

Nitration of phenolic compounds and oxidation of hydroquinones using tetrabutylammonium chromate and dichromate under aprotic conditions

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Abstract. In this work, we have reported a mild, efficient and selective method for the mononitration of phenolic compounds using sodium nitrite in the presence of tetrabutylammonium dichromate (TBAD) and oxidation of hydroquinones to quinones with TBAD in CH_2Cl_2 . Using this method, high yields of nitrophenols and quinones were obtained under neutral aprotic conditions. Tetrabutylammonium chromate (TBAC) can also be used as oxidant at same conditions.

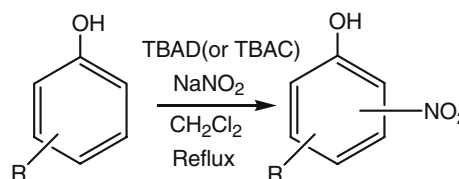
Keywords. Ammonium salt; chromate; hydroquinone; nitration; phenol.

1. Introduction

Nitration of aromatic compounds is an industrially important organic reaction since the nitro aromatic compounds are key intermediates for fine chemicals and also many useful materials such as dyes, pharmaceuticals, agrochemicals, perfumes, and plastics.^{1–3} Traditionally, the nitration of aromatic rings was accomplished with mixed concentrated nitric-sulfuric acids. This reaction is notoriously unselective for nitration of substituted aromatic compounds such as phenols and anilines because they may be oxidized or polynitrated under these conditions. Furthermore, disposal of the corrosive and acidic liquors presents a serious environmental concern, which makes this method uneconomical and non-safe. Due to the importance of nitrophenols as organic intermediates, it is interesting to develop new synthetic methods for selective nitration of phenolic compounds. In recent years, various methodologies have been reported for nitration of phenols such as HNO_3 /zeolite,^{4,5} HNO_3 /TBAB,⁶ HNO_3 /CTAB,⁷ HNO_3 (40%)/bentonite clay,⁸ HNO_3 /Ac₂O/ $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$,⁹ HNO_3 /ZnCl₂ under ultrasonic conditions,¹⁰ HNO_3 (60%)/Zr or Hf oxychloride complex and KSF,¹¹ HNO_3 (30%)/

ZSTA,¹² N_2O_5 and ClNO_2 ,¹³ $\text{AcONO}_2/\text{HNO}_3$.¹⁴ Although it has been shown that these reagents are selective and efficient nitrating systems for phenolic compounds, they are environmentally unfavourable and have some other disadvantages including acidic conditions, using unavailable and expensive catalysts or reagents and tedious handling. Also, many methods have been reported by using metal nitrates or nitrites as source of nitronium ion under mild acidic or neutral conditions.^{15–23}


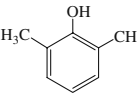
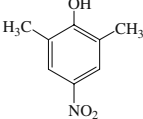
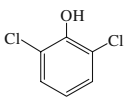
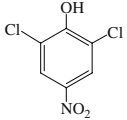

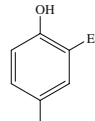

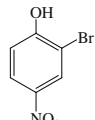

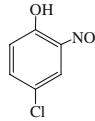

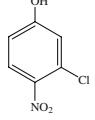
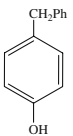
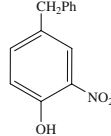
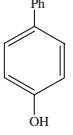
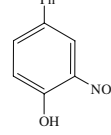
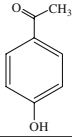
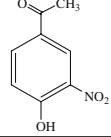
On the other hand, the use of quaternary ammonium salts as phase transfer catalysts has been extensively used for functional group interconversions. Furthermore, it is attractive to use quaternary ammonium salts as reagents for organic transformations. Because of good solubility of these salts in organic solvents, high selectivity and absence of side reactions, many easily prepared or commercially available crystalline quaternary ammonium salts having different oxidizing anions have found some



Scheme 1. Nitration of phenolic compounds.

*For correspondence

Table 1. Nitration of phenolic compounds using NaNO₂ in the presence of TBAD or TBAC in CH₂Cl₂ under reflux conditions.

Entry	Substrate	Product	TBAD ^a Time /h (isolated yield/%)	TBAC ^b Time /h (isolated yield/%)
1		<i>para</i> -Nitrophenol	(40)	(36)
		<i>ortho</i> -Nitrophenol	(40)	(44)
2			24(98)	23(99)
3			23(98)	45(98)
4			94(90)	95(70)
5			50(75)	90(95)
6			48(95)	48(90)
7			48 (90)	69(98)
8			96(80)	52(80)
9			45(85)	69(90)
10			100(80)	100(82)

^a Substrate/TBAD ratio is 1:1^b Substrate/TBAC ratio is 1:2

applications in the oxidation of functional groups in organic synthesis. Quaternary ammonium salts of nitrate,²⁴ nitrite,²⁵ periodate,²⁶ peroxodisulfate,²⁷ dichromate,²⁸ chromate²⁹ and chlorochromate³⁰ are examples of these reagents. TBAD and TBAC have been used as a very mild oxidizing agent for the selective conversion of unsaturated alcohols including allylic and benzylic alcohols to the corresponding aldehydes.^{28,29}

2. Experimental

Tetrabutylammonium dichromate (TBAD) and chromate (TBAC) were prepared according to literature.^{28,29} Other chemicals were obtained from Merck chemical company. The progress of the reaction was monitored by thin-layer chromatography on commercial Merck precoated TLC plates (silica gel 60 F₂₅₄) and GLC on a Varian CP-3800 instrument. All products are known. They were identified by comparison of their physical and spectroscopic data with those of authentic samples after purification by column chromatography. Melting points were determined by using open capillary tubes with a Buchi 510 apparatus and corrected. FT-IR spectra were recorded on a Perkin Elmer RXI spectrometer.

2.1 Nitration of phenol by using TBAD and NaNO₂

To 0.188 g phenol (2 mmol) dissolved in 20 cm³ CH₂Cl₂, 0.138 g NaNO₂ (2 mmol) and 1.40 g TBAD (2 mmol) were added. The mixture was refluxed for 48 h, cooled, and after adding 20 cm³ distilled water, the mixture was extracted with 3 × 20 cm³ CH₂Cl₂. Organic layer was separated and dried over MgSO₄ and the solvent was evaporated. Chromatography on TLC plates yields 0.111 g (40%) *o*-nitrophenol, mp 44–46°C (Ref.³¹ mp 46°C); and 0.111 g, (40%) *p*-nitrophenol mp 112–114°C (Ref.³¹ mp 112–113°C).

2.2 Nitration of 4-chlorophenol by using TBAC and NaNO₂

To 0.257 g 4-chlorophenol (2 mmol) dissolved in 20 cm³ CH₂Cl₂, 0.138 g NaNO₂ (2 mmol) and 1.44 g TBAC (4 mmol) were added. The mixture was refluxed for 48 h, cooled, and after adding 20 cm³ distilled water, the mixture was extracted with 3 × 20 cm³ CH₂Cl₂. Organic layer was separated and dried over MgSO₄ and the solvent was evaporated. Chromatography on TLC plates yields 0.231 g (90%) 4-chloro-2-nitrophenol, mp 87–90°C (Ref.³¹ mp 88–89°C).

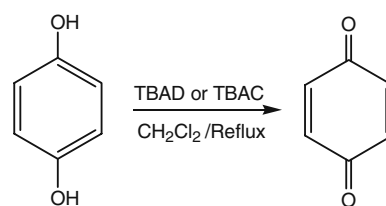
2.3 Oxidation of hydroquinone by using TBAD

To 0.220 g hydroquinone (2 mmol) dissolved in 20 cm³ CH₂Cl₂, 1.40 g TBAD (2 mmol) were added. The mixture was refluxed for 15 min. After adding 20 cm³ distilled water, the mixture was extracted with 3 × 20 cm³ CH₂Cl₂. Organic layer was separated and dried over MgSO₄ and the solvent was evaporated. Chromatography on a TLC plate afforded 0.207 g (95%) *p*-benzoquinone, mp 112–114°C (Ref.³¹ mp 113–114°C).

3. Results and discussion

Recently, we have reported the efficient and mild conversion of oximes to carbonyl compounds using TBAC in aprotic conditions.³² Now, we report a mild and selective nitration of phenols using sodium nitrite and tetrabutylammonium dichromate (TBAD) or chromate (TBAC) in CH₂Cl₂ at reflux conditions (scheme 1).

First, for optimizing reaction conditions, we conducted the reaction between phenol, sodium nitrite, and TBAD in various organic solvents with different polarities at room temperature and reflux conditions. For mononitration of phenol, best results were obtained when it was reacted with NaNO₂ (1 eq.) and TBAD (1 eq.) in CH₂Cl₂ under reflux conditions. The progress of reaction was monitored by thin layer chromatography and GLC. After completion of the reaction (48 h), the mixture was worked-up according to experimental. Products of the reaction were separated by chromatography on TLC plates. This afforded *p*-nitrophenol and *o*-nitrophenol each in 40% isolated yields. Other phenols were efficiently nitrated under these conditions with high yields (table 1). In these reactions, phenols were selectively converted to the corresponding mononitrated phenolic compounds. Dinitrated phenols were not observed in all reactions. Benzene and other non-activated aromatics were not reacted in these conditions.



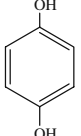
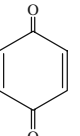
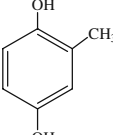
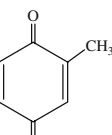
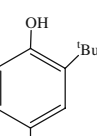
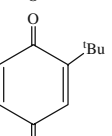
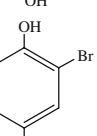
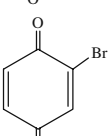
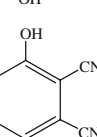
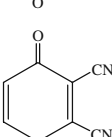
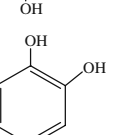
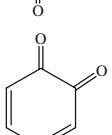
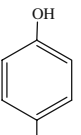
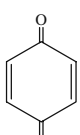
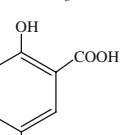
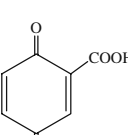
Scheme 2. Oxidation of hydroquinones.

Also, we conducted the reaction of phenol (1 mmol) with NaNO_2 (1 mmol) and TBAC (2 mmol) in CH_2Cl_2 under reflux conditions. After 48 h, work-up of the reaction afforded 36% *p*-nitrophenol and 44% *o*-nitro-

phenol. Other structurally different phenols were efficiently nitrated by TBAC with high yields (table 1).

Hydroquinone and its derivatives were easily oxidized at the reaction conditions and the corresponding

Table 2. Oxidation of hydroquinones and other oxidizable aromatic compounds to quinones using TBAD or TBAC in CH_2Cl_2 under reflux conditions.

Entry	Substrate	Product	TBAD ^a Time/min. (isolated yield / %)	TBAC ^b Time/min. (isolated yield / %)
1			15(95)	10(98)
2			10(99)	7(99)
3			9(99)	20(98)
4			14(98)	30(99)
5			16(98)	20(98)
6			7(99)	10(99)
7			50(96)	90(95)
8			8(99)	15(99)

^a Substrate/TBAD ratio is 1:1

^b Substrate/TBAC ratio is 1:2

nitro compounds were not produced. We observed that hydroquinone was oxidized with TBAD in CH_2Cl_2 under reflux conditions in 10 min and *p*-benzoquinone was obtained with 95% isolated yield (scheme 2). Also, in the presence of TBAC, hydroquinone was converted to the *p*-benzoquinone in CH_2Cl_2 under reflux conditions with 98% isolated yield.

As shown in table 2, substituted hydroquinones (entries 2–5), 1,2-dihydroxy benzene (entry 6), 4-methoxy phenol (entry 7), and 2-hydroxy-5-amino-benzoic acid (entry 8) were efficiently oxidized by TBAD and TBAC to the corresponding quinones with high yields. In the case of 4-methoxy phenol, demethylation followed by oxidation afforded benzoquinone.

4. Conclusion

In conclusion, efficient and selective mononitration of structurally different phenolic compounds was performed using sodium nitrite in the presence of TBAD and TBAC under non-acidic and aprotic conditions. High yields, mildness and good handling of the reagents are other advantages of this method. Also, oxidation of dihydroxy benzenes was performed in short times with TBAD or TBAC to afford the quinones.

Acknowledgement

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