


A New Method for Nitration of Phenolic Compounds

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Received: June 9, 2003; Accepted: August 8, 2003

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Abstract: Phenolic compounds can be nitrated by 65% nitric acid in the presence of catalytic amounts of montmorillonite KSF and bismuth(III) nitrate to give the corresponding nitrated products in good yields in a heterogeneous phase. The co-catalyst of KSF and $\text{Bi}(\text{NO}_3)_3$ can be easily recovered and reused in the next batch of nitration.

Keywords: bismuth(III) nitrate; catalytic nitration; montmorillonite KSF; nitric acid; phenols; synthetic methods

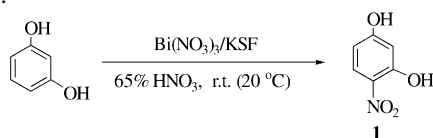
Nitration of aromatic compounds is one of the most important industrial processes.^[1] Especially, nitrated phenolic compounds are very useful intermediates in the preparation of fine chemicals.^[2–4]

In fact, nitration of phenolic compounds is very effortless. It is readily carried out at room temperature with dilute nitric(V) acid (6 wt % HNO_3). A particular case is that in the nitration of phenol, a mixture of 2-nitrophenol and 4-nitrophenol is usually formed. However, since the concentration of nitronium ions (NO_2^+) present in dilute nitric(V) acid is very small, the NO_2^+ ion is unlikely to play a significant part in the nitration process. There is evidence that the electrophile involved is the nitrosonium ion (NO^+), namely, the electrophilic substitution of a hydrogen atom with $-\text{NO}$ group is a major reaction path. The nitric(V) acid present oxidizes the $-\text{NO}$ group to the $-\text{NO}_2$ group forming the desired 2- and 4-nitrophenols. On the other hand, phenolic compounds are in general very sensitive to oxidants. It is very difficult to find a good means to nitrate them in high yields because this nitration process is usually accompanied by oxidized by-products of nitric(V) acid. In industry, the nitration of phenol may be achieved in a two-step process involving the sulphonation of phenol and subsequent nitration with mixed acid. The replacement of sulphonic acid groups must be completed to minimize the losses due to the solubility of the sulphonated compounds in water. The other popular method

for the preparation of nitrophenols is the hydrolysis of the corresponding nitrochlorobenzene with dilute alkali using aqueous sodium hydroxide at elevated temperature of 160 °C for 4 hours. But these ways are all inconvenient.

Much effort has been expended by many chemists to solve the problem in the nitration of phenolic substrates. There is a large body of literature so far. Using HNO_3 , AgNO_3 , NaNO_3 or $\text{Ca}(\text{NO}_3)_2$ as an NO_2^+ carrier and H_2SO_4 or BF_3 as an acid catalyst in CH_3CN , CHCl_3 or aromatic solvents, the nitrated phenolic compounds were obtained in good yields.^[5] Some other methods, for example, using $\text{Cu}(\text{NO}_3)_2/\text{K10}$ as a catalyst and 100% HNO_3 as an NO_2^+ carrier in acetic anhydride are also useful in the nitration of phenolic substrates.^[6] In addition, $\text{Fe}(\text{NO}_3)_3 \cdot 1.5 \text{N}_2\text{O}_4$, $\text{Cr}(\text{NO}_3)_3 \cdot 2 \text{N}_2\text{O}_4$ and $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ can be used as NO_2^+ carrier in this nitration reaction.^[7] Recently, the nitration of phenol with 6 wt % nitric acid in the presence of a phase-transfer catalyst has also been reported.^[8] However, most of the methods have some drawbacks, such as regioselectivity, over-nitration, and competitive oxidation of the phenolic substrates.^[9] In this paper, we report a new method for the nitration of phenolic compounds under mild conditions.

4,6-Dinitroresorcinol is used to prepare 4,6-diaminoresorcinol, which is a precursor to polybenzoxazoles (PBOs), polymers that are useful as insulators, solar arrays, and cut-resistant gloves. They are usually prepared by the reactions of 4,6-diaminoresorcinol with bisacids, bisacid halides, bisesters, bisamides, or bisnitriles.^[10] Efforts to prepare 4,6-dinitroresorcinol in one step from resorcinol and nitric acid in yields exceeding 30 percent have been unsuccessful due to the formation of high levels of undesirable by-products such as 2,4-dinitroresorcinol and 2,4,6-trinitroresorcinol.^[11] Improved yields of the desired 4,6-isomer have been obtained by introducing bulky protecting groups at the 1- and 3-positions of resorcinol, thereby inhibiting nitration at the 2-position.^[12] Based on these previous results, it is very clear that the preparation of mono- or dinitrated resorcinol as a sole product in high yield is difficult by using nitric acid. Thus, from the beginning we decide to select resorcinol as a substrate in our experi-

Table 1. The nitration of resorcinol catalyzed by $\text{Bi}(\text{NO}_3)_3/\text{KSF}$.

| Entry ^[a] | Solvent | Time [h] | Yield [%] ^[b] |
|----------------------|--------------------------|----------|--------------------------|
| 1 | Et_2O | 1.0 | 50 |
| 2 | Et_2O | 16 | 61 |
| 3 | THF | 1.0 | 52 |
| 4 | THF | 16 | 70 |
| 5 | DME | 16 | 68 |
| 6 | CH_2Cl_2 | 16 | 20 |
| 7 | CH_3NO_2 | 16 | 35 |

^[a] The reaction was carried out by use of $\text{Bi}(\text{NO}_3)_3$ (39 mg, 0.1 mmol) and 500 mg of KSF and resorcinol (110 mg, 1.0 mmol) with 65% HNO_3 (0.1 mL, 1.4 mmol).

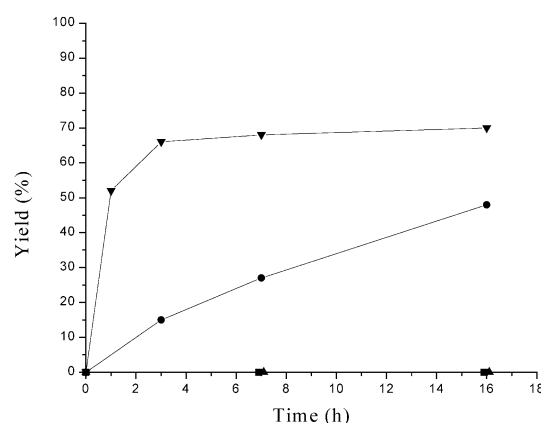
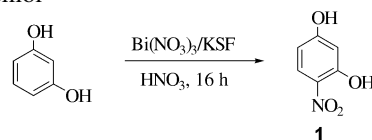
^[b] Isolated yields.

ments to seek out a mild nitration method in the preparation of the corresponding nitrated phenolic compounds.

In 2000, Susanta reported that the nitration of aromatic compounds can be achieved by using $\text{Bi}(\text{NO}_3)_3$ as a nitration reagent and KSF as a catalyst.^[13] Investigations on the nitration of aromatic compounds,^[14] we found that $\text{Bi}(\text{NO}_3)_3/\text{KSF}$ [(39 mg, 0.1 mmol)/500 mg] is a good catalyst for nitration. First of all, we utilized $\text{Bi}(\text{NO}_3)_3/\text{KSF}$ as a catalyst to nitrate resorcinol in ether with 65% nitric acid. The mono-nitrated product was obtained in 50% after 1 h, and in 61% after 16 h at room temperature (20 °C) (Table 1, entries 1 and 2). This result suggests that $\text{Bi}(\text{NO}_3)_3/\text{KSF}$ is a very effective catalyst for mono-nitration of phenolic compounds. Then we examined the effects of solvent on this nitration. These results are summarized in Table 1. As can be seen from Table 1, we found that this nitration process proceeded very well in ether, DME or THF (Table 1, entries 1, 4, and 5). The best result was obtained when using THF as a solvent in which the corresponding mono-nitrated product was obtained in 52% after 1 h and in 70% after 16 h. Nevertheless, in the other kinds of solvents, for example, dichloromethane or nitromethane, the yields are very low (Table 1, entries 6 and 7).

The control experiment showed that using only $\text{Bi}(\text{NO}_3)_3$ as a catalyst or without a catalyst, no reaction occurred under the same conditions (Figure 1). The combination of $\text{Bi}(\text{NO}_3)_3/\text{KSF}$ is more efficient than only using KSF as a catalyst in the nitration of resorcinol (Figure 1).

We also examined this catalytic nitration reaction with different concentrations of nitric acid under the same conditions. When the concentration of nitric acid was

**Figure 1.** The yields of the nitration of resorcinol in the presence or absence of catalyst versus time with 65% HNO_3 . ▼ $\text{Bi}(\text{NO}_3)_3/\text{KSF}$; ● only KSF; ■ only $\text{Bi}(\text{NO}_3)_3$; ■ no catalyst.**Table 2.** The concentration of nitric acid on the nitration of resorcinol^[a]

| Entry | Percent of nitric acid | Temp. [°C] | Amount of KSF | Yield [%] ^[b] |
|-------|------------------------|------------|---------------|--------------------------|
| 1 | 20% ^[c] | 30 | 1000 mg | 53 |
| 2 | 65% ^[d] | 20 | 500 mg | 70 |
| 3 | 95% ^[e] | 0 | 500 mg | 75 |

^[a] Resorcinol (110 mg, 1.0 mmol) and 39 mg (0.1 mmol) of $\text{Bi}(\text{NO}_3)_3$ were employed.

^[b] Isolated yields.

^[c] 20% of HNO_3 (0.5 mL, 1.6 mmol) was employed.

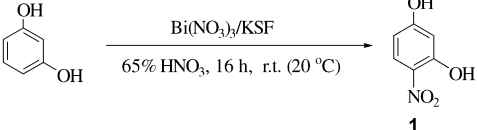
^[d] 65% of HNO_3 (0.1 mL, 1.4 mmol) was employed.

^[e] 95% of HNO_3 (0.08 mL, 2.0 mmol) was employed.

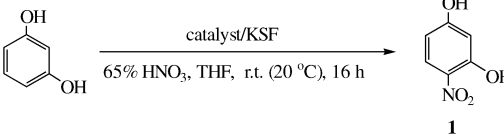
changed from 20% to 65% and 95%, we found that the nitration reaction rate became faster. The results are listed in Table 2. Using 20% nitric acid, the nitration reaction is sluggish. The nitrated resorcinol was obtained in 50% at higher temperature (30 °C) and in the presence of 1.0 g of KSF (Table 2, entry 1).^[15] Using 95% of nitric acid, the nitration reaction proceeded quickly to give the corresponding nitrated product **1** along with many unidentified products at room temperature because of the further oxidation with 95% nitric acid. But at 0 °C, the reaction proceeded very well to give **1** in 75% (Table 2, entry 3). Considering the safety of the operation, we decided to use 65% nitric acid in the nitration of the phenolic compounds.

It should be emphasized here that the $\text{Bi}(\text{NO}_3)_3/\text{KSF}$ catalyst can be easily recovered from the reaction mixture just by filtration and reused many times after

Table 3. The recovered catalyst in the nitration of resorcinol.

|  | | |
|---|---------------|--------------------------|
| Entry | Amount of KSF | Yield [%] ^[a] |
| 1 | 500 mg | 61 |
| 2 ^[b] | 500 mg | 60 |
| 3 ^[b] | 500 mg | 71 |

^[a] Isolated yields.^[b] The recovered catalyst was used.**Table 4.** Nitration of resorcinol catalyzed by catalyst/KSF.

|  | | |
|---|--------------------------------|--------------------------|
| Entry | Catalyst ^[a] | Yield [%] ^[b] |
| 1 | Bi ₂ O ₃ | 73 |
| 2 | BiCl ₃ | 58 |
| 3 | SeO ₂ | 52 |
| 4 | Sb ₂ O ₃ | 60 |
| 5 | GeO ₂ | 60 |

^[a] 0.1 mol of catalyst was employed.^[b] Isolated yields.

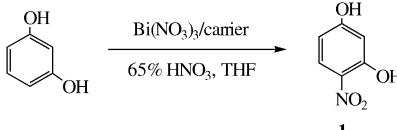
it has been re-activated by heating in an oven at 120 °C. In our experiment, we reused the catalyst for three times and it still has good activity (Table 3, entries 1–3).

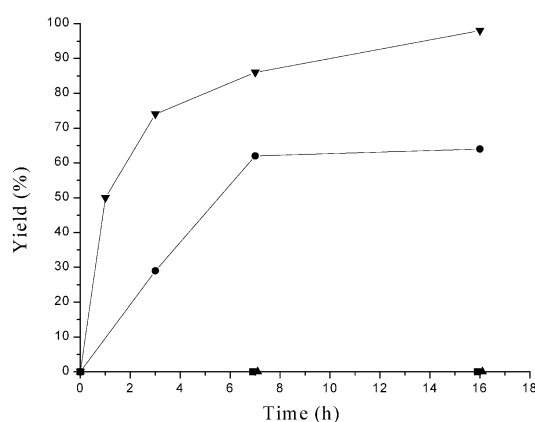
We also examined other metal salts (BiCl₃) or metal oxides (Bi₂O₃, SeO₂, Sb₂O₃, GeO₂) in this nitration process. The results are summarized in Table 4. Among all our examined metal salts and metal oxides, Bi₂O₃ also gave a good result. The yield of nitrated resorcinol is 73% (Table 4, entry 2).

In addition, we also tried to find other carriers to replace KSF. During our own examinations, we found that Bi(NO₃)₃/SiO₂ can catalyze this nitration reaction at a higher temperature (50 °C) to give the corresponding **1** in similar yield as that of Bi(NO₃)₃/KSF along with some unidentified by-products, although it has no activity at room temperature (20 °C) (Table 5, entries 1 and 2). However, molecular sieves 4 Å showed no activity (Table 5, entry 3). From our experiments, the best catalyst is Bi(NO₃)₃/KSF for nitration of phenolic substrates at room temperature.

Based on the above investigations, we decided to use Bi(NO₃)₃/KSF as a catalyst to nitrate other phenolic substrates under mild conditions. We first utilized

Table 5. Nitration of resorcinol catalyzed by Bi(NO₃)₃/carrier.

|  | | | |
|--|---------------------------------|------------|--------------------------|
| Entry | Carrier | Temp. [°C] | Yield [%] ^[a] |
| 1 | SiO ₂ ^[b] | 20 | no reaction |
| 2 | SiO ₂ ^[b] | 50 | 70 |
| 3 | MS 4 Å ^[b] | 50 | no reaction |

^[a] Isolated yields.^[b] 500 mg of SiO₂ or MS 4 Å were employed.**Figure 2.** The yields of the nitration of *p*-chlorophenol in the presence or absence of catalyst versus time with 65% HNO₃. ▼ Bi(NO₃)₃/KSF; ● only KSF; ■ only Bi(NO₃)₃; ▲ no catalyst.

phenol as a substrate for this method. The yield of nitrophenol is 88% (*p*:*o* = 31:49). If phenol was directly nitrated only by nitric acid, the product was a black solid and no nitrophenol was formed. In order to further clarify the effects of the catalyst Bi(NO₃)₃/KSF in other phenolic compounds control experiments were carried out using Bi(NO₃)₃, KSF or Bi(NO₃)₃/KSF as the catalysts in the nitration of *p*-chlorophenol and *p*-bromophenol. The results are shown in Figures 2 and 3. We found that the nitration of *p*-chlorophenol did not occur in the absence of catalyst or using only Bi(NO₃)₃ as catalyst. The catalyst Bi(NO₃)₃/KSF is better than KSF alone as catalyst in this nitration process. The difference is very distinctive. The yield reached 98% within 16 h under mild conditions. Similar results were obtained in the nitration of *p*-bromophenol (Figure 3).

This electrophilic aromatic nitration reaction proceeded very well for many phenolic substrates. The results are shown in Table 6. *p*-Chlorophenol, *p*-bromophenol and *p*-fluorophenol reacted smoothly to afford a single mono-nitrated product in excellent yields (Ta-

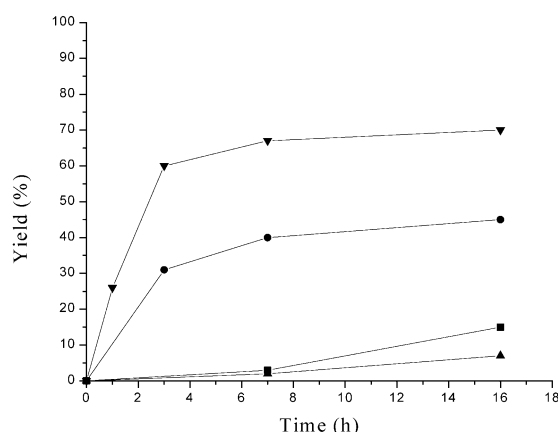
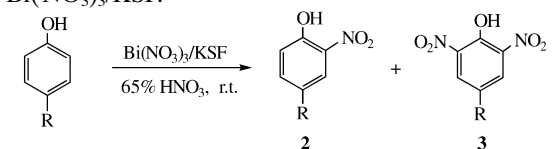


Figure 3. The yields of the nitration of *p*-bromophenol in the presence or absence of catalyst versus time with 65% HNO₃. ▼ Bi(NO₃)₃/KSF; ● only KSF; ■ only Bi(NO₃)₃; ▲ no catalyst.

Table 6. Nitration of phenolic compounds catalyzed by Bi(NO₃)₃/KSF.



| Entry | R | Time [h] | Yield [%] ^[a] | |
|-------|--------------|----------|--|-------------------------|
| | | | 2 | 3 |
| 1 | H | 16 | 2a (31 ^[b]) 2a' (49 ^[b]) | |
| 2 | Cl | 4 | 2b (98) | – |
| 3 | Br | 16 | 2c (70) | – |
| 4 | F | 16 | 2d (82) | – |
| 5 | <i>t</i> -Bu | 4 | 2e (75) | 3e (21) |
| 6 | <i>t</i> -Bu | 16 | 2e (50) | 3e (38) |
| 7 | OMe | 16 | – | 3f (71 ^[c]) |
| 8 | <i>i</i> -Pr | 16 | 2g (74) | – |
| 9 | | 4 | 2h (76 ^[d]) | – |

^[a] Isolated yields.

^[b] The products are 2-nitrophenol **2a** (31%) and 4-nitrophenol **2a'** (49%).

^[c] 2.2 equivs. of nitric acid were employed.

^[d] The product is 1,4-dimethoxy-2-nitrobenzene **2h**.

ble 6, entries 2–4). For the nitration of 4-*tert*-butylphenol, two products, mono-nitrated and dinitrated, were obtained in total 96% yield and the yield of dinitrated product **3e** increased when the reaction time was prolonged (Table 6, entries 5 and 6). In the case of the activated phenolic aromatic compound, *p*-methoxyphenol, a single dinitrated product was observed in 71% yield under mild conditions (Table 6, entry 7). For the

Table 7. Nitration of cresols catalyzed by Bi(NO₃)₃/KSF.

| Entry | Cresol | Time [h] | Yield [%] ^[a] | |
|-------|--------------------------------------|----------|--------------------------|----------|
| | | | 4 | 5 |
| 1 | 4-MeC ₆ H ₄ OH | 16 | | |
| | | | 4i (53) | 5i (26) |
| 2 | 3-MeC ₆ H ₄ OH | 16 | | |
| | | | 4j (53) | 4j' (21) |
| 3 | 2-MeC ₆ H ₄ OH | 16 | | |
| | | | 4k (24) | 4k' (26) |
| | | | | 5k (22) |

^[a] Isolated yields.

nitration of 4-*iso*-propylphenol and 1,4-dimethoxybenzene, the corresponding mono-nitrated phenolic compound was exclusively formed (Table 6, entries 8 and 9). On the other hand, we also examined the nitration reaction of 2-cresol, 3-cresol and 4-cresol. In the case of 3-cresol, two mono-nitrated phenolic products **4j** and **4j'** were obtained in good yields (Table 7, entry 2). However, in the nitration of 4-cresol and 2-cresol, both mono-nitrated and dinitrated products were obtained at the same time (Table 7, entries 1 and 3).

In conclusion, we have found a good method for the nitration of phenolic compounds under mild conditions. In the presence of Bi(NO₃)₃/KSF catalyst, 65% nitric acid can be used in the nitration of phenolic compounds to give the nitrated products in good yields. The use of concentrated or fuming nitric acid can be avoided by this catalytic system. Moreover, Bi(NO₃)₃ and KSF are very cheap catalysts in industry and can be recovered and reused by simple treatment. This nitration method was carried out in ether or THF, an environmentally safer solvent. Overall we believe this method is an eco-safer and environment-benign way for the nitration of phenolic compounds.

Experimental Section

General Remarks

Mp's were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer for solutions in CDCl_3 with tetramethylsilane (TMS) as internal standard; J values are in Hz. All of the solid compounds reported in this paper gave satisfactory C,H,N microanalyses with a Carlo-Erba 1106 analyzer. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured by a Finnigan MA^+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. The orientation of nitration was determined by NMR analysis. Flash column chromatography was carried out using 200–300 mesh silica gel.

General Procedure for the Nitration of Phenolic Compounds

KSF (500 mg) was put into a glass vessel and then the vessel was flame-dried under reduced pressure. A solution of resorcinol (110 mg, 1.0 mmol) and bismuth nitrate (39 mg, 0.1 mmol) in THF (or other solvent, 5 mL) was added into the dried glass vessel. Nitric acid (65%, 0.10 mL, 1.4 mmol) was slowly added dropwise and the mixture was stirred for 16 hours at room temperature. After filtration, the catalyst was recovered and the reaction mixture was extracted with dichloromethane (CH_2Cl_2). The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatograph (eluent: petroleum ether/EtOAc, 10/1) to give the product as a yellow solid; yield: 108 mg (70%).

Recovery of the Employed Catalysts and the Reusing Procedure

The catalyst can be easily recovered from the reaction mixture just by filtration and reused for many times after it had been activated by heating in an oven at 120°C . The recovered catalyst was employed in the same manner as that described above. After filtration, the catalyst was recovered and the reaction mixture was extracted with dichloromethane (CH_2Cl_2). The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatograph (eluent: petroleum ether/EtOAc, 10/1) to give the product as a yellow solid; yield: 110 mg (71%).

4-Nitro-resorcinol (1): A yellow solid; yield: 170 mg (73%); mp $117\text{--}119^\circ\text{C}$, IR (KCl): $\nu = 1532, 1397$ (NO_2), $3354, 1255\text{ cm}^{-1}$ (OH); ^1H NMR (CDCl_3 , 300 MHz, TMS): $\delta = 6.47$ (1H, dd, $J = 9.2\text{ Hz}, 3.4\text{ Hz}$, Ar), 6.52 (1H, d, $J = 3.4\text{ Hz}$, Ar), 8.05 (1H, d, $J = 9.2\text{ Hz}$, Ar), 10.97 (1H, s, ArOH); MS (EI): $m/z = 155$ (M^+ , 47.40), 125 ($\text{M}^+ - 30$, 100), 97 ($\text{M}^+ - 58$, 94.90), 77 ($\text{M}^+ - 78$, 6.77), 51 ($\text{M}^+ - 104$, 65.02); anal. calcd. for $\text{C}_6\text{H}_5\text{NO}_4$ (%): C 46.46, H 3.25, N 9.03; found: C 46.48, H 3.44, N 9.02.

Acknowledgements

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China for financial support (20025206, 203900502, and 20272069).

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