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Side Chain Bromination of 4 – Nitro Toluene by an Electro Chemical Method

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Abstract - *A simple method for the preparation of 4 – Nitro Benzyl Bromide from 4 – Nitro Toluene is reported. The electrolysis was carried out in a two compartment electrochemical cell fitted with graphite electrodes at Room Temperature. The maximum conversion of 4 – Nitro Toluene is above 95% and the selectivity is observed as above 95%. The effects of different electrode, solvent, and current density are studied and reported.*

Keywords: *Electrochemistry, Bromination, Two compartment divided electrochemical cell, Emulsion electrolysis, 4 – Nitro Benzyl Bromide.*

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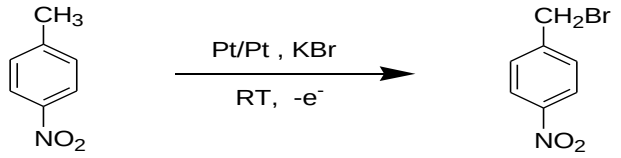
I. Introduction

Brominated aromatic compounds are valuable intermediates in organic synthesis and they have been use widely in industrially important products,[1] and biologically active substrates as antitumor, antifungal, antibacterial, antineoplastic and antiviral compounds[2]. The electrochemical method has received significant interest from both academia and industry, over regular chemical methods because it is an environmentally benign process for organic synthesis[3,4]. The need for isomerically pure bromoaromatics has led to investigations into more selective brominating agents, and several methods have been reported in the literature. Reactions making use of organic ammonium tribromides(OATB) such as tetrabutylammonium tribromide(TBATB),[5,6] 1,8-diazabicyclo[5,4,0]-tetrabutylammoniumtribromide[7] and pyridine hydrobromide perbromide, together with methods employing anodic brominations in organic solvents[8] and bromine triflouride [9] have been fully investigated. In particular, the electrochemical reactions serve as excellent method for the generation of reactive species under mild conditions[10] which do not require large quantities of toxics or corrosive reagents. In the homogeneous system, less selectivity is observed due to oxidation of the substrate on the surface of the electrode giving mixtures of nuclear (ortho and para isomers) and side-chain brominated products[11].

Electrochemical bromination has been investigated in different solvents [12–19] and most of the work deals with ring brominated products. We present a simple and regio selective electrochemical method for the α-bromination of 4 - Nitro Toluene to 4- Nitro benzyl bromide in very good yield by electrolysis method using an aqueous 80 percentage of KBr solution as the supporting electrolyte at room temperature [20] in a two compartment electrochemical cell. Some of the reagent reported for bromination offer low yield, very toxic, expensive, not readily available need to be freshly prepared, require drastic condition or prolonged reaction times and involve tedious work up.



4- Nitro Toluene 4- Nitro Benzylchloride

II. Experimental

2.1 Materials and analysis

In a 150 ml capacity of two compartment electrochemical cell, 31.6 ml of 2M H_2SO_4 , aqueous KBr (50 ml of 80% solution) and 7ml of Acetonitrilie containing 1.37 g of 4- nitro toluene (10 mmol) were taken as anolyte and the catholyte was the equal volume of the solution as mentioned above without depolariser. The graphite was used as electrodes (4.0 cm x 2.5 cm) and 2F of electricity was passed galvanostatically at a current density of 100 mA cm at the room temperature and the whole solution was stirred constantly throughout the electrolysis. In some cases more amount of current (4F, 6F) was passed to get maximum conversion. Saturated solution of Potassium Bromide containing catalytic amount of sulphuric acid (2M) and acetronitrile was used as electrolyte. The electrolysis was monitored by HPLC (Shimadzu, Japan, Model. no. CLASS. VP-10) using Shimpack ODS-18 column (125mm×4.5 mm) as stationary phase. The eluent consisted of methanol/water (70:30) at a flow rate of 1 ml/min. Samples were analysed at a wavelength of 254 nm with a UV detector (Shimadzu UV–vis detector) coupled to a printer.

2.2 Experimental Procedure

An amount of 1.37 gm of 4 - Nitro Toluene (10 mmol) was dissolved in 7 ml of Acetonitrile and the solution was transferred into the electrolytic cell. 50 ml aqueous KBr (50 ml of 80% solution) and 31.6ml of 2M H_2SO_4 was added over the above solution in a 150 ml capacity two compartment electrochemical cell. The organic phase alone was stirred with

magnetic stirrer at a rate of 40 rpm . After electrolysis the aqueous electrolyte solution was extracted twice with 25ml of diethyl either in order to remove the organic phase. The ether layer was then washed with water (2X10 ml) and dried over anhydrous sodium sulphate. Then the filtered organic extract was distilled to get the crude product. The material yield and current efficiency were calculated for the isolated products based was analyzed and characterized by ^{1}H NMR, ^{13}C NMR(400 MHz, BRUKER), FT-IR spectra(Perkin Elmer model paragon 500).

III. Product Analysis

The electrochemical reaction was monitored by Shimadzu HPLC with LC-8A column (250mm×4.6 mm) as stationary phase. The eluent consisted of acetonitrile and water (60:40) at a flow rate of 1 ml/min. Samples were analyzed at a wavelength of 254 nm with a UV detector coupled to a printer. Authentic samples were used to calculate the peak areas of the respective experimental products for yield calculation. HPLC analysis of the crude product indicates the presence of 4 - Nitro Benzyl bromide. The product was analyzed and characterized by ^{1}H NMR, ^{13}C NMR(400 MHz, BRUKER), FT-IR spectra(Perkin Elmer model paragon 500).

3.1 Chemicals and Solvents Used

The following chemicals and solvents were used for the present study.

1. 4 – Nitro toluene, (AR)
2. Sulphuric acid (LR)
3. Diethyl ether (LR)
4. Acetonitrile (LR)
5. n-Hexane (LR)
6. Anhydrous sodium sulphate (LR)
7. TLC Silica gel 60 F_{254} plates.

IV. Results And Discussion

Galvanostatic electrolysis was carried out for the synthesis of 4 – Nitro Benzyl bromide from 4 – Nitro Toluene**.** The experimental parameters such as current density, solvent, current passed (F/mol) and anode material for the bromination of 4 – Nitro Toluene to 4 - Nitro Benzyl bromide was studied and the results are summarized in Table. At the optimum electrolytic condition platinum electrodes were used at a current density of 5 A/dm^2 in acetonitrile solvent.

4.1 Effect of solvent

A total charge of 2F/mole was passed at different densities of 3, 5, and 7A/dm^2 using graphite electrodes and acetonitrile as a solvent. The yield of product 4 - Nitro Benzyl bromide is obtained of 76%, 84% and 63% with 3, 5, and 7 A/dm^2 respectively.

When the electrolysis was carried out using Dichloromethane as a solvent, at a current density of 3, 5 and 7 A/dm^2 the product obtained is with a yield of 65%, 79% and 57% respectively.

In the case of 1-Butanol as an another solvent, with a current density of 3, 5 and 7 A/dm^2 the product is obtained with an yield of 55%, 62% and 43% respectively. From the above set of experiments the maximum yield of product is obtained using acetonitrile as a solvent.

4.2 Effect of Electrode

The electrochemical Bromination of 4 – Nitro Toluene was carried out using different electrodes of platinum and graphite under various solvents of acetonitrile ,Dichloromethane and 1–Butanol as solvent the following results are observed.

When the electrolysis was carried out with platinum as electrodes and acetonitrile as solvent, the product 4 - Nitro Benzyl bromide was obtained with a yield of 82%, 99%, and 74% at a current densitiy of 3, 5 and 7 A/dm^2 respectively. In the case of Dichloromethane as a solvent, the yield obtained was 78%, 86%, and 66% at the current densities of 3, 5 and 7 A/dm^2 respectively.

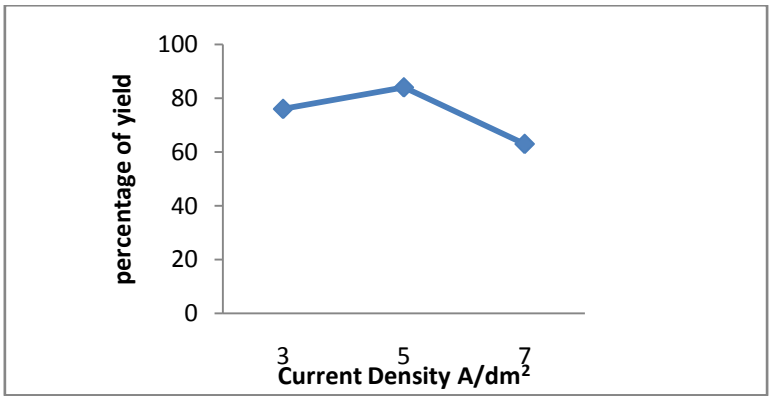
Similarly when 1-Butanol was used as solvent, the yield obtained was 51%, 67%, and 45% at the current densities of 3, 5 and 7 A/dm^2 respectively. From the above results it is concluded that usage of platinum electrodes gives a maximum yield of 99% product.

Electrochemical Bromination of 4 – Nitro Toluene to 4 - Nitro Benzyl bromide
Effect of current density using Graphite electrode in Acetonitrile

Electrolytic cell : Two – compartment electrochemical cell
Electrolyte : 31.6ml of 2M H_2SO_4 + 7ml of Acetonitrile
Electrode : Graphite (Cathode) & Graphite (Anode) (Area = 4.0 cm x 2.5 cm)
Temperature : Room Temperature
Cell Voltage : 2.0- 5.0 V

Table 1

No.	Weight of 4 – Nitro Toluene taken for Bromination(g)	Current density (A/dm^2)	Current passed (F/mole)	Weight of the product obtained (g)	Material yield %	Current efficiency%
1	1.37	3.0	2.0	1.79	76	76
2	1.37	5.0	4.0	1.98	84	42
3	1.37	7.0	6.0	1.48	63	21

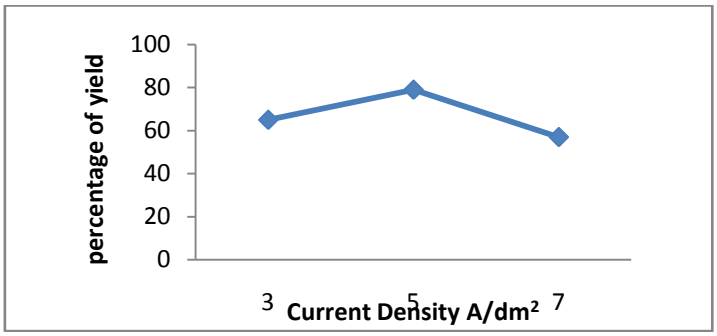


Effect of current density using Graphite electrode in Dichloro Methane

Electrolytic cell : Two – compartment electrochemical cell
Electrolyte : 31.6 ml of 2M H_2SO_4 + 7ml of Dichloromethane
Electrode : Graphite (Cathode) & Graphite (Anode) (Area = 4.0 cm x 2.5 cm)
Temperature : Room Temperature
Cell Voltage : 2.0- 5.0 V

Table 2

No.	Weight of 4 – Nitro Toluene taken for Bromination (g)	Current density (A/dm^2)	Current passed (F/mole)	Weight of the product obtained (g)	Product yield %	Current efficiency%
1	1.37	3.0	2.0	1.53	65	65
2	1.37	5.0	4.0	1.86	79	40
3	1.37	7.0	6.0	1.34	57	29

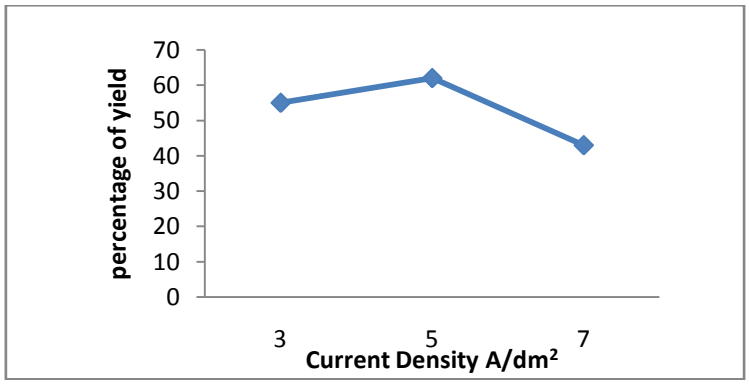


Effect of current density using Graphite electrode in 1- Butanol

Electrolytic cell : Two – compartment electrochemical cell
Electrolyte : 31.6 ml of 2M H_2SO_4 + 7ml of 1- Butanol
Electrode : Graphite (Cathode) & Graphite (Anode) (Area = 4.0 cm x 2.5 cm)
Temperature : Room Temperature.
Cell Voltage : 2.0- 5.0 V

Table 3

No.	Weight of 4 – Nitro Toluene taken for Bromination (g)	Current density (A/dm^2)	Current passed (F/mole)	Weight of the product obtained (g)	Product yield %	Current efficiency%
1	1.37	3.0	2.0	1.30	55	55
2	1.37	5.0	4.0	1.46	62	31
3	1.37	7.0	6.0	1.01	43	14

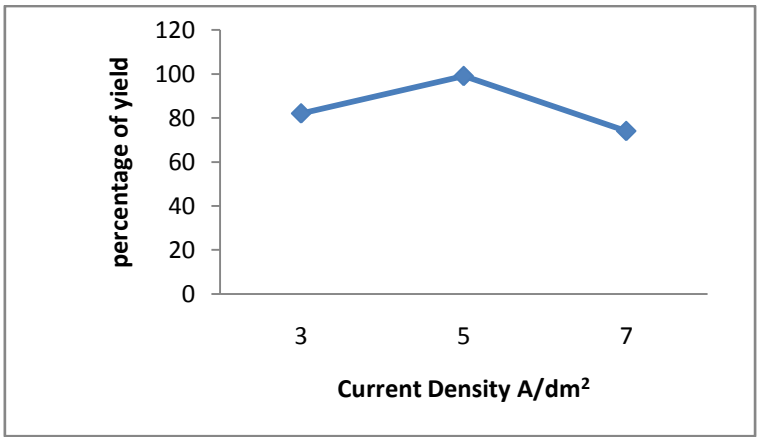


Effect of current density using Platinum electrode in Acetonitrile

Electrolytic cell : Two – compartment electrochemical cell
Electrolyte : 31.6 ml of 2M H_2SO_4 + 7ml of acetonitrile
Electrode : Platinum (Cathode) & Platinum (Anode) (Area = 4.0 cm x 2.5 cm)
Temperature : Room Temperature
Cell Voltage : 2.0- 5.0 V

Table 4

No.	Weight of 4 – Nitro Toluene taken for Bromination (g)	Current density (A/dm^2)	Current passed (F/mole)	Weight of the product obtained (g)	Product yield %	Current efficiency%
1	1.37	3.0	2.0	1.93	82	82
2	1.37	5.0	4.0	2.33	99	49
3	1.37	7.0	6.0	1.74	74	25

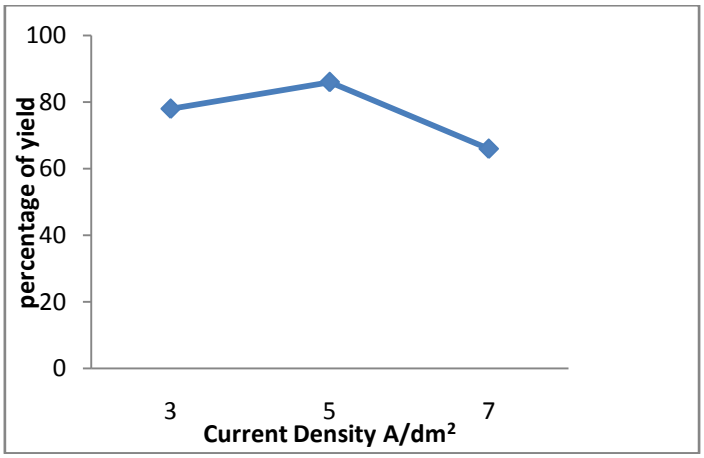


Effect of current density using Platinum electrode in Dichloro Methane

Electrolytic cell : Two – compartment electrochemical cell
Electrolyte : 31.6 ml of 2M H_2SO_4 + 7ml of Dichloromethane
Electrode : Platinum (Cathode) & Platinum (Anode) (Area = 4.0 cm x 2.5 cm)
Temperature : Room Temperature
Cell Voltage : 2.0- 5.0 V

TABLE 5

No.	Weight of 4 – Nitro Toluene taken for Bromination (g)	Current density (A/dm^2)	Current passed (F/mole)	Weight of the product obtained (g)	Product yield %	Current efficiency%
1	1.37	3.0	2.0	1.84	78	78
2	1.37	5.0	4.0	2.02	86	43
3	1.37	7.0	6.0	1.55	66	22

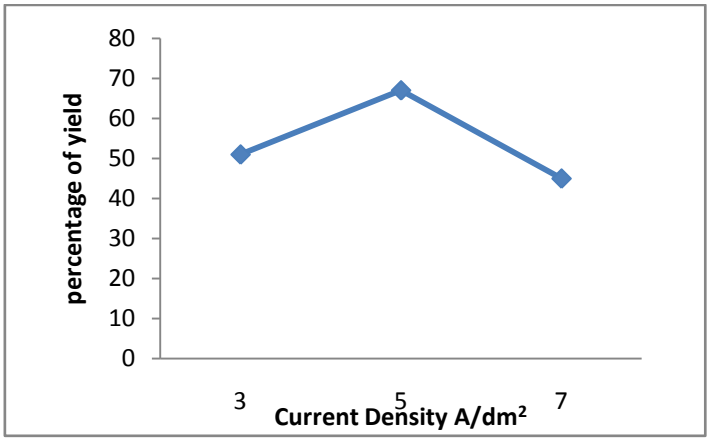


Effect of current density using Platinum electrode in 1- Butanol

Electrolytic cell : Two – compartment electrochemical cell
Electrolyte : 31.6 ml of 2M H_2SO_4 + 7ml of 1- Butanol
Electrode : Platinum (Cathode) & Platinum (Anode) (Area = 4.0 cm x 2.5 cm)
Temperature : Room Temperature
Cell Voltage : 2.0- 5.0 V

TABLE 6

No.	Weight of 4 – Nitro Toluene taken for Bromination(g)	Current density (A/dm^2)	Current passed (F/mole)	Weight of the product obtained (g)	Material yield %	Current efficiency %
1	1.37	3.0	2.0	1.20	51	51
2	1.37	5.0	4.0	1.58	67	34
3	1.50	7.0	6.0	1.06	45	15



* Experiment carried out in an Two compartment electrochemical cell

4.3 Effect of Current Passed (F / mole)

The electrochemical bromination of 4 – Nitro Toluene is found to be quite facile, the theoretically required current of 2F/mole is quite sufficient for the conversion of 4 – Nitro Toluene with maximum yield of 4 - Nitro Benzyl bromide. When more than theoretical amount of current, 4F/ mole and 6F/mole were passed for electrolysis, low yield was obtained due to competitive O_2 evolution.

Hence the optimum conditions for the direct anodic oxidation of 4 – Nitro Toluene to 4 - Nitro Benzyl bromide is found to be at 5.0 A/dm^2 current density with platinum electrodes in acetonitrile solvent with theoretical amount of current.

V. Product Analysis

5.1 High Performance Liquid Chromatography (HPLC)

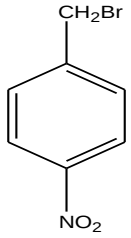
Typical HPLC graphs of standard and experimental samples of 4 - Nitro Benzyl bromide were analysed. The retention time of electro chemically synthesized 4 - Nitro Benzyl bromide is 4.4 min. The percentage purity of 4 - Nitro Benzyl bromide in the product mixture was found out by HPLC as above 99% and the yield of 4 - Nitro Benzyl bromide was calculated based on the peak area.

5.2 FTIR Spectroscopy

The FT-IR Spectrum of electro chemically prepared 4 – Nitro Toluene synthesized was analysed. The characteristic alkane C-H stretching absorption is found at 2861 cm^{-1}, aromatic C-H stretching absorption is found at 3081 cm^{-1}, C-Br absorption of alkyl halide is observed at 598$cm^{-1}$and and aromatic N-O stretching absorption is found at1539 cm^{-1}. These values coincide well with the literature value and hence the 4 - Nitro Benzyl bromide formation is confirmed.

5.3 Proton NMR Spectrum

Proton NMR Spectrum of 4 - Nitro Benzyl bromide prepared in our present work was analysed. The chemical shift values δ observed in the product spectrum is comparable with the literature value.

Compound Name	Chemical Shift δ values			
	^{1}H		^{13}C	
	Observed	Reported	Observed	Reported
	4.52	4.56	31.0	38.4
	7.26	7.32	124.04	123.9
	7.55	7.32	129.96	130.1
	8.19	8.07	144.84	144.1
	8.20	8.07	147.64	148.6
4 - Nitro Benzyl bromide				

The δ values of aromatic protons are observed at 7.26 – 8.20 and methyl protons at 4.52 in the product. The δ values of aromatic carbon are observed at 124.04 & 147.64, and methyl protons at 31.0 are observed in the product which is comparable with the literature value.

VI. Conclusion

The present investigation has established a method for the direct anodic bromination of 4 – Nitro Toluene using platinum electrode in an Two compartment electrochemical cell with aqueous sulphuric acid medium containing a solvent of acetonitrile to get 4 - Nitro Benzyl bromide as product in excellent yield (99%). The optimum current density for the bromination is at 5.0 A/dm^2. Platinum electrodes gave maximum yield than the graphite.

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