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AN ENVIRONMENTALLY FRIENDLY, EFFICIENT, AND FACILE METHODOLOGY FOR THE NITRATION OF AROMATIC COMPOUNDS USING UREA NITRATE

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ABSTRACT

An efficient, environmentally friendly, and facile methodology is developed for room temperature nitration of variously substituted aromatic compounds using urea nitrate and concentrated sulphuric acid. The method uses a simple aqueous workup without organic solvents and results in the formation of mono-nitro compounds in excellent yields. Amides are nitrated smoothly without hydrolysis of the amide function.

Keywords: Aromatic Nitration, Urea Nitrate, Room Temperature Nitration, Regioselective Nitration, Mononitration.
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INTRODUCTION

Nitration of aromatic substrates is a classical reaction of immense synthetic utility, engaging the unabated interest of researchers even today. The nitroaromatic compounds find many applications as intermediates in dyes, pharmaceuticals, explosives, plastics, and other industries. Classically nitration has been carried out chiefly with mixtures of concentrated nitric acid and concentrated sulphuric acid, known as mixed acid nitration. Newer reagents and preparative methods have evolved, each with specific attributes.[1] With the growth of environmentally friendly methods of synthesis over the past few decades, several reports on greener and safer methods of synthesis have appeared in the literature.[2,3] Aromatic nitration reactions using urea nitrate have been reported in the literature to yield synthetically significant and useful results.[4-8] Regioselectivity and mononitration are among the important advantages. Side reactions, which accompany classical mixed acid nitration reactions are usually not observed in nitration reactions using urea nitrate.[9-10] This, coupled with the ease of preparation and low cost of urea nitrate, and milder reaction conditions, makes it an attractive method for the nitration of aromatic compounds. This paper presents the results of the nitration of aromatic compounds using urea nitrate and concentrated sulphuric acid, applied to compounds having substituents with different directive influences including those which are susceptible to hydrolysis such as amides and anilides. All reactions were accomplished smoothly at room temperature, even in the case of toluene, chlorobenzene, and bromobenzene which normally require heating in classical mixed-acid nitration methods.

EXPERIMENTAL

Materials and Equipment

All starting materials were purchased from chemical suppliers and purified by crystallization or distillation before use. Solvents for crystallization were also distilled before use. Melting points were determined using a novel apparatus, BODMEL.[11] This is a safe and highly reliable method and uses only a small volume (~2 mL) of concentrated sulphuric acid as compared to the conventional methods that use larger volumes.[12] Authentic samples for comparisons were purchased from Sigma Aldrich.

Preparation of Urea Nitrate (UN)

Urea nitrate (UN) was prepared according to a recent literature procedure by adding concentrated nitric acid (5.75mL) dropwise with stirring to a cold (10^0C) nearly saturated aqueous solution of urea (10.8g).[13] A white crystalline solid separated almost immediately. It was washed with ice-cold water. Air drying gave

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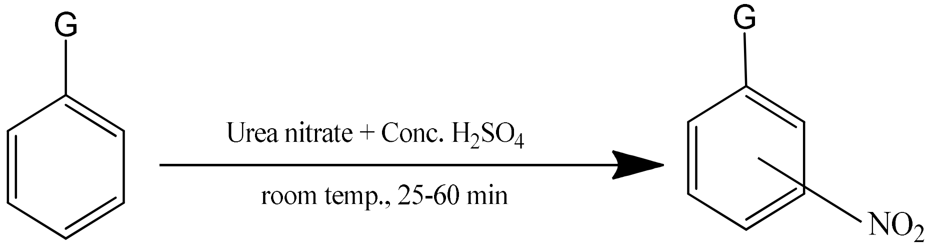
a sharp melting (160^{0}C) solid. The compound is stable at ambient temperatures and requires no special treatment for storage. Simply storing it in desiccators keeps it free from moisture for many days. Its ability to cause nitration remains unaffected by storage over long periods.

Typical Nitration Procedure

The reaction between urea nitrate and concentrated sulphuric acid is exothermic and requires cooling. A typical procedure for nitration involves taking up 4 mmol of the compound in concentrated sulphuric acid (2-3 mL) at ice bath temperature and adding 5 mmol of urea nitrate in small lots and mixing thoroughly. After complete addition, the reaction mixture is stirred for 25-60 minutes at ambient room temperature (27^0-30^{0}C). For o-and p-nitrophenols (entries 4 and 5, Table 1), the reaction mixture after the initial mixing of the reactants is warmed briefly at 60-70 degrees C for a few seconds in order to dissolve the compounds. The crude products were separated by pouring the reaction mixture over crushed ice with brisk stirring. Liberal washing with ice-cold water and crystallization from ethyl alcohol water (80:20) yielded pure products (single spots on TLC). The products were identified by melting points, co-TLC, and mixed melting points with authentic samples. A graphical description of the reaction is presented in Scheme-1.



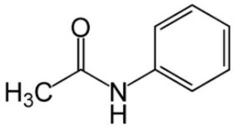
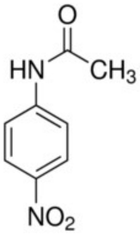
Scheme-1: Nitration of Aromatic Compounds using UN-cH2SO4

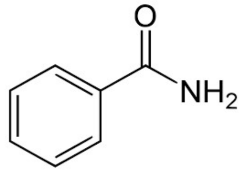
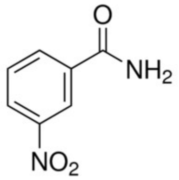
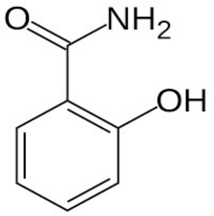
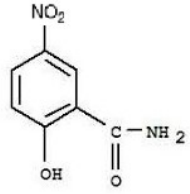
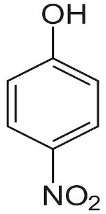
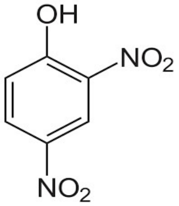
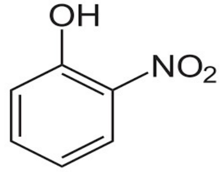
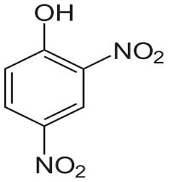
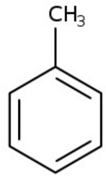
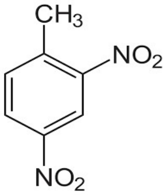
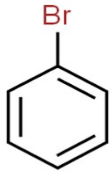
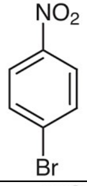
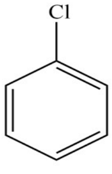
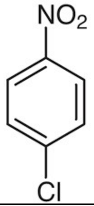
RESULTS AND DISCUSSION

Urea nitrate and aromatic compound were reacted in 1:1, 1:2, and 1:3 molar ratios to determine the effect on yield and extent of nitration. 1:1 Molar ratio showed optimum results in terms of yield and only mononitration was observed in all cases except toluene (entry 6, Table-1). Mononitration was observed in 1:2 and 1:3 ratios also, however, the yields decreased with increasing amounts of UN. Literature reports on the use of urea nitrate for nitration of aromatic compounds deal with deactivated aromatics.[4-5] The present report includes activated, moderately activated, deactivated, and hydrolysis-prone substrates represented by acetanilide, benzamide, salicylamide, p-nitrophenol, o-nitrophenol, toluene, bromobenzene, and chlorobenzene as listed in Table-1. All the reactions were accomplished at ambient laboratory temperatures and took between 25min and 60 min to afford the products. Continuing reactions beyond the specified time periods did not increase the yield of products. Acetanilide, salicylamide, and benzamide gave nitration products smoothly without hydrolysis of the acetyl or amide function, an often- encountered side reaction in mixed-acid classical nitration procedure.[13]

Toluene gave a gummy mass when reacted with UN-cH_2SO_4 in 1:1 ratio. However, when this ratio was changed to 1:2, dinitration took place and 2,4-dinitrotoluene was isolated.

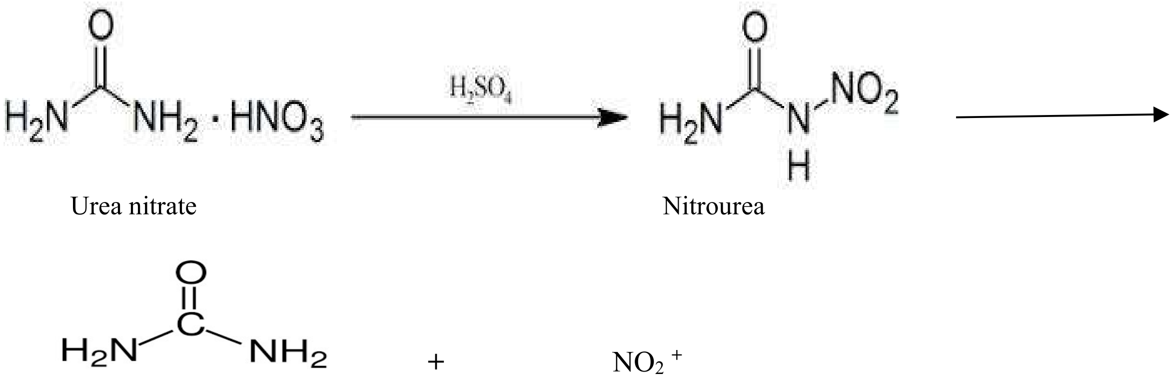
Table-1: UN-cH_2SO_4 Nitration of Aromatic Compounds

Entry	Compound	Time (min)	Product	Yield (%)
1.		20		95

2.		60		55
3.		25		68
4.		60		74
5.		60		72
6.		30		50
7.		25		68
8.		30		52

Further change in ratio to 1:3 and 1:4 had no effect and resulted in only the dinitro product. Dinitration has previously been reported in the case of nitration of anisole using urea nitrate-polyphosphoric acid.[14] This may presumably be due to the influence of activating methyl group in toluene and methoxy group in anisole that predisposes these compounds to dinitration.

Bromobenzene is reported to yield p-nitro bromobenzene in 66% yield using UN-polyphosphoric acid at 100^{0}C for 1 hour.[14] However, we found that regioselective mononitration happens in the case of bromobenzene to give p-nitro bromobenzene at room temperature in much less time (25 min/68 % yield) using UN-cH_2SO_4 reagent. As no heating is required and the time taken is less than half of the reported time, this method is an improved, environmentally friendly method as it conserves both time and heat energy. No $CHCl_3$ or organic solvents were used for the isolation of products.[4] The nitro products were isolated by simple environmentally friendly aqueous workup and gravity filtration. Even for recrystallization, only an ethyl alcohol-water (80: 20) mixture was used. The mechanism of aromatic nitration by UN-cH_2SO_4 reagent is believed to involve dehydration of urea nitrate to nitrourea in presence of concentrated H_2SO_4[4] Nitrourea then provides nitronium ions for the nitration reaction as outlined in Scheme-2.



Scheme-2: Generation of Nitronium Ions in Aromatic Nitrations using UN-cH2SO4

CONCLUSION

The nitration of variously substituted aromatic compounds having activating, moderately activating, deactivating, and hydrolysis-prone groups by the UN-cH_2SO_4 method has been accomplished with regioselectivity and mononitration in shorter reaction times and at room temperature. It provides a safer and more environmentally friendly synthetic route to aromatic nitro compounds as compared to the classical mixed-acid protocol which uses concentrated sulphuric acid and concentrated nitric acid. The use of solid urea nitrate in place of corrosive concentrated nitric acid makes it a milder reagent and ice bath-room temperature operating conditions of the reactions make it safer to use. As the reactions are carried out at room temperature, the method provides a definite advantage for the nitration of bromobenzene, chlorobenzene, and toluene where heating is required for the completion of nitration by the classical mixed-acid protocol. This method has advantages for teaching laboratories also since urea nitrate is inexpensive, easy to prepare, and safe to handle.

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