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Melamine trisulfonic acid catalyzed regioselective nitration of aromatic compounds under solvent-free conditions

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A simple, mild and efficient method for the regioselective nitration of various aromatic compounds using poly(4-vinylpyridinium nitrate) (P_4VPyN) in the presence of melamine trisulfonic acid (MTSA), is reported. This method provides several advantages such as good selectiveity between ortho and para positions of aromatic compounds, clean procedure, simple work-up, short reaction times, solvent-free conditions and high yields of products. This methodology is useful for nitration of activated and deactivated aromatic rings.

Keywords: Melamine trisulfonic acid; Nitration; Aromatic compounds

1. INTRODUCTION

Nitro aromatic compounds are important chemicals that have application such as solvents, dyes, pharmaceuticals, perfumes, explosives, and plastics in industry [1]. They can also be employed as intermediates for preparation of other compounds, particularly amines, by reduction [2]. Nitration tipically requires the use of a mixture of concentrated sulfuric acid with nitric acid, leading to an excssive waste stream. However, the majority of this method suffers from disadvantages such as low regioselectivity, over nitration, strongly acidic media, tedious work-up and oxidation of the reagents. Therefore, various methods have been reported in which regioselectivity, over nitration and competitive oxidation of substrates has been the subject of investigation [3-10]. Although many useful procedures for nitration of different aromatic compounds have been reported, the main disadvantage of these is the relative difficulty in the preparation of the reagents and in the working-up of the reaction mixture. Moreover in the case of active aromatic compounds, such as anilines and phenols, nitration usually results in a complex mixture of mono and even dinitrated products. It is especially difficult to perform selective mononitration of highly activated aromatic compounds, such as aniline and phenol derivatives. Recently the method have been reported for the mono nitration of aromatic compounds using poly(4-vinylpyridinium nitrate) as the source of nitrate [11]. However, in spite of its application potentials, this method suffer from disadvantages such as using toxic solvent, relatively high reaction times and tedious work-up. Mostly, compunds containing electron donating were studied. Also it has been observed that chemoselective conversion of aromatic compounds to their *ortho* substituted products was achieved. Such drawbacks could be obviated by perform the reaction under solvent-free conditions. Reaction under solvent-free conditions has attracted attention. The advantage of these methods over conventional classical method is that they are cleaner reactions, decreased reaction time, and easier workup. In the previous research, we have reported preparation of melamine trisulfunic acid (MTSA) and its applications, as a new and efficient solid acid catalyst in the promotion of the protection of different types of functional groups and the synthesis of dihydropyrimidons and coumarins[12-16]. This catalyst is safe, easy to handle, environmentally benign and presents fewer disposal problems. Therefore, We decide to perform the nitration reaction in the presence of MTSA under solvent-free conditions and hoped to obtain good results.

2. EXPERIMENTAL

2.1. General

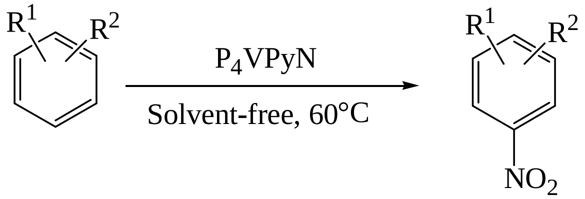
All products were identified by comparison of their spectral, TLC and physical data with authentic samples. Chemicals were purchased from Fluka, Merck and Aldrich Chemical companies. Poly(4-vinylpyridinium nitrate), was prepared according to a previously reported method [17]. Yields refer to isolated pure products.

2.2 General procedure for nitration of aromatic compounds

A mixture of aromatic compound (1 mmol), Poly(4-vinylpyridinium nitrate) (0.4g) and MTSA (0.1 mmol), was heated in an oil bath (60 ºC) for the appropriate time (Table 1). After completion of the reaction as followed by TLC, 5 mL of ethyl acetate was added to the mixture and filtered. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from ethanol gave the corresponding nitrated compounds in good to excellent yields.

3. RESULTS AND DISCUSSION

In continuation of our research on the nitration of aromatic compounds [18], we have found that aromatic rings can be nitrated using poly(4-vinylpyridinium nitrate) (P_4VPyN) as the source of nitrate in the presence of melamine trisulfonic acid under solvent-free conditions (Scheme1).



Scheme 1. Regioselective nitration of aromatic compounds catalyzed by MTSA.

At first we examined the reactions in the absence of melamin trisulfonic acid, but observed that aromatic compounds remain intact. Therefore the nitration reactions were performed in the presence of this catalyst. All the reactions were performed under solvent-free conditions for the appropriate times. A wide range of various aromatic compounds, were successfully reacted to afford the desired mono nitrated products in excellent yields with complete regioselectivity. Among the various substrates studied, compounds containing electron donating were found to be most reactive and converted to the corresponding mono-nitrated products in shorter reaction times. However, the rate of the reaction was slower when the ring contained an electron-withdrawing group (Table 1, entries 16, 17, 18). It has been observed that chemoselective conversion of aromatic compounds to their *para* substituted products was achieved in excellent yields. When the *para*-position was blocked, mononitrated products were obtained over longer reaction times (Table 1, entry 3, 4, 13, 14). Phenol gave mainly the *para* isomer as the major product in short reaction time(Tables 1 entry 1), However 4-chloro phenol was reacted after 15 min to afford 2-nitro-4-choloro phenol (Table 1,entry 3). Also, it was observed that *p*-orientation is more favorable than *o*-orientation from the fact that 2,6-dimethyl phenol was more readily nitrated than 2,4-dimethyl phenol (Table 1, entries 5, 6). *Ortho*-cholorophenol and *ortho-nitro phenol* were quantitatively converted to the *para* nitrated products with respect to the hydroxyl groups in good yields (Table 1, entries 2, 12). The substrate was nitrated *ortho* to the phenolic OH only when the *para* position was occupied (entries 3, 4, 6,14, 15). It is very important to note that the method can also be employed for the nitration of bezaldehyde and some activated bezaldehyde derivatives to the corresponding products in good yields (Table 1, entries 13-16).

Table 1. Regioselective nitration of aromatic compounds catalyzed by MTSA.

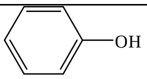
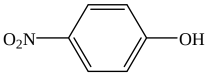
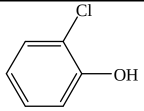
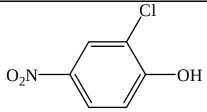
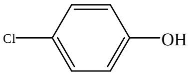
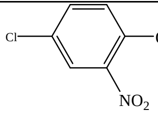
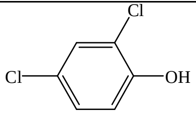
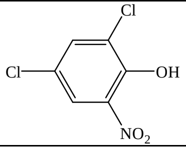
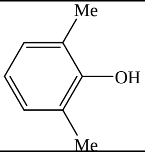
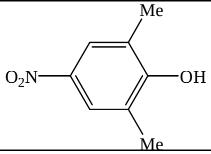
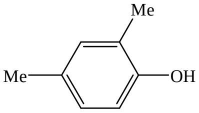
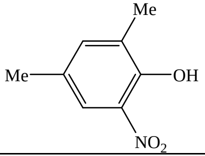
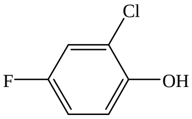
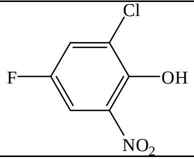
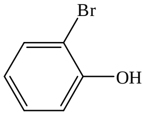
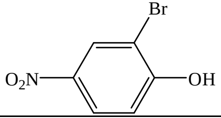
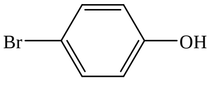
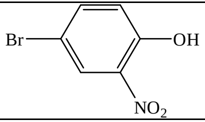
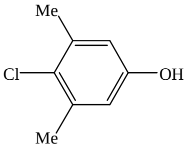
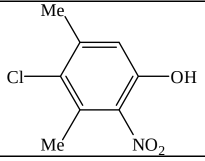
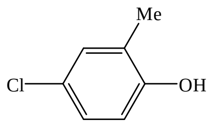
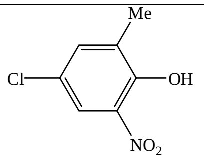
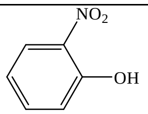
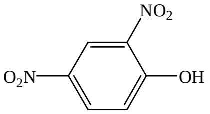
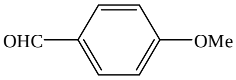
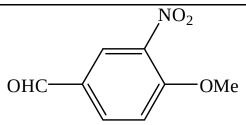
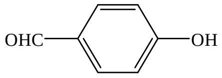
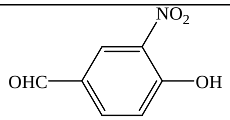
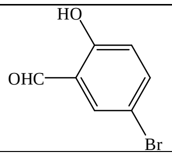
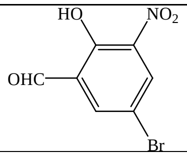
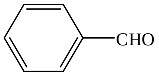
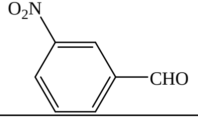
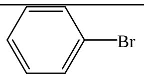
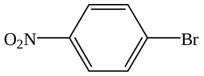
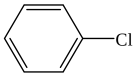
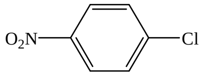
Entry	Substrate	Product	Time(min)	Yield (%) [a]
1			8	87
2			25	89
3			25	90
4			25	88
5			5	93
6			15	87
7			25	88
8			12	89
9			20	90
10			30	89

Table1.Continued

11			20	90
12			30	89
13			30	88
14			30	85
15			30	88
16			30	79
17			18	89
18			22	87

In conclusion, we have described that poly(4-vinylpyridinium nitrate) as a polymeric reagent is efficiently able to chemoselective nitration of aromatic compounds in the presence of melamine trisulfonic acid under solvent-free conditions. Green procedure, easy to handle, Simple work-up, good chemoselectivity, high yields of the products and short reaction times, will make this procedure a useful addition to the available methods.

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