

Nitration of Aromatic Compounds on Silica Sulfuric Acid

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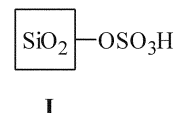
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Nitration of organic compounds has long been a very active and rewarding area of research and is the subject of a large body of literature.¹ Also nitro-aromatics compounds are extensively utilised and act as chemical feedstocks for a wide range of useful materials such as dyes, pharmaceuticals, perfumes, and plastics.² Therefore, the nitration of aromatic rings has received considerable attention of late, due to unsolved problems pertaining to regioselectivity, overnitration and competitive oxidation of substrates.³ Nitration of phenol taken as a special case has been studied by various nitrating agents under different conditions.⁴ The nitration of benzene and toluene is one of the most important routes to substituted aromatics in the production of chemical intermediates.⁵ The industrial nitration of toluene is performed by means of mixed acid, a mixture of nitric acid, sulfuric acid, and water^{5a} which leading to excessive acid waste streams and added expense.^{5b} Also, the separation of the products from the acid is often a difficult and energy consuming process that habitually implies a basic aqueous work-up. Moreover, sulfuric acid is corrosive and is dangerous to transport and handle.⁶ The above mentioned disadvantages of the commercial manufacturing process currently used has led to a substantial effort to develop viable alternatives, inter idea using solid acid catalyst,^{1,2,5-8} other sources of NO₂^{+,3,9,10} organic nitrating agents,^{11,12} metal nitrates,^{13,14} other acids replacing sulfuric acid such as inorganic acidic salts (NaHSO₄·H₂O, Mg(HSO₄), Oxone[®], ...) ¹⁵ and silica sulfuric acid,^{6,16} etc.

Our goal, in undertaking this line of work, was three-fold: a) to overcome the limitations and drawbacks of the reported methods such as tedious work-up,^{17,18} strongly acidic media,¹³ 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),^{13,14} (b) to perform solvent-free organic synthesis which seems to be a highly useful technique, especially for industry possessing many advantages like: reduced pollution, low costs, as well as simplicity in process and handling (these factors are especially important in industry),¹⁹ (c) moreover, to develop an high-yielding one-pot synthesis of nitro-aromatics using a novel combination

of reagents.

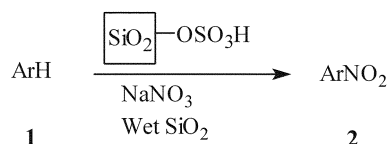
In addition, any reduction in the amount of liquid acids needed and/or any simplification in handling procedures would be highly convenient in terms of risk control, economic advantage and environment protection.¹⁹ Recently, we have reported the preparation of silica sulfuric acid **I** as a stable acidic reagent (solid acid) and showed its catalytic activity in synthetic methodology.^{16,20} In continuation of our studies in this regard, we have found that aromatic rings can be nitrated by using a combination of silica sulfuric acid **I**, NaNO₃ and wet SiO₂ under solvent free conditions. Therefore, we wish to report here a one-pot solid phase procedure for the nitration of different kind of aromatic compounds.



A good range of aromatic compounds **1** were also subjected to nitration in the presence of silica sulfuric acid **I**, NaNO₃, and wet SiO₂ (60% w/w) under solvent free conditions (Scheme 1). The nitration reactions were performed under mild conditions with moderate to good yields (Scheme 1 and Table) by simply placing the nitrating agents and substrates **1** in a reaction vessel and efficiently shaking the resulting mixture. Highly pure nitro compounds can be obtained by simple extraction and subsequent evaporation of the solvent. For this new system the in-situ generation of nitronium ion mechanism may be proposed (See Schemes 2 and 3).

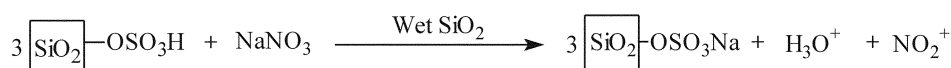
Experimental Section

General. Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. Yields refer to isolated

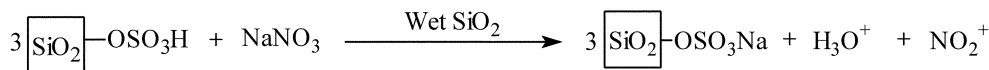


Scheme 1

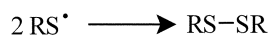
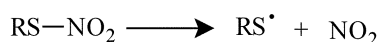
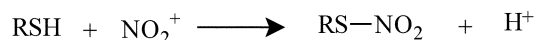
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Scheme 2



I



Scheme 3

Table 1. Nitration of aromatic rings with silica sulfuric acid (I), sodium nitrate, and wet SiO₂ (60% w/w) under solvent free condition

Entry	Substrate	T (°C)	Time (min)	Yield (%)	Product	Mp (Bp) °C	
						Found	Reported ²¹
1	Benzene	25	2-3	80	Nitrobenzene	(208-210)	(210)
2	Toluene	25	2-3	85	4-Nitrotoluene	53-55	54
3	<i>p</i> -Xylene	25	2-3	90	2-Nitro- <i>p</i> -xylene	(232-233)	(234)
4	<i>o</i> -Xylene	25	2-3	85	4-Nitro- <i>o</i> -xylene	30-31	30
5	Thiophenol	25	6-7	90	Diphenyl disulfide	62-64	62
6	Phenol	25	12	85	4-Nitrophenol	113-114	114
7	Bromobenzene	25	3-4	85	4-Nitrobromobenzene	125-126	127
8	Chlorobenzene	25	3-4	80	4-Nitrochlorobenzene	82-83	83
9	Anisol	25	2-3	85	4-Nitroanisol	52-53	54
10	Biphenyl	60 ^a	30-35	75	4-nitrobiphenyl	112-113	114
11	3-Chlorophenol	25	10-12	81	2-Nitro-5-chlorophenol	40-43	42
12	<i>N,N</i> -Dimethyl aniline	25	1-2	94	4-Nitro- <i>N,N</i> -dimethylaniline	160-163	163
13	4-Methoxy benzaldehyde	25	6-7	74	3-Nitro-4-methoxybenzaldehyde	83-85	86
14	Naphthalene	50	15	91	1-Nitronaphthalene	70-71	71

^awas pulverized in a mortar in 25 °C for 1 min and then heated until 60 °C for 30-35 min.

pure products. The nitration products were characterized by comparison of their spectral (IR, ¹H-NMR), TLC and physical data with authentic samples.

General Procedure. A mixture of silica sulfuric acid I (0.6 g), sodium nitrate (1 mmol, 0.085 g), wet SiO₂ (0.5 g, 60% w/w) and aromatic compound 1 (1 mmol) was pulverized in a mortar for 2-35 min (the progress of the reaction was monitored by TLC), followed by CH₂Cl₂ (10 mL) addition and filtration of the resulting mixture. Dichloromethane was finally removed and the nitro compounds were obtained with moderate to good yields.

IR and ¹H-NMR of some of the nitrated products.

4-Nitro, *N,N*-Dimethyl aniline: IR (KBr) 800, 1300, 1350, 1500, 1525, 1600, 2900-3000 cm⁻¹; ¹H NMR (CDCl₃) δ_{ppm} 2.89 (s, 6H), 6.32 (d), 7.8 (d).

p-Nitrophenol: ¹H NMR (CDCl₃) δ_{ppm} 6.9 (d, 2H), 8.1 (d, 2H), 10 (s, 1H, O-H).

1-Nitronaphthalene: IR (KBr) 1330, 1520, 3050 cm⁻¹; ¹H NMR (CDCl₃) δ_{ppm} 8.43 (d, 1H), 7.17-8.1 (m, 6H).

1-Bromo-4-Nitrobenzene: ¹H NMR (CDCl₃) δ_{ppm} 7.8 (d,

2H), 8.3 (d, 2H).

2-Nitro-*p*-xylene: ¹H NMR (CDCl₃) δ_{ppm} 2.4 (s, 3H), 2.7 (s, 3H), 7.5 (s, 2H), 8.1 (s, 1H).

Diphenyl disulfide: ¹H NMR (CDCl₃) δ_{ppm} 7.3-7.8 (m, 10H) ppm.

3-Nitro-4-methoxy benzaldehyde: ¹H NMR (CDCl₃) δ_{ppm} 10 (s, 1H), 8.5 (sbr, 1H), 8.2 (dd, 1H), 7.3 (dbr, 1H), 4.1 (s, 3H).

5-Chloro-2-Nitro phenol: ¹H NMR (CDCl₃) δ_{ppm} 11 (s, 1H, OH), 8 (d, 1H), 7.6 (d, 1H), 7 (dd, 1H).

4-Nitrobiphenyl: ¹H NMR (CDCl₃) δ_{ppm} 8.5 (d, 2H), 7.8 (d, 2H), 7.3-7.7 (m, 5H).

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