, it has to be recycled by complex techniques. Moreover, sulfuric acid is corrosive and dangerous to transport and handle [1,2]. The above mentioned disadvantages for the application of concentrated sulfuric acid have led to a substantial effort to develop viable alternatives, inter idea using some deferent types of new solid acids replacing sulfuric acid [3–8].

Nitration of phenols is a fundamental process, because nitrophenols are important intermediates for the manufacture of drugs and pharmaceuticals. Also these compounds are of the most important substances in environmental chemistry. Nitration of phenols reaction as a special case has been studied using various nitrating agents under different conditions [9–13]. Considering some draw backs from these reactions, there is still a good scope for research towards finding green and eco-friendly protocol for the nitration of phenols.

Bisphenol A, commonly abbreviated as BPA, was first reported by Dianin in 1891 [14]. It is prepared by the condensation of acetone (hence the suffix A in the name) with two equivalents of phenol. The reaction is catalyzed by an acid, such as hydrochloric acid (HCl) or a sulfonated polystyrene resin [15,16].

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1. Experimental

1.1. Preparation of melamine-(H_2SO_4)$_3$ [17]

In a 50 mL beaker, 6 g of H_2SO_4 (98%) and 2.52 g of melamine were stirred for 10 min and a white solid [melamine-(H_2SO_4)$_3$] was obtained.

1.2. Preparation of PVP-(H_2SO_4)$_n$ [18]

In a 50 mL beaker, 2.2 g of H_2SO_4 (98%) and 2.4 g of poly vinylpyrrolidone (PVP) were stirred for 15 min and a white solid *PVP-(H_2SO_4)$_n$* was obtained.

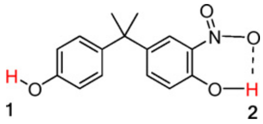
1.3. Mono-nitration of bisphenol A with melamine-(H_2SO_4)$_3$/NH_4NO_3 system—a typical procedure

To a solution of bisphenol A (0.228 g, 1 mmol) in $CHCl_3$ (5 mL), was added NH_4NO_3 (0.16 g, 2 mmol), melamine-(H_2SO_4)$_3$ (0.28 g, 0.7 mmol), and wet SiO_2 (50%, w/w) (0.4 g) and the resulting mixture stirred under the reflux. The reaction was completed after 20 min. The product was extracted with $CHCl_3$ (2 × 10 mL) and dried over anhydrous Na_2SO_4 (5 g). Evaporation of the solvent afforded the crude product (0.117 g, 43%).

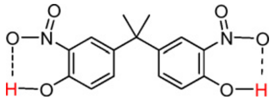
Melamine-(H_2SO_4)$_3$: White solid, IR (KBr): 3133(b), 2613(w), 1721(m), 1652(s), 1506(w), 1176(s) cm^{-1}.

PVP-(H_2SO_4)$_n$: White solid, IR (KBr): 2750–3650(b), 1170(s), 1176(s), 1072(m), 852.5 (m), 576.7(m) cm^{-1}.

2-Nitrobisphenol A: Yellow oil, IR (KBr): 3396(b), 2970(w), 1703(s), 1628(m), 1536(s), 1176(s), 1231(s), 834(m) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.73 (s, 6H), 4.81 [b, 1H (phenolic H, No 1)], 6.88–7.42 (m, 5H); 7.95 (s, 2H); 10.4 [s, 1H (phenolic H, No 2)].



2,2′-Dinitrobisphenol A: Yellow solid, Mp: 120 °C, IR (KBr): 3254(w), 2968(w), 1714(w), 1629(m), 1539(s), 1481(m), 1419(m), 1326(s), 1261(m) cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 1.76 (s, 6H), 7.06–7.016 (m, 2H); 7.49-7.58 (m, 2H); 8.04 (d, 2H); 10.37 (s, 2H).

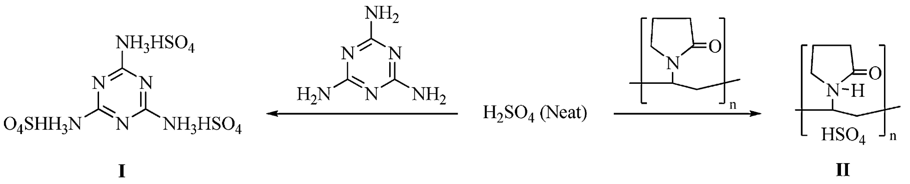


2. Results and discussion

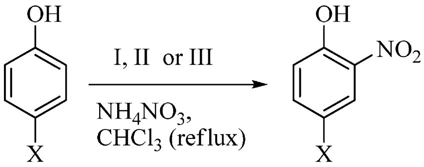
Our goal, in undertaking this line of work, was four folds: (a) to overcome the limitations and draw-backs of the reported methods for the nitration of phenols such as tedious work-up [19] strongly acidic media [20], oxidation ability of the reagents and safety problems (storage, handling, using and also presence of toxic transition metal cations such as Cr^{3+}, Hg^{2+}, Cu^{2+}, within molecular structure of the reagents), (b) design and synthesis of new organic solid acid in a simple protocol, (c) moreover, to develop an high-yielding one-pot synthesis of nitrophenols using a novel combination of reagents and (d) first mono- and di-nitaration of bisphenol A.

In continuation of our studies on the application of solid acids [3–7] and nitration of phenols [10,19] as well as melamine-H_2O_2 and PVP-(H_2O_2)$_n$ [21], we found that melamine or poly vinylpyrrolidone (PVP) readily reacts with concentrated sulfuric acid to give melamine-(H_2SO_4)$_3$ (**I**) and PVP-(H_2SO_4)$_n$ (**II**). It is interesting to note that these exothermic reactions are fast, easy and clean not requiring any work-up (Scheme 1).

In order to running acid mediated reactions under mild and heterogeneous conditions, we decided to apply these solid acids for the nitration of phenols in the presence of NH_4NO_3 and wet SiO_2. Phenol and different kinds of 4-substituted phenols (**2**) were converted to nitro-phenol derivatives in the presence of melamine-(H_2SO_4)$_3$ (**I**) and PVP-



Scheme 1.



Scheme 2.

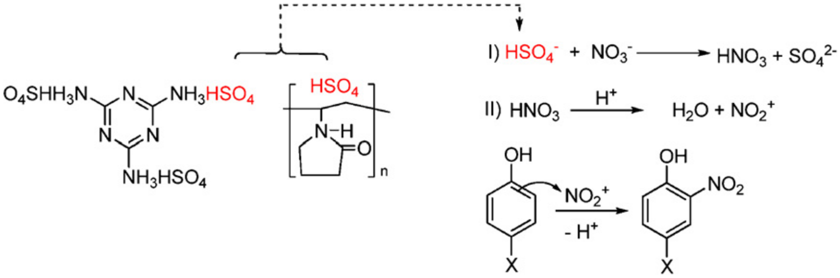
$(H_2SO_4)_n$ (**II**), NH_4NO_3, and wet SiO_2 (50%, w/w) in a reaction vessel and efficiently stirring the resultant heterogeneous mixture under the reflux of chloroform (Scheme 2, Table 1). In order to comparing the efficiency of these novel solid acids with respect to the silica sulfuric acid [4] (**III**) for the nitration of phenols, we used silica sulfuric acid in the same reaction conditions (Scheme 2, Table 1). As it is clear from table, the efficiency of melamine-$(H_2SO_4)_3$ (**I**) and PVP-$(H_2SO_4)_n$ (**II**) are comparable to silica sulfuric acid in terms of yields, reaction times and amount of the reagent for successful nitration reaction.

We also applied our new reaction protocols for the first report on the mono and di-nitration of bisphenol A (Table 1, entry 15 and 16). Spectral and physical data for the obtained products are in close agreement with their structures. We also accomplished mono and di-nitration of bisphenol A with some acid *i.e.* HCl, *p*-Toluene sulfonic acid and Sulfamic acid (table, entry 17-21). Results show that HCl and *p*-Toluene sulfonic acid could perform this reaction but sulfamic acid

Table 1
Mononitration of phenols (1 mmol) with the combination of melamine-$(H_2SO_4)_3$ (**I**), PVP-$(H_2SO_4)_n$ (**II**) or silica sulfuric acid (**III**) and NH_4NO_3 (2 mmol) in the presence of wet SiO_2 (50%) under the reflux of $CHCl_3$.

Entry	Substrates[a]	Acid (g)			Time			Yields (%)[b]		
		I	**II**	**III**	**I** (min)	**II** (h)	**III** (h)	**I**	**II**	**III**
1	Phenol	0.28	0.42	0.25	60	1.2	1.5	41	46	50
								20	25	32
2	4-F-Phenol	0.28	0.42	0.25	15	3.3	7	77	88	70
3	4-Cl-Phenol	0.28	0.42	0.25	15	2	10	75	79	65
4	4-Br-Phenol	0.28	0.42	0.25	20	3	7	77	70	83
5	4-CN-Phenol	0.28	0.42	0.25	90	24	7	81	97	82
6	4-Ph-Phenol	0.28	0.21	0.25	20	12	9.5	66	70	70
7	4-COPh-Phenol	0.28	0.42	0.25	30	11	9	74	78	71
8	4-OCH_3-Phenol	0.28	0.42	0.25	5	15(min)	4	69	64	60
9	4-$COCH_3$-Phenol	0.28	0.84	0.25	30	12	6	75	83	94
10	4-CH_2Ph-Phenol	0.28	0.42	0.25	20	1	14	90	95	79
11	4-NHOAc-Phenol	0.28	0.42	0.25	10	5(min)	0.5	77	65	97
12	4-NH_2-Phenol	0.28	0.84	0.25	30	0.5	0.5	–	–	–
13	4-CH_2-Phenol	0.28	0.42	0.25	15	16	7.5	69	80	80
14	2,4-Cl_2-Phenol	0.28	0.42	0.25	3	5(min)	8	72	81	63
15	Bisphenol A	0.28	0.42	0.4	20	60	25	43	51	69
16	Bisphenol A[c]	0.42	0.6	0.6	30	75	50	65	82	77
17	Bisphenol A	HCl/NH_4NO_3 (1.5/1 mmol)				20 min			60	
18	Bisphenol A[c]	HCl/NH_4NO_3 (2/3 mmol)				50 min			71	
19	Bisphenol A	4-Me-Ph-SO_3H/NH_4NO_3 (1.5/1 mmol)				Fast			62	
20	Bisphenol A[c]	4-Me-Ph-SO_3H/NH_4NO_3 (2/3 mmol)				Fast			73	
21	Bisphenol A	Sulfamic acid/NH_4NO_3 (1.5/1 mmol)				80 min			No reaction	

[a] 1 mmol substrate: 0.4 g wet SiO_2 (50%).
[b] Isolated yield.
[c] For the di-nitration of bisphenol A (1 mmol substrate: 3 mmol NH_4NO_3).



Scheme 3.

could not. Literature survey indicates that the mixture of H_2SO_4 and NO_3^- generates NO_2^+ ion [22]. Thus we proposed that the reaction mechanism proceeds via in situ generation of NO_2^+. A reasonable mechanism for the nitration of phenols in the presence a mixture of melamine-$(H_2SO_4)_3$ or PVP-$(H_2SO_4)_n$ and NH_4NO_3 is outlined in Scheme 3.

3. Conclusions

Melamine-$(H_2SO_4)_3$ and PVP-$(H_2SO_4)_n$ are two superior proton source considering convenience, cost effectiveness and simplicity of their production procedure. Also, they are insoluble in most of the organic solvents and are excellent proton mediated sources for the organic reactions under heterogeneous conditions. As illustrated in table, the acidic powers of these solid acids are very good and are comparable with silica sulfuric acid as well as other known acids. Also, in this paper we reported mono- and di-nitro bisphenol A for the first time.

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