Synthesis Of p-Nitrophenol From p-Nitrochlorobenzene and Sodium Hydroxide

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Abstract—**The present study focuses on the preparation of p-Nitrophenol from p-Nitro chlorobenzene using Sodium Hydroxide through a nucleophilic aromatic substitution reaction. The process involves the hydrolysis of p-nitro chlorobenzene in the presence of aqueous sodium hydroxide under controlled temperature and pressure conditions, leading to the replacement of the chlorine atom by a hydroxyl group to form p-nitrophenol. The synthesized product was subsequently isolated, purified, and characterized using standard analytical techniques such as melting point determination, thin-layer chromatography, and spectroscopic analysis. The objective of this work was to optimize reaction parameters including temperature, reaction time, concentration of sodium hydroxide, and pressure in order to maximize product yield and purity. The effect of various operating conditions on the conversion efficiency was systematically studied. The obtained results demonstrated that higher temperatures and appropriate alkali concentration significantly enhanced the reaction rate and product formation. The final product exhibited satisfactory purity and yield, confirming the effectiveness of the adopted synthesis method. This study highlights the industrial importance of p-nitrophenol as an intermediate in the manufacture of pharmaceuticals, dyes, pesticides, and fine chemicals. The developed method offers a simple, economical, and efficient route for the synthesis of p-nitrophenol from p-nitro chlorobenzene using sodium hydroxide.**

Index Terms—**p-Nitrophenol, para-nitrophenol,4-Nitrophenol, PNP,4-NP, p-Hydroxynitrobenzene,1-Hydroxy-4-nitrobenzene.**

I. INTRODUCTION

Aromatic nucleophilic substitution reactions constitute an important class of organic transformations in both laboratory and industrial chemistry. Among these, the alkaline hydrolysis of p-nitro chlorobenzene (PNCB) to produce p-nitrophenol (PNP) represents a well-established and industrially significant reaction.

p-Nitrophenol is a valuable intermediate extensively utilized in the synthesis of pharmaceuticals, agrochemicals, dyes, antioxidants, and photographic developers. It also serves as a precursor in the manufacture of paracetamol (acetaminophen) and other biologically active compounds, highlighting its considerable pharmaceutical relevance.

The hydrolysis of aryl halides is generally challenging due to the partial double-bond character of the carbon–halogen bond and the inherent stability of the aromatic ring. However, the presence of strong electron-withdrawing substituents, such as the nitro (-NO) group, significantly enhances the susceptibility of the aromatic nucleus to nucleophilic attack. In p-nitro chlorobenzene, the para-positioned nitro group activates the ring toward nucleophilic aromatic substitution (SNAr) by stabilizing the negatively charged intermediate formed during the reaction. This electronic activation enables the replacement of the chlorine atom by a hydroxyl group under strongly alkaline conditions, typically using aqueous sodium hydroxide at elevated temperatures and pressures. Mechanistically, the reaction proceeds via an addition–elimination pathway involving the formation of a Meisenheimer complex (σ-complex). Initially, the hydroxide ion attacks the carbon atom bearing the chlorine substituent, forming a resonance-stabilized intermediate. Subsequent elimination of the chloride ion restores aromaticity, yielding p-nitrophenol. The efficiency of this transformation depends on several parameters, including alkali concentration, reaction temperature, pressure, solvent composition, and reaction time. Industrial processes often require temperatures above 150–170°C and high-pressure reactors to achieve

acceptable conversion rates and yields.From a pharmaceutical manufacturing perspective, process optimization is crucial to ensure high purity, minimal by-product formation, and cost-effectiveness'-Nitro chlorobenzene (1-chloro-4-nitrobenzene) is an aromatic compound with a benzene ring substituted by a chlorine atom (-Cl) at position 1 and a nitro group (-NO) at the para position (position 4). The nitro group is a strong electron-withdrawing group due to its -M (resonance) and -I (inductive) effects, which deplete electron density from the ring, particularly at the ortho and para positions relative to itself, making the carbon attached to chlorine more susceptible to nucleophilic attack. Alkaline hydrolysis of p-nitro chlorobenzene involves nucleophilic aromatic substitution (SNAr), where hydroxide ion (OH) from NaOH replaces the chlorine. Unlike chlorobenzene, which resists hydrolysis due to high C-Cl bond strength and poor leaving group activation The para-nitro group stabilizes the negatively charged Meisenheimer complex intermediate through resonance delocalization, lowering the activation energy and enabling reaction under milder conditions.

II. CHEMICAL AND REAGENT

Table.2 List of chemical and reagents used:

Identify	Abbreviation	Grade
Para nitro choloro benzene.	$C_6H_4ClNO_2$	99%
Sodium Hydroxide	NaOH	98%
Ethanol	C_2H_5OH	99%
Hydrochloric Acid	HCL	98%
Demineralized water	H_2O	-------

III. EXPERIMENTAL WORK

Phase-1: Preparation of Reaction Mixture:

1. In a 100 ml round bottom flask, add 10 gm of paranitrochlorobenzene and 20 ml of ethanol.
2. Ethanol or Methanol used as a solvent.
3. Add the NaOH solution (4 gm of NaOH in 20 ML water) to the flask.

$$NO_2\text{-}C_6H_4\text{-}Cl + CH_3CH_2OH \longrightarrow NO_2\text{-}C_6H_4\text{-}OCH_2CH_3 + NaCl + H_2O$$

Phase-2: Reflux the mixture:

1. Attach a reflux condenser to the flask and heat the mixture to reflux (around 80 to 90) for 3 hours.
2. Monitor the reaction progressing TLC(silica gel, hexane: ethyl acetate).

Fig:1 Assembly during addition

Fig: 2 After 1hr of heating (Reflux condenser)

Phase-3: Neutralize and Extract:

1. Cool the reaction mixture and neutralize with dilute HCL (PH 6 to 7).
2. Transfer the mixture to a separating funnel and extract the product with ethyl acetate.(2x20 ML)

Fig: 3. Dilute HCL

Fig: 4. Neutralize the product

Fig:5 Ethyl Acetate

Phase-4: Purify the product:

1. Wash the combined extract with water and dry it.

Fig:6 Separation of layer

Fig:7 Drying on water bath Safety

Precautions:

- ✓ Wear Personnel protective equipment (PPE): Gloves, goggles, lab coat etc.
- ✓ Handle NaOH and HCL with care, avoid skin contact.

Use proper ventilation and fallow local regulation for handling chemicals

IV. IDENTIFICATION OF FUNCTIONAL GROUP IN PARA-NITRO BENZENE:

Spectroscopic Identification (IR Spectroscopy):

IR spectroscopy is the most common and definitive method for identifying the nitro group by its characteristic absorption peaks. The nitro group gives rise to two strong and sharp N-O stretching vibration bands due to symmetric and asymmetric stretches.

- Asymmetric N-O stretch: Strong band typically found around 1550-1475 cm $^{-1}$.
- Symmetric N-O stretch: Strong band typically found around 1360-1290 cm $^{-1}$.

The presence of these two distinct, strong peaks in the specified range provides strong evidence for the nitro group in the para-nitrophenol product. Other techniques like Gas Chromatography-Mass Spectrometry (GC-MS) can also confirm the compound's identity and molecular weight (139.11 g/mol). The IR spectra of the synthesized compounds were recorded using a Shimadzu FT-IR 8400 spectrophotometer. The KBr pellet method was employed for sample preparation. The spectra were analyzed to identify various functional groups present in the compounds. Functional groups were assigned based on their characteristic absorption frequencies in the infrared region.

Fig: 8 Expected graph

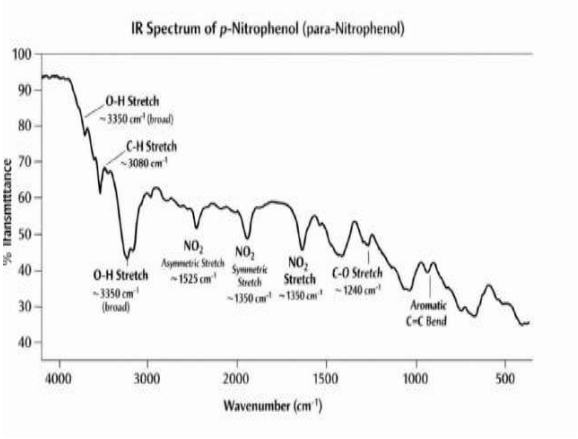
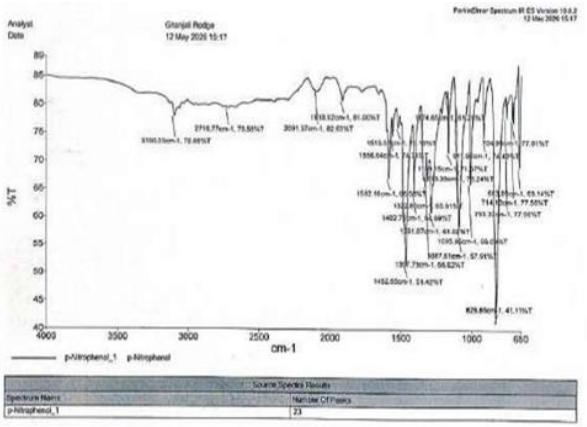


Fig: 9 IR of p-Nitrophenol



PerkinElmer Spectrum IR ES Version 10.6.2
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List of Peak Area/Height		
Peak Number	X (cm-1)	Y (%T)
1	3100.30	78.08
2	2719.77	79.58
3	2091.37	82.63
4	1910.92	81.00
5	1582.16	66.98
6	1556.64	74.74
7	1515.57	76.19
8	1462.65	51.42
9	1402.71	64.69
10	1322.80	55.61
11	1307.73	56.62
12	1281.07	61.03
13	1174.65	81.29
14	1159.15	71.57
15	1110.35	76.24
16	1087.61	57.91
17	1005.96	66.09
18	911.99	74.42
19	826.85	41.11
20	753.32	77.96
21	714.10	77.56
22	704.99	77.01
23	663.09	69.14

List of Peaks		
Peak Number	Wavelength (cm-1)	Functional groups
1.	3100.30	Aromatic or alkene C-H stretch
2.	2719.77	Aldehyde C-H stretch
3.	2091.37	Alkyne or Nitrile stretch
4.	1910.92	Anhydrous or Asymmetric stretch of cumulated double bond
5.	1582.16	Aromatic C=C stretch or N-H bending
6.	1556.64	Aromatic C=C stretch or Nitro group
7.	1515.57	Aromatic C=C stretch or N-O asymmetric
8.	1462.65	C-H bending (methyl/ methylene)
9.	1402.71	C-H bending or O-H bending
10.	1322.80	C-N stretch or C-O stretch
11.	1307.77	C-O stretch or C-H in-plane bend
12.	1281.07	C-O stretch (ester/ether)
13.	1174.65	C-O stretch (alcohol/ester)
14.	1159.15	C-O stretch or C-N stretch
15.	1110.35	C-O stretch(ether)
16.	1087.61	C-O stretch or Si-O stretch
17.	1005.96	C-O stretch or aromatic C-H bend
18.	911.99	C-H out-of-plane bend(alkene)
19.	826.85	Aromatic C-H out-Of-plane bend
20.	753.32	Aromatic C-H out-of-pane (ortho/meta substitution)

Chemical Test (Baker-Mulliken's Test) :

A common qualitative chemical test to detect the presence of a nitro group is the Baker-Mulliken's test, which relies on reducing the nitro group to an amine.

Required Reagent:

1. Test compound solution:

25 mg sample dissolved in 6 mL ethanol.

2. Ammonium chloride solution:

10%w/v NH4Cl solution

(5 gm ammonium chloride in 100 mL distilled water).

3. Zinc dust

Weigh 0.5 gm zinc dust.

4. Tollen' s reagent (freshly prepared)

1% silver nitrate solution

Dilute ammonia solution added until precipitate

dissolves.

Procedure:
Step 1.: Reduction of Nitro Group.
- Take a 2 mL test sample.
- Add 2mL of 10% ammonium chloride solution and 0.5 g of zinc dust.
- Heat gently for 2-3 minutes in a water bath.
- Cool and filter the mixture.

Step 2.: Detection with Tolen's Reagent:
- Take 2mL filtrate add 2 mL Fresh Tolen's Reagent.

Observation:
Formation of grey precipitate followed by a black silver mirror on the walls of the test tube indicates the presence of a nitro group.
Reaction:
Reduction of nitro compound:
R-NO →R-NHOH → R-NH
1. Reduction: The compound is treated with zinc dust and ammonium chloride solution and heated. This mixture reduces the nitro group (-NO) to a hydroxylamine group (-NHOH) or further to an amine group (-NH).
2. Detection: The resulting solution is filtered, and the filtrate is treated with Tollen's reagent (ammoniacal silver nitrate solution).
3. Observation: The formation of a grey precipitate that turns into a black silver mirror on the test tube walls indicates a positive result for the nitro group's presence.
p-Nitrophenol (4-Nitrophenol)

Physical Properties:
- Chemical formula: C H NO
- Molar mass: ~139.11 g/mol
- Appearance: Black to brownish crystalline solid
- Odour: Slight phenolic smell
- Melting point: 113–114 °C
- Boiling point: ~279 °C (with decomposition)
- Solubility:
  - Slightly soluble in cold water
  - More soluble in hot water
  - Freely soluble in alcohol, ether, benzene
  - Soluble in aqueous alkali (forms yellow phenoxide salt)

1. Physical Examination
- Colour: Black to brownish crystalline solid
- Odour: Phenolic smell
- Melting point: 113–114 °C
  - This is the most important confirmation
  - (o-nitrophenol melts at ~45 °C)

A high melting point strongly indicates para-nitro.

2. Ferric Chloride Test (Phenol Test) Principle:
Phenolic compound react with ferric chloride solution to produce coloured complex.

Reagent: Neutral Ferric chloride solution.(5%w/v)
Preparation of 5% ferric chloride solution:
Dissolve 1.25 g ferric chloride in 25 mL distilled water

Procedure:
1. Dissolve the 50 g sample in 2mL distilled water.
2. Add 2-3 drops of neutral ferric chloride solution.
3. Observe the colour formation. 4.

Observation:
Reddish brown colour observed.
Result:
Colour development confirms the phenolic group present

Soddium hydroxide test-
p-Nitrophenol dissolves in NaOH forming a yellow sodium salt. Upon acidification.
Free p-nitrophenol precipitates again.
Reagents: Sodium hydroxide solution(10%w/v) and dilute HCL.

Preparation:
10%NaOH solution: Dissolve 10 g NaOH in 100 mL water. Dilute HCL: Mix equal volume of concentrated HCL and water.

Procedure:
- ✓ Dissolve 50 g of sample in water.
- ✓ Add 10 NaOH solution.
- ✓ Observe the yellow colour.
- ✓ Add dilute HCL dropwise.

Observation:
Intense yellow colour with NaOH.
On acidification, yellow precipitate reappears.

V. RESULT:

p-nitrophenol is a most widely used compound in industrial intermediate. Its structure like a benzene ring with hydroxyl group and nitro group positioned para to each other. Its melting point 112 to 116.Its colour appears Black to brownish crystalline solid. Its having abundant use in dyes and other industries. By above methods and experiments I sure these is pure product that is p-nitrophenol performed above all methodology in lab scale and all results are true hence we stated that these is a pure form of p-nitrophenol. Mechanistically, the reaction proceeds via an addition–elimination pathway involving the formation of a Meisenheimer complex (σ-complex). Initially, the hydroxide ion attacks the carbon atom bearing the chlorine substituent, forming a resonance-stabilized intermediate

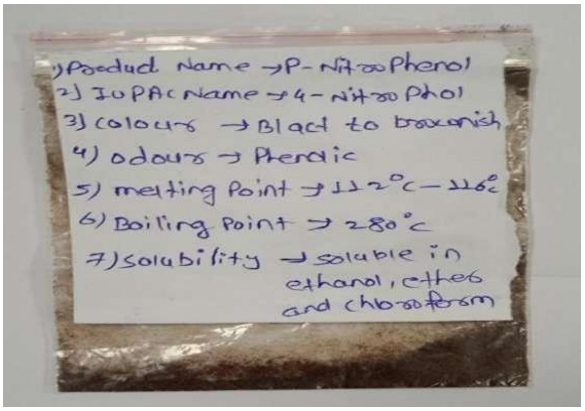

Fig: 21 p-Nitrophenol

VI. CONCLUSION:

The alkaline hydrolysis of p-nitrochlorobenzene represents a classical yet industrially significant example of nucleophilic aromatic substitution (SNAr) applied to the synthesis of p-nitrophenol, an essential intermediate in pharmaceutical, agrochemical, dye, and specialty chemical industries. The reaction exemplifies the fundamental principles of aromatic reactivity, particularly the activation of aryl halides by strong electron withdrawing groups.

The presence of the para-nitro substituent plays a decisive role by stabilizing the negatively charged Meisenheimer (σ) complex, thereby lowering the activation energy and enabling substitution under strongly alkaline conditions. Mechanistic and kinetic investigations consistently support an addition–elimination pathway, with nucleophilic addition as the rate-determining step and restoration of aromaticity providing the primary thermodynamic driving force. Industrial implementation of this transformation relies on elevated temperatures and pressures to achieve high conversion rates, while careful optimization of alkali concentration, solvent composition, and reaction time ensures improved yield and minimized by-product formation.

Downstream processing—including acidification, crystallization, and purification—is equally critical, particularly for pharmaceutical-grade material where stringent regulatory and quality standards apply. Despite its robustness and economic viability, the conventional process presents environmental and safety challenges, including high energy consumption and saline effluent generation.

VII. FUTURE SCOPE

Basic Reaction:

p-Nitrochlorobenzene + NaOH→ p-Nitrophenol + NaCl

Research-Oriented Future Scope of p-Nitrophenol (PNP)

1. Industrial Importance:

- Paracetamol (Acetaminophen) synthesis
- Dye intermediates
- Agrochemicals
- Fungicides and pesticides
- Rubber chemicals
- Photographic developers
- Pharmaceutical intermediates

The PNP market is strongly linked to pharmaceutical and agrochemical growth.

2. Green Chemistry and Sustainable Manufacturing:

✓ Current production generates:

- Chloride waste
- Phenolic wastewater
- High-temperature alkaline effluents
- Low-waste processes
- Recyclable catalysts
- Microwave-assisted synthesis
- Phase-transfer catalysis

- Continuous reactor technology

Recent industry reports show increasing investments in greener PNP production technologies due to environmental regulations.

3. Catalysis Research:

✓ PNP is widely used as a model pollutant in catalytic reduction studies.

✓ Many nano catalysts are tested using the reduction of p-nitrophenol to p-aminophenol because:

- Reaction is easy to monitor by UV-Visible spectroscopy
- Good benchmark for catalyst efficiency

4. Agrochemical and Dye Industry Expansion

✓ PNP derivatives are important in:

- Herbicides
- Insecticides
- Fungicides
- Sulfur dyes
- Pigments

✓ Asia-Pacific, especially India and China, dominates future market growth because of:

- Textile industry expansion
- Agricultural chemical demand
- Specialty chemical manufacturing

5. Research Scope Environmental

✓ PNP itself is considered a toxic pollutant, creating research demand in:

- Wastewater remediation
- Biodegradation
- Adsorption technologies
- Advanced oxidation processes
- Photocatalysis

✓ This makes PNP both:

1. An industrial product
2. A research model contaminant
3. Removal of nitrophenols from industrial wastewater
4. Bioremediation using microbes.

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