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### A CONVENIENT METHOD FOR SELECTIVE MONO OR DINITRATION OF PHENOL UNDER MILD CONDITIONS

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**Abstract**:. Nitrophenol can be obtained via nitrosation-oxidation of phenol with  $C_2H_2O_4.2H_2O$ , NaNO<sub>2</sub>, and wet SiO<sub>2</sub> at room temperature in high yield. Direct mono or dinitration of phenol was also performed with  $C_2H_2O_4.2H_2O$ , metal nitrates (ionic) and wet SiO<sub>2</sub> under different reaction conditions.

Nitration of the phenol as a special case has been studied by various nitrating agents under different conditions.<sup>1-5</sup> Although a survey of the literature indicates the lack of entire selectivity of para nitration of phenol but almost selective ortho nitration of phenol was performed with  $N_2O_4$  and pyridine derivatives carrying transferable nitro group.<sup>2</sup> It is clear that, on the basis of the above facts there is a need for more regioselective control of nitration of aromatic compounds. However, we report here an one-pot heterogeneous procedure for mono or dinitration of phenol.

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During the course of our studies on the utilization of  $C_2H_2O_4.2H_2O$  and  $NaNO_2$  as an efficient and chemose lective heterogeneous system for the nitrosation of secondary amines, thiols and oxidation of urazoles to their corresponding triazolinediones<sup>6</sup> we found that a combination of  $C_2H_2O_4.2H_2O$  and  $Mg(NO_3)_2.6H_2O$  in usable solvent ( $CH_2Cl_2$ ,  $Et_2O$ , THF, Acetone etc.) lead to nitration of phenol under mild and heterogeneous conditions via *in situ* generation of HNO<sub>3</sub><sup>3d</sup> (Scheme 1, Table 1).



Scheme 1

Similarly, we think that phenol must be converted to the p-nitrosophenol selectively by  $C_2H_2O_4.2H_2O(2 \text{ eq})$ , NaNO<sub>2</sub> (1 eq) and wet SiO<sub>2</sub> (50% w/w) in CH<sub>2</sub>Cl<sub>2</sub> as usable solvent via in situ generation of HNO<sub>2</sub>. Since that, phenol nitrosation is rapid and yields almost entirely the para isomers which can be readily converted to p-nitrophenol via mild oxidation with HNO3.4 Therefore, we decided to produces p-nitrophenol via nitrosation-oxidation strategy<sup>4,5</sup> in one pot reaction under mild and heterogeneous condition by addition of  $Mg(NO_3)_2.6H_2O$  to the reaction mixture (as a source for in situ generation of  $HNO_3$  in the presence of  $C_2H_2O_4.2H_2O$  and wet  $SiO_2$  ) after performing the nitrosation reaction. Whereas, in contrast to the reported procedures under aqueous media<sup>4,5</sup> we observed that nitrosation and oxidation were occurring simultaneously without addition of any oxidant to the reaction mixture for the oxidation of nitrosophenol. Hence, in this reaction mono nitration has occurred

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Table 1. Mononitration of Phenol (I) with a Combination of C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O (II), Wet SiO<sub>2</sub> (50% w/w, 2g) and metal nitrite (III) or metal nitrate (IV).

III or IV	Solvent	Reagent (m	nol)	Reaction Con	ditions	Product Dis	tribution <sup>a</sup>
		ши	IV	Reflux (Min)	RT(Min)	Ortho(2)%	Para(3)%
NaNO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	10 30 20		1	30	35	65
NaNO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	10 20	20	I	20	33	45
NaNO <sub>3</sub>	- <b>4</b>	10 20	20		20	35	50
$Ca(NO_1), .4H_2O$	Et <sub>2</sub> O	10 10	10	•	48(h)	40	45
$Mg(NO_3)_2.6H_2O$	$CH_2CI_2$	10 10	10		20	30	50
$Mg(NO_3)_2.6H_2O$	Et <sub>2</sub> O	10 10	10	8 1	20	40	49
Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	د	10 12.5	20	-	20	25	21
<sup>a</sup> Isolated yields after colun	nn chromatography.	1	<sup>b</sup> Solid phase	. <sup>c</sup> Solid	phase without w	et SiO <sub>2</sub> .	

and o-nitrophenol ( 35%) and p-nitrophenol (65%) were obtained (Scheme 1, Table 1).

Whereas, the mono nitration of phenol with other alkali and alkaline earth metal nitrates such as : NaNO<sub>3</sub>, KNO<sub>3</sub>, Ba(NO<sub>3</sub>)<sub>2</sub> and Sr(NO<sub>3</sub>)<sub>2</sub> in the presence of  $C_2H_2O_4.2H_2O$  were not occurred but the nitration of phenol with  $C_2H_2O_4.2H_2O$  and Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O in Et<sub>2</sub>O was performed after 48 h (Table 1). All the aforementioned ionic alkali and alkaline earth metal nitrates are able to nitrate phenol in the presence of wet SiO<sub>2</sub> (Scheme 1, Table 1).



Table 2. Dinitration of Phenol (I) with a Combination of C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> .2H<sub>2</sub>O (II), Wet SiO<sub>2</sub> (50% w/w, 2g) and metal nitrate (III) in refluxing EtOAc.

III	Reagent (mmol)			Time	Yields <sup>a</sup>
	I	II	III	(h)	%
NaNO <sub>3</sub>	10	20	40	24	85
$Ca(NO_3)_2.4H_2O$	10	10	10	24	89
$Mg(NO_3)_2.6H_2O$	10	10	10	24	90
$Ba(NO_3)_2$	10	10	10	24	90

<sup>a</sup> Isolated yields after column chromatography.

Dinitration of phenol with three equivalent amounts of reagent was easily performed in refluxing EtOAc and 2,4-dinitrophenol was obtained in excellent yield (Scheme 2, Table 2).

In conclusion, the cheapness and the availability of the reagents, easy and clean work-up, and high yields make this method for the large-scale operations.

#### **EXPERIMENTAL SECTION**

## Mononitration of Phenol with CH<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O, NaNO<sub>2</sub> and Wet SiO<sub>2</sub> A Typical Procedure:

Phenol (1.88 g, 0.02 mol),  $C_2H_2O_4.2H_2O$  (2.52 g, 0.02 mol), NaNO<sub>2</sub> (1.38 g, 0.02 mol) and wet SiO<sub>2</sub> (50% w/w, 2 g) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) were stirred magnetically at room temperature. The reaction was completed after 30 minutes. The solvent was evaporated and the resulting mixture was mixed with silica gel (5 g). The resulting powder mixture was applied on silica gel column and eluted with petroleum ether:acetone (9:1). The solvent of each fraction was evaporated. o-Nitrophenol ,1 g 35% , mp 46 °C [ lit<sup>3</sup> mp 44 °C ] and p-nitrophenol ,1.8 g, 65%, mp 112-113 °C [ lit<sup>3</sup> mp 114 °C ] were obtained (Table 1, Scheme 1).

# Dinitration of Phenol with $CH_2O_4.2H_2O$ , NaNO<sub>2</sub> and Wet SiO<sub>2</sub>. A Typical Procedure:

Phenol (0.94 g, 0.01 mol),  $C_2H_2O_4.2H_2O$  (2.52 g, 0.02 mol), NaNO<sub>3</sub> (3.40 g, 0.04 mol) and wet SiO<sub>2</sub> (50% w/w, 2 g) were added together in EtOAc (20 ml). The resulting mixture was stirred vigorously under reflux conditions for 24 h. The solvent was evaporated and the reaction mixture was mixed with silica gel (5 g) and it was applied on a short column of silica gel (5 g) and eluted with petroleum ether: acetone (3:1). The solvent was evaporated and 2,4-dinitrophenol was obtained as pale yellow crystals ,1.56 g (85%), mp 112-113 °C [ lit<sup>3</sup> mp 113 °C ] (Table 2, Scheme 2).

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