

## SHORT COMMUNICATION

### HETEROPOLYACIDS AS AN EFFICIENT AND REUSABLE CATALYTIC SYSTEM FOR THE REGIOSPECIFIC NITRATION OF PHENOLS WITH METAL NITRATES

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**ABSTRACT.** Highly regiospecific mononitration of phenols and substituted phenols is accomplished employing a metal nitrate and a catalytic amount of heteropolyacid in acetonitrile. An exclusive ortho-selectivity was observed with excellent yields. A variety of metal nitrates were used to obtain o-nitrophenols exclusively in good to excellent yields. The use of heteropolyacid is key for the selectivity observed.

**KEY WORDS:** Heteropolyacids, Phenol, Nitration, Regiospecific

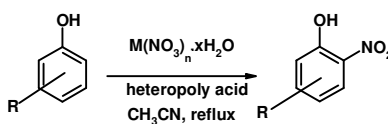
## INTRODUCTION

Aromatic nitro compounds are important starting materials for the manufacture of various industrial products such as pharmaceuticals, dyes and plastics.

The nitration of aromatic is one of the oldest and most important processes in the chemical industry for the production of intermediates. Extensive and well-documented reviews have been published about the mechanism [1-3] and using various nitrating agents under different conditions [4-25], most of them are not usually selective and cause environmental concerns regarding the disposal of large volumes of mixed acids typically employed in this process [26, 27]. A mixture of concentrated nitric acid and sulfuric acid is used as the most common nitrating reagent for the nitration of benzene, alkyl benzene, and less reactive aromatic compounds [28, 29], highly reactive aromatic compounds, phenols and pyrroles, etc., require mild nitration condition, thus a wide variety of nitration methods have been developed [24, 25, 30, 31]. Conventional methods for the nitration of aromatic compounds utilize a mixture of nitric and sulfuric acids or nitronium tetrafluoroborate. However their use is always associated with the formation of dinitro compounds, oxidized products and unspecified resinous tarry materials from over-oxidation of the substrate. Furthermore, it is noteworthy that the typical yield of direct nitration never exceeds 60% [26] because of the above mentioned side reactions in most cases, which makes these existing processes uneconomical. On the other hand, the use of metal nitrates like ceric ammonium nitrate [8], copper nitrate [32, 33] and vanadium nitrate [34], ferric nitrate [7] have contributed significantly, enhancing the scope of the nitration process however, there are concerns regarding achieving efficient regioselectivity. All these methods also suffer from other drawbacks, for example some of the nitrates must be prepared from dinitrogen pentoxide, or they must either use the clay supported or absorbed on silica gel prior to their use as nitrating agents. Recently, solid acids have attracted much attention in organic synthesis owing to their easy work-up procedures, easy filtration, and minimization of

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cost and waste generation due to reuse and recycling of these catalysts [35]. The application of heteropolyacids, HPAs, as catalytic materials is growing continuously in the catalytic field. These compounds possess unique properties such as: well-defined structure, Brønsted acidity, possibility to modify their acid-base and redox properties by changing their chemical composition (substituted HPAs), ability to accept and release electrons, high proton mobility, being environmentally benign and presenting fewer disposal problems [36]. Because of their stronger acidity, they generally exhibit higher catalytic activity than conventional catalysts such as mineral acids, ion exchange resins, mixed oxides, zeolites, etc [37]. They are used as industrial catalysts for several liquid phase reactions [38], such as alcohol dehydration [39], alkylation [40] and esterification [41]. Recently,  $H_3PW_{12}O_{40}$  was used on the nitration of phenols by  $Fe(NO_3)_3 \cdot 9H_2O$  in low yields [42] and in our lab, we used nitric acid as a strongly acidic media in the presence of HPAs to the nitration of phenols [43]. Because of our studies towards the development of new routes to the synthesis of heterocyclic compounds [44-49] in mild nitration condition, we decided to use metal nitrates as a safe nitrating reagent on the nitration of phenols in the presence of a catalytic amount of various type of HPAs including,  $H_{14}[NaP_5W_{30}O_{110}]$ ,  $H_4[PMo_{11}VO_{40}]$ ,  $H_5[PMo_{10}V_2O_{40}]$  and  $H_6[P_2W_{18}O_{62}]$  (Scheme 1) in good yields (Table 2, 3).



Scheme 1

## RESULTS AND DISCUSSION

Nitration of phenol in the presence of a catalytic amount of HPAs with a variety of metal nitrates was screened and the results are summarized in Table 1. The use of a catalytic amount of HPAs is key for the reaction to proceed with high regioselectivity and each of the metal nitrates used afforded *o*-nitrophenols as a single regioisomer in good to excellent yields. Even though the reaction proceeds with various metal nitrates, the time required for completion of the reaction was found to be less and the yields are more effective with  $Th(NO_3)_4 \cdot 5H_2O$ . Phenols were treated with a metal nitrate and HPAs in acetonitrile at reflux to afford *o*-nitrophenol as the exclusive product in satisfactory to good yields (Scheme 1). The scope and generality of the method is illustrated with several examples in Table 3 and all of them yielded the *o*-nitro product exclusively in good to excellent yields. Phenols with electron donating groups (entries 2, 6, 7 in Table 2) behaved very well to afford the *o*-nitrophenols as the exclusive products in excellent isolated yields. Phenols with moderately deactivating groups (entries 3,4 in Table 2) also yielded the *o*-nitrophenols in good yields.

In a systematic study and aimed work, the reaction has been examined with various type of HPAs and the effects of the catalyst type, the reaction temperature and solvent have also been studied.

*Effect of the catalyst type.* As shown in Table 2, among heteropolyacids with Keggin, Preyssler and Wells-Dawson structures used in present study,  $H_{14}[NaP_5W_{30}O_{110}]$  shows higher activity and the yield of product decreases in the following order:

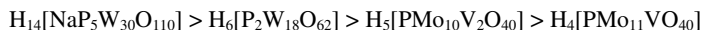


Table 1. Nitration of phenol with metal nitrates using various heteropolyacids under refluxing condition.

Entry	M(NO <sub>3</sub> ) <sub>n</sub> ·xH <sub>2</sub> O	Catalyst	Time (min)	<i>o</i> -nitro phenol (%) <sup>a</sup>
1	Th(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O	H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ]	25	95
	Th(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O	H <sub>6</sub> [P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ]	30	90
	Th(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O	H <sub>5</sub> [PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	35	89
	Th(NO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O	H <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	35	85
2	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ]	30	90
	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	H <sub>6</sub> [P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ]	35	83
	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	H <sub>5</sub> [PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	40	80
	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	H <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	40	80
3	Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ]	40	88
	Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	H <sub>6</sub> [P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ]	45	83
	Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	H <sub>5</sub> [PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	45	81
	Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	H <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	45	79
4	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ]	50	85
	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	H <sub>6</sub> [P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ]	60	79
	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	H <sub>5</sub> [PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	60	75
	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	H <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	60	73
5	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ]	50	85
	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>6</sub> [P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ]	60	82
	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>5</sub> [PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	60	80
	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	H <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	60	79
6	NaNO <sub>3</sub>	H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ]	50	80
	NaNO <sub>3</sub>	H <sub>6</sub> [P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ]	60	77
	NaNO <sub>3</sub>	H <sub>5</sub> [PMo <sub>10</sub> V <sub>2</sub> O <sub>40</sub> ]	60	72
	NaNO <sub>3</sub>	H <sub>4</sub> [PMo <sub>11</sub> VO <sub>40</sub> ]	60	70

<sup>a</sup>Yields were analyzed by GC.Table 2. Nitration of phenols with Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O and H<sub>14</sub>[NaP<sub>5</sub>W<sub>30</sub>O<sub>110</sub>].

Entry	Substrate	Product	Time (min)	Yield (%) <sup>a</sup>		
				25 °C	50 °C	82 °C
1	Phenol	<i>o</i> -Nitrophenol	25	75	85	95
2	4-Methoxy phenol	4-Methoxy-2-nitro phenol	10	80	90	98
3	4-Nitro phenol	2,4-Dinitro phenol	60	70	79	88
4	4-Bromo phenol	4-Bromo-2-nitro phenol	60	70	80	87
5	1,3-Benzen diol	2-Nitro-1,3-benzen diol	25	70	80	87
6	2-Methyl phenol	2-Methyl-2-nitro phenol	20	81	88	98
7	4-Methyl phenol	4-methyl-2-nitro phenol	10	80	86	98
8	2-Naphthol	1-Nitro-2-naphthol	25	72	80	93
9	1-Naphthol	2-Nitro-1-naphthol	25	71	80	93

<sup>a</sup>Yields were analyzed by GC.

In acid-catalyzed reactions by heteropolyacids, several types of acid sites are present [50-53]. They are including: proton sites in bulk heteropolyacids, Lewis acid sites in salts of them (metal counteractions), proton sites in acidic salts, proton sites generated by dissociation of coordinated water and reduction of salts, and proton generated by partial hydrolysis of polyanions. Generally reactions catalyzed by heteropolyacids may be represented by the conventional mechanisms of Bronsted acid catalysis. The mechanism may include the protonation of the substrate followed by the conversion of the ionic intermediate to yield the reaction product [50, 51]. Misono and co-workers advanced two types of catalysis for heterogeneous acid catalysis by heteropolyacids as surface type and bulk type [52, 53]. In

surface type catalysis, the reactions occur on the surface of bulk or supported heteropoly compounds and the catalytic activity usually depends on the surface acidity of heteropolyacid. In this case, the reaction rate and yield is parallel to the number and the strength of the accessible surface acid sites. The bulk type of mechanism is largely relevant to reactions of polar substrates on bulk heteropoly compounds. These substrates are capable of absorbing into the catalyst bulk, and thus all protons both in the bulk and on the surface of heteropolyacid, are suggested to participate in the catalytic reaction. Unfortunately, unlike the Keggin-type heteropolyacids that have been widely used as acid and oxidation catalysts for organic syntheses, the role of Preyssler catalyst is largely overlooked and there is not sufficient information. We believe that the large anion of Preyssler with the larger number of tungsten atoms, provides many "sites" on the oval shaped molecule that are likely to render the catalyst effective. Also the larger number of protons in Preyssler catalyst may lower the activation barrier for nitration reactions.

Preyssler's anion,  $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ , has an approximate  $D_{3h}$  symmetry and consists of a cyclic assembly of five  $\text{PW}_6\text{O}_{22}$  units. A sodium ion is located within the polyanion on the fivefold axis and 1.25 above the pseudo mirror plane that contains the five phosphorus atoms [51, 54]. Preyssler polyanion as a large anion can provide many "sites" on the oval shaped molecule that are likely to render the catalyst effective. The Keggin anions have an assembly of 12 corner shared octahedral  $\text{MoO}_6$  from trimetallic groups  $[\text{Mo}_3\text{O}_{13}]$  around a heteroatom tetrahedron  $\text{PO}_4$  [54]. The introduction of vanadium(V) into the Keggin framework of  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  is beneficial for catalysis reactions [55]. Usually positional isomers are possible and coexist when two or more vanadium atoms are incorporated into the Keggin structure [56]. Studies on these isomers in catalytic reactions indicate that different isomers cause to show different reactivities [57]. With respect to the catalytic performances for these catalysts and the overall effects of all isomers, for synthesizing of them, we cannot control the reaction conditions to synthesis of positional vanadium-substituted isomers separately, revealing the relationship between the structures of  $\text{H}_{3+x}\text{PMo}_{12-x}\text{V}_x\text{O}_{40}$  ( $x = 1-2$ ) and hence study of their catalytic activity, is difficult. However, because the metal substitution may modify the energy and composition of the LUMO and redox properties, for mentioned heteropolyacids with different charges, the energy and composition of the LUMOs have significant effects on the catalytic activity [58]. Substitution of vanadium ions into the molybdenum framework stabilize the LUMOs because these orbitals derive, in part from vanadium d-orbitals which have been assumed to be more stable than those of molybdenum and tungsten [59].

The abundance of different isomers may also play an important role in catalytic performance. In addition, different positional Mo atom(s) substituted by the V atom(s) in  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  may create different vanadium chemical environments, thus causing these catalysts to exhibit varying catalytic performances.

*Effect of the solvent.* Influences of solvents are the important parameter for the determination of yield of the product. Table 3 shows the effect of various solvents on the nitration reaction. The performance of various solvents are in the following the order:

acetonitrile > ethyl acetate > acetone > THF > chloroform > dichloromethane.

Acetonitrile shows better yield as compared with other solvents. In addition, the time required for completion of the reaction was found to be less in acetonitrile. Because of large negative charge of polyoxoanions, all of the HOMOs and LUMOs of them have very high energy levels. These highly charged heteropolyanions do not exist in the gas phase and that the external field generated by the solvent is crucial to stabilize them. With regard to the heteropolyanions which are reducible easily and is required in catalytic reactions, the energy of the LUMO must be sufficiently low to accept the electrons in catalytic reactions. The solvent

molecules can place these molecular orbitals at the appropriate level. As shown in Table 3, the solvent effects change in parallel to the charges of the anions. The greater negative charge lead to the greater solvent effects and finally the higher yields. It is suggested that the solvent effects are dominated by the interactions of the polarized polyanions with the solvent, to place the molecular orbitals at the appropriate level and or to lower the activation energy. Apparently this effect is higher for acetonitrile.

Table 3. Synthesis of o-nitro phenol in the presence of different solvents with  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  using various heteropolyacids under refluxing condition.

Entry	Solvent	Catalyst	Temperature (°C)	Time (min)	Yield (%) <sup>a</sup>
1	Acetonitrile	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	Reflux	25	95
	Acetonitrile	$\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$	Reflux	30	93
	Acetonitrile	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	Reflux	30	80
	Acetonitrile	$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	Reflux	30	89
2	Ethylacetate	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	Reflux	30	92
	Ethylacetate	$\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$	Reflux	35	90
	Ethylacetate	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	Reflux	40	88
	Ethylacetate	$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	Reflux	40	85
3	Acetone	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	Reflux	35	90
	Acetone	$\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$	Reflux	40	88
	Acetone	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	Reflux	40	85
	Acetone	$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	Reflux	40	85
4	THF	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	Reflux	45	89
	THF	$\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$	Reflux	50	87
	THF	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	Reflux	50	86
	THF	$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	Reflux	50	83
5	$\text{CHCl}_3$	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	Reflux	50	87
	$\text{CHCl}_3$	$\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$	Reflux	55	85
	$\text{CHCl}_3$	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	Reflux	60	82
	$\text{CHCl}_3$	$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	Reflux	60	80
6	$\text{CH}_2\text{Cl}_2$	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	Reflux	50	86
	$\text{CH}_2\text{Cl}_2$	$\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$	Reflux	55	84
	$\text{CH}_2\text{Cl}_2$	$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	Reflux	60	80
	$\text{CH}_2\text{Cl}_2$	$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	Reflux	60	79

<sup>a</sup>Yields were analyzed by GC.

*Effect of the reaction temperature.* The temperature effect on the nitration of phenol in the solvent of choice (acetonitrile) was also carefully investigated. The reaction was carried out in the presence of  $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$  and the temperature varied from room temperature (25 °C to 82 °C). The results are shown in Table 3. As can be seen in Table 3 the highest yield is obtained at 82 °C (reflux temperature), and the yields are lower when the reactions are carried out at temperatures lower than reflux temperature. We believe that increasing in the temperature for accelerating the reaction is apparently favorable.

## CONCLUSIONS

In conclusion, the mono-nitration of phenols with a metal nitrate and HPAs has been achieved with high regioselectivity and with excellent isolated yields. In general, exclusive ortho-selectivity was observed for all the phenols subjected to this protocol. The high regioselectivity, with excellent isolated yields and the use of inexpensive and easily accessible HPAs as the catalyst makes this methodology of wide synthetic and commercial utility. This method offers

some advantages in terms of simplicity of performance, easy work-up, use of inexpensive, available and easy to handle catalyst and high yields of products and relatively short reaction times.

### EXPERIMENTAL

*Chemical and apparatus.* All the chemicals were obtained from Merck Company and used as received.  $H_{14}[NaP_5W_{30}O_{110}]$  was prepared according to earlier works [44-49, 60, 61].  $H_4[PMo_{11}VO_{40}]$ ,  $H_5[PMo_{10}V_2O_{40}]$  and  $H_6[P_2W_{18}O_{62}]$  were prepared according to the literatures [50]. The integrity of the synthesized heteropolyacids has been proven by comparing of spectral data with those reported in literature [51, 54, 62, 63]. All products are known compounds and were characterized by m.p., IR,  $^1H$  NMR and GC/MS. Melting points were measured by using the capillary tube method with an electrothermal 9200 apparatus.  $^1H$  NMR spectra were recorded on a Bruker AQS AVANCE-300 MHz spectrometer using TMS as an internal standard ( $CDCl_3$  solution). IR spectra were recorded from KBr disk on the FT-IR Bruker Tensor 27 spectrometer. GC/MS analysis using an Agilent (Denver, CO, USA) 6890 GC system Hp-5 capillary 30 m  $\times$  530  $\mu$ m  $\times$  1.5  $\mu$ m nominal. Thin layer chromatography (TLC) on commercial aluminium backed plates of silica gel, 60 F254 was used to monitor the progress of reactions.

*Typical experimental procedure.* To a stirred solution of the phenol (1 mmol) in acetonitrile (5 mL) was added metal nitrate (1 mmol) followed by a catalytic amount of HPAs (0.01 mmol) and the reaction mixture was refluxed until all the phenol was consumed. The progress of the reaction was monitored by TLC using petroleum ether:ethyl acetate (4:1) as eluent. After completion of the reaction, the catalyst was filtered. The mixture was then washed with saturated sodium hydrogen carbonate (10 mL) and the product extracted into dichloromethane (2  $\times$  5 mL). The combined organic extracts were washed with distilled water (10 mL), dried over anhydrous  $MgSO_4$  and the solvent was removed by evaporation to afford the *o*-nitrophenol, m.p. 91-92  $^{\circ}C$  (lit. [64] m.p. 92  $^{\circ}C$ ).

*Reusability of the catalyst.* The catalyst was recovered after the reaction and reused as a catalyst in the nitration reactions. Several times recoveries had only slightly decreased the catalytic activity, pointing to the stability and retention capability of this useful polyanion. At the end of the reaction, the catalyst was filtered, washed with diethyl ether, dried at 130  $^{\circ}C$  for 1 h, and reused in another reaction. As shown in Table 4, the recycled catalyst was used for three reactions without observation of appreciable lost in its catalytic activities.

Table 4. Reuse of the  $H_{14}[NaP_5W_{30}O_{110}]$  for synthesis of *o*-nitro phenol with  $Th(NO_3)_4 \cdot 5H_2O$ .

Entry	Time (min)	Yield (%) <sup>a</sup>
1	25	95
2	30	94
3	40	92
4	50	86
5	60	85

<sup>a</sup>Yields were analyzed by GC.

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