



Nitration Ortho Dihydroxyl Benzene (Catechol) Using Bismuth Nitrate on the Solid Phase Montmorillonite

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Abstract

Nitro catechols via 2 hydroxyl group and a nitro group have a wide range of functions including reagents form stable complexes with more than 40 elements in the fields of analytical chemistry, biochemistry, coordination chemistry, environmental chemistry, atrium exploration, organic chemistry, pharmacy, etc. Moreover, the nitro to amine recovery has a potential function in different fields. In recent years the use of various nitration factors including metal nitrates with environmentally friendly features, and in order to reduce pollution as an alternative to nitric acid/ sulfuric acid has been reported. High-performance trivalent bismuth nitrate nitration has been reported in the literature. In this work, impregnated nitrate bismuth on solid montmorillonite KSS and KSF in catechol ring nitration was used in conditions of largely different polarity solvents. Under the condition of the use of montmorillonite KSF as the solid phase and dichloromethane solvent, conversion of catechol to nitrate derivatives will be quantitative.

Keywords: Nitration, Catechol, Bismuth nitrate, Montmorillonite.

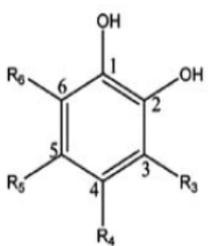
1. Introduction

The nitration of aromatic compound is one of the most important key in organic synthesis. Nitrophenols are the most important Precursors for synthesis of dyes and pigments. This group of reagent has other application too, such as: photography material and pharmacology [1-6].

Nitro reagents could be used as precursors for synthesis of different amines [1, 2 and 7]. In classical nitration method of aromatic compound, concentrated sulfuric and nitric acid have been used. But in this way acid can make the oxide compound of the precursors. Therefore the yield of the reaction decreases. However, using of sulfuric acid can be hazardous and expensive [3, 8].

Catechols, have been known by benedict at the first time [9]. Nitro derivatives of catechol (NDCS) are important reagents in aromatic compound. They have 2 hydroxyl groups in ortho position and at least a nitro group has been bonded to benzene circle. The result of researches about NDCS could be reported in every part of chemistry such as analytical chemistry, biochemistry, environment chemistry and organic chemistry. Table 1 shows some new derivatives of catechol. They are hot spot for researchers in the future [10].

Table 1. Different derivatives of catechol.

General formula	Names and abbreviations	R ₃	R ₄	R ₅	R ₆	Mol. mass	Melting point/ °C
	3-nitrobenzene-1,2-diol (3-nitrocatechol, 3-NC)	NO ₂	H	H	H	155.11	86-87
	4-nitrobenzene-1,2-diol (4-nitrocatechol, 4-NC)	H	NO ₂	H	H	155.11	174-176
	3,4-dinitrobenzene-1,2-diol (3,4-dinitrocatechol, 3,4-DNC)	NO ₂	NO ₂	H	H	200.11	147-148
	3,5-dinitrobenzene-1,2-diol (3,5-dinitrocatechol, 3,5-DNC)	NO ₂	H	NO ₂	H	200.11	166.8-167.1
	4,5-dinitrobenzene-1,2-diol (4,5-dinitrocatechol, 4,5-DNC)	H	NO ₂	NO ₂	H	200.11	166.5-167.5

A literature survey shows that various methods have been reported using different catalysts such silica sulfuric acid (SSA) [11], COCl₂ [12], tetrabutyl ammonium dichromate (TBAD) and tertabutyl ammonium chromate (TBAC) [13], [MSIM] Cl [14]. However, these methods show varying degrees of success as well as limitations such as prolonged reaction times, low yields and use of expensive catalysis. Herein we disclose a general high yielding protocol for nitration of catechol. With Bismuth nitrate and also montmorillonite (KSF) as solid phase, in dichloromethane and reflux condition (Figure 1).

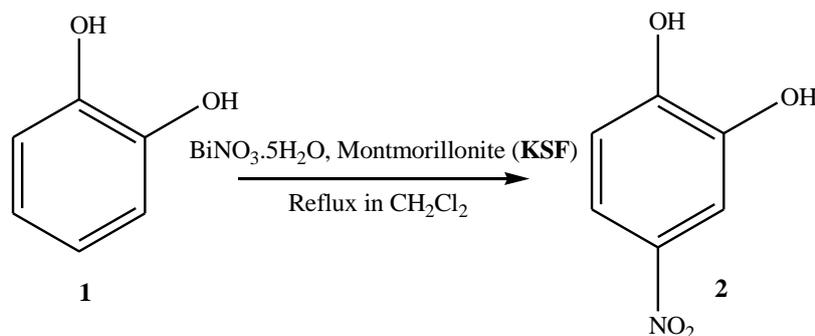


Fig 1. Nitration of catechol using bismuth nitrate on the solid phase montmorillonite.

2. Material and methods

All chemicals were obtained from Fluka or Merck and were used without further purification. A mixture of catechol (0.11 g, 0.001 mmol), bismuth nitrate (1.44 g, 0.003 mmol) and montmorillonite, KSF (0.5 g) was dissolved in 20 ml dichloromethane and stirred at room temperature for 10 minutes. In the next step the mixture of reaction refluxed at 35 °C for 2 h. The mixture was filtered and washed with dichloromethane for several times. Then the solvent was removed under reduced pressure, and the pure product was finally obtained.

3. Results and discussion

Firstly, the study was carried out by choosing the reaction of catechol No 1 in the presence of montmorillonite, KSF or KSS and Bismuth nitrate in different solvents. Different conditions have been checked too, all the results have been reported in table 2. Finally best condition for the reaction has been found (table 2 entry7). The structure of compound 2 was confirmed from IR and ^1H -NMR spectra. The ^1H -NMR spectrum of No 2 in CH_2Cl_2 exhibited two doublets ($\delta = 7.37, 8.49$ ppm) for 2 H, and a singlet ($\delta = 9.1$ ppm) for ^1H .

Table 2. Evaluation of different conditions for nitration of catechol.

Entry	Bismuth nitrate (mol)	Montmorillonite (g)	Solvent	reaction condition	Time (h)	Yield (%)
1	0.001	0.05 KSS	Acetone	r.t ^a	4	-
2	0.003	0.05 KSS	Acetone	r.t	4	10
3	0.001	0.05 KSS	Dichloromethane	r.t	4	70
4	0.001	0.05 KSS	Dichloromethane	r.t	2	70
5	0.003	0.05 KSS	Dichloromethane	r.t	2	80
6	0.003	0.05 KSF	Dichloromethane	r.t	2	10
7	0.003	0.05 KSF	Dichloromethane	R.f^b	2	90
8	0.003	0.05 KSF	Water	r.t	2	15
9	0.003	0.05 KSF	Water	R.f	2	65

^aRoom temperature.^bReflux.

4. Conclusion:

In summary we describe an efficient method of nitration of catechol in the presence of KSF and Bismuth nitrate, under reflux radiation. The advantage of the present procedure is that the reaction is performed by simple mixing of the starting materials using an inexpensive and available reagent in a short time. So the products No 2 are prepared in good yield. This method was successfully applied to nitration of catechol.

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