

REVIEW PAPER

Electrochemical bromination and oxidation of alkyl aromatic compounds by two-phase electrolysis

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Abstract—A simple, regioselective, environmentally clean and economical method for the preparation of side chain/ring brominated aromatic compounds is reported in 70-98% yield by an electrochemical method using two phase electrolysis technique. Electrochemical reactions were carried out using aqueous 25-50 wt% sodium bromide containing catalytic amount (5 wt%) of hydrobromic acid as an aqueous phase and chloroform containing alkyl aromatic compounds as an organic phase, at a temperature of 0-30 °C in an undivided cell. The same two-phase electrolytic system can be used for the oxidation of benzylic alcohols to the corresponding benzaldehydes in 80-94% yield without over oxidation to carboxylic acids. The advantage of this very mild procedure is a room temperature reaction used with an undivided cell. Excellent conversions are observed. After completion of alcohol oxidation the electrolyte can be reused for a number of times, demonstrating “spent reagent” free electro organic reaction as an attractive one. In the case of side chain/ring bromination of alkyl aromatic compounds, the electrolyte can be reused after making up the concentration of the electrolyte with 47 wt% HBr solution. In some cases homogeneous electrolysis is applied, where the two-phase electrolysis did not work. Styrene epoxidation and α -bromination of ketones underwent homogeneous electrolysis at room temperature without any catalyst. The reaction was performed in CH_3CN -water (3 : 2) using equimolar amount of NaBr as an electrolyte to get 68% of styrene epoxide. Use of an ionic liquid 1-butyl 3-methyl imidazolium bromide (Bmim) Br, instead of NaBr improved the yield and current efficiency of styrene epoxide to 86%.

Keywords: Two-phase Electrolysis, Oxidation, Chlorination, Bromination, Aromatic Compounds, Current Density, Electrolyte, Selectivity

INTRODUCTION

Electrochemistry is a clean and convenient method for the generation on a preparative scale of many reactive intermediates. This forms the basis of organic electrosynthesis and conditions have been devised for selective and useful chemical conversions. The *in-situ* electro generation and regeneration of redox reagents in non stoichiometric amounts and the related redox catalysis is proving to be an attractive, indirect, electro synthetic approach. And mechanistic insights into useful preparative reactions are now at an advanced stage. Among the halogenation processes, bromination is considered important because chlorination is generally less selective than bromination. Fluorination is not only even less selective than chlorination but also highly exothermic, and care must be taken to prevent violent reaction. The bromine substituted organic compound gives increase of product yield as the bromide is a better leaving group than other halides like fluoride, chloride. Bromination is involved in the synthesis of many important drug molecules. Benzylic bromides are used to prepare a variety of organic intermediates (Fig. 1). Chemical bromination was carried out using different types of brominating agents which are costly and difficult to handle. This chapter outlines the use of Br^-/Br_2 mediator for the side chain/ring bromination, oxidation of alcohols, epoxidation of alkenes and α -bromination of ketones in an operationally simple and environmentally

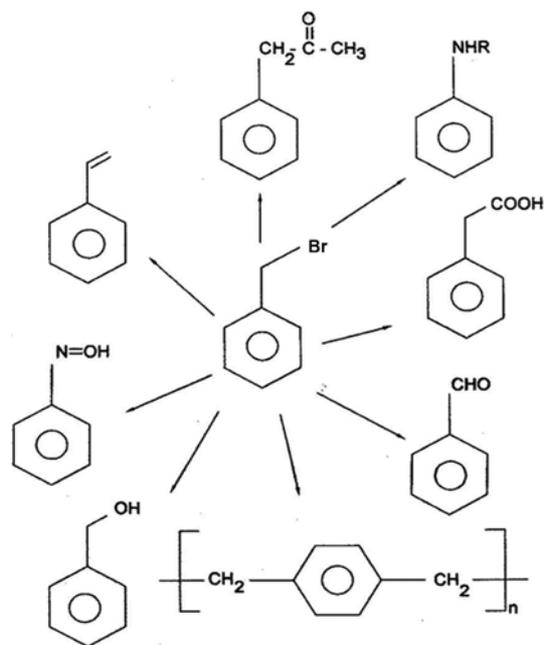


Fig. 1. Functionalization of benzylic bromides into other useful products.

friendly electrochemical method at room temperature.

1. Chemical Bromination

1-1. Use of Molecular Bromine

The direct bromination of aromatic compounds using bromine

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generates toxic and corrosive HBr along with product. The product may also include mono and polybrominated compounds that require the separation of unwanted product. Molecular bromine itself is very difficult to handle as it is a highly dense (density=3.11) and corrosive liquid. Consequently, various brominating agents have been developed.

1-2. In-situ Generation of Bromine

Alkali metal bromide or HBr is taken along with an oxidizing agent such as KMnO_4 , sodium bromate or hydrogen peroxide to oxidize the metal bromide to generate bromine molecule. During the course of reaction, one out of two bromine atoms in a bromine molecule becomes part of the product, the other atom released as corrosive HBr. This has to be neutralized before discharge. Hence this reaction is environmental unfriendly. This reaction gives low atomic yield, as part of the bromine formed the unwanted hydrobromic acid. The methyl group of alkyl benzenes and alkanes are brominated in excellent yield using NaIO_4 in 10% H_2SO_4 and LiBr as reagents in methanolic medium at 110 °C [1]. In this case, though, the yield is satisfactory the chemicals involved in this reaction are very costly.

1-3. *N*-bromosuccinimide

N-bromosuccinimide is one of the reagents often used for introduction of bromine into organic molecules. Because of ease of handling and availability, *N*-bromosuccinimide is generally used for the bromination of aromatic compounds instead of corrosive liquid bromine. However, the disadvantages of this reagent include high temperature reaction, and after completion of reaction, the side product succinimide formed has to be either disposed off or recycled [2]. In some cases unsatisfactory yields are also observed [3].

1-4. Combined Bromide - H_2O_2

Recently, combined bromide - H_2O_2 was used for benzylic bromination of aromatic compounds. Though this brominating system works at room temperature, it uses three equivalents of hydrogen peroxide and three equivalents of acid in presence of UV irradiation. After completion of reaction excess H_2O_2 has to be removed by washing with 40 wt% NaHSO_3 solution. The product yield falls at a range of 40-80% with by-product formation [4].

2. Electrochemical Method

The electrochemical method has received significant research interest from both academia and industry, over regular chemical methods because it is an environmentally benign process for organic synthesis [5,6]. In particular, the electrochemical reactions serve as excellent method for the generation of reactive species under mild conditions [7] which do not require large quantities of noxious or corrosive reagents. It has been widely used in many areas such as synthesis of pharmaceutical drugs, amino acids, dye stuff, perfumery and organic reagents, and has received much attention in recent years.

The electrochemical method is very simple and does not require complex and expensive equipment. The other commercially available brominating agents are irritants and sensitive. Their storage and handling requires serious caution. The main advantage of the present electrochemical method is that these reactive species can be formed *in-situ*, avoiding the above mentioned problems. The electrochemical reaction is an excellent dosage control reaction (by simple current control), which is not easy in many classical methods when a solid should be gradually introduced into the reaction

mixture—this procedure might be recommended as a superior one.

In general, electrochemistry waned because i) electrodes were easily poisoned or not catalytic, separators were frail (porous pots/membranes), and materials of construction were not robust enough. In two-phase electrolysis, an ideal electrolytic condition is formed and electrode poisoning is negligible as the electrolyte and electrodes are present in aqueous phase and organic substrate in organic phase. Absence of the separator makes the cell set-up simple and ultimately we can select the material of construction for cell as per our choice. Electrohalogenation is one of the general classes of electro organic process, which has been studied for several years. Among these electrochemical halogenation processes, electrobromination is considered an important one.

HALOGENATION AND OXIDATION BY TWO PHASE ELECTROLYSIS

1. Two-phase Electrolysis

Two phase electrolysis has distinct advantages over conventional homogeneous electrolysis [8,9]. With electrochemical technology it is possible to carry out desired reaction via two-phase electrolytic reaction resulting in high yields and selectivity. In the case of electrochemical halogenation in homogeneous systems less selectivity is observed due to oxidation of the substrate on the surface of the electrode giving a mixture of nuclear (ortho/para isomers) and side chain halogenated products [10]. In a two-phase electrolysis system the reactive species formed by the electrolytic oxidation of a halide ion in the aqueous phase can be taken continuously into the organic phase and then reacted with the substrate to give the regioselective products in very high yield [11]. The electrolysis takes place in the aqueous phase, where the conductivity is high and the cell voltage is consequently low. This leads to low power costs and favorable economics. Separation of product is also easy by simple phase separation, which further improves process economics.

2. Side Chain Chlorination

Substitution of C-H bonds in alkyl aromatic compounds by radical halogenation is one of the most important reactions for functionalization of alkyl aromatics. Krishnan et al. attempted electrochemical chlorination of toluene in 10 wt% HCl solution as electrolyte in a divided cell containing porous pot as a diaphragm and they obtained ring chlorinated product *o*-, *p*-chlorotoluenes in a mole ratio of 66 : 33, respectively [12]. Similarly, chlorination of *p*-xylene, afforded a mixture of 2,5-dichloro *p*-xylene (ring chlorinated products) in 79% yield [13]. The electrodes used were ruthenium oxide coated over titanium metal as anode and stainless steel as cathode. In this case *p*-xylene was taken as a neat solution, and while stirring it formed droplets in aqueous 10 wt% HCl solution. In another experimental condition (two-phase electrolysis) 81% of benzyl chloride

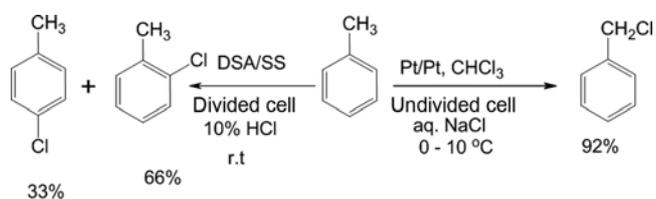


Fig. 2. Two-phase electrolysis by different electrolysis conditions.

was obtained, i.e., the side chain halogenated product, rather than ring halogenated product [14] as shown in Fig. 2. In this case, 30 wt% NaCl solution containing 5 wt% sulphuric acid was used as electrolyte. Among the two phases the aqueous NaCl solution was present as top layer and chloroform containing toluene as bottom layer. While electrolysis proceeded, the two layers were maintained by simply stirring the bottom chloroform layer alone and the electrodes were placed in the aqueous phase.

3. Electrochemical Bromination by Two-phase Electrolysis

Electrochemical bromination was investigated in different solvents and most of the work deals with ring brominated products [15]. Side chain bromination was not much explored. A simple and regioselective side chain bromination of toluene and substituted toluenes was reported in 80-94% yield by two phase electrolysis in an undivided cell as shown in Fig. 3. Bromination occurs at the α -position of the side chain without formation of any polybrominated product. A number of alkyl aromatics and substituted alkyl aromatic compounds were subjected to side-chain bromination by two-phase electrolysis using an aqueous 25-50 wt% NaBr solution as the supporting electrolyte and as a bromine source. The product distribu-

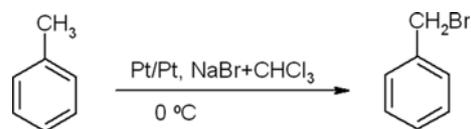


Fig. 3. Electrochemical bromination of toluene by two-phase electrolysis.

tions from the reactions are listed in Table 1. The reaction proceeds under mild conditions and in an efficient way in the presence of a less hazardous brominating agent than Br_2 , *N*-bromosuccinimide and pyridinium tribromide. In contrast to the exclusive benzylic bromination of alkyl benzenes, alkyl naphthalene was brominated mainly on the aromatic ring. 2-methylnaphthalene, for example, gave 1-bromo-2-methylnaphthalene as the only isolated brominated product.

In the electrolysis of NaBr solution, the two electrode reactions are the generation of Br_2 at the anode, the formation of hydroxide ion and H_2 at the cathode. If the products of both of these cell reactions are allowed to mix, then the dissolved bromine undergoes further reactions to form hypobromous acid, which depends on the elec-

Table 1. Side chain bromination of alkyl aromatic compounds by two-phase electrolysis

Entry	Reactant	Product	Charge passed (F/mole)	Yield (%)	Current efficiency (%)
1			4.3	95	44
2			4.5	85	37
3			4.0	57	35
4			3.0	50	33
			6.0	48	32
			9.0	90	41
5			6.0	80	26

trolyte concentration, pH and temperature [16].

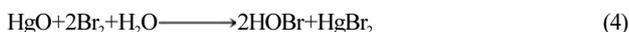
The oxyacids of bromine are strong oxidants, but they are unstable at ordinary temperature and stable only in solution [17]. There are some evidences about the formation of hypobromous acid (HOBr) [16]. Side chain bromination of toluene follows a free radical mechanism and the brominating species is dibromine monoxide (Br_2O), which is formed as shown in Eqs. (1) and (2). In the first step, electrochemically generated bromine is combined with water giving hypobromous acid and hydrogen bromide. In presence of HBr, one molecule of water is removed from two molecules of hypobromous acid as a hydronium ion resulting in the formation of Br_2O as the brominating species, which is extracted by the organic phase where the selective bromination occurs.



As the reactive species Br_2O is unstable, it is cleaved homolytically into Br^\bullet and $^\bullet\text{OBr}$. The more reactive $^\bullet\text{OBr}$ abstracts benzylic hydrogen to form HOBr. Subsequently, the bromine radical attacks the benzyl radical and benzyl bromide is formed as the product. Although dibromine monoxide is exceptionally reactive in the bromination of non-activated and deactivated alkyl aromatic compounds, an activated compound like 4-methoxytoluene gave higher percentage of nuclear brominated product rather than side chain brominated product. This is due to ring bromination of activated aromatics by the attack of Br^\bullet , which is generated from HOBr as shown in Eq. (3).



If HOBr alone was present as the brominating agent in the absence of HBr, then the product obtained from toluene was a mixture of side chain brominated (54%) and nuclear brominated (47%) products (a mixture of 22% *ortho*-bromo toluene and 25% *para*-bromo toluene). The formation of the products was confirmed by chemically generating HOBr as in Eq. (4), followed by the reaction with toluene afforded the same product.



Furthermore, dibromine monoxide was prepared chemically in CCl_4 as shown in Eq. (5) and the toluene was brominated at 0-5 °C. The product obtained was benzyl bromide as a sole product.

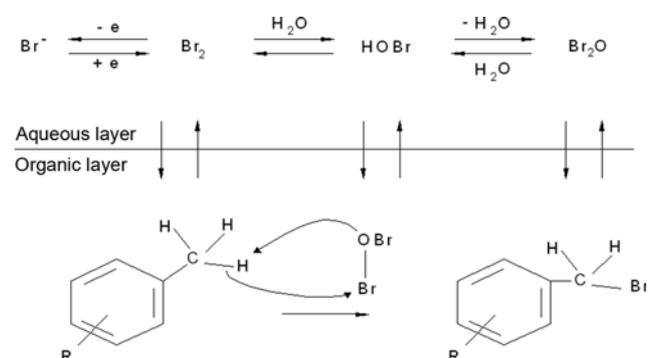


Fig. 4. Two-phase electrolysis mechanism.

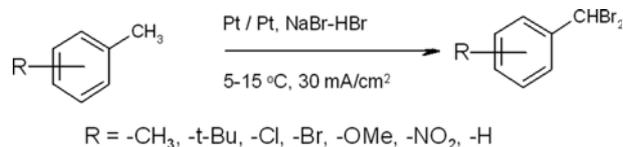


Fig. 5. Electrochemical method for the preparation of dibromomethyl alkyl aromatic compounds.

The electrochemical method for side chain bromination of toluene to yield benzyl bromide by two-phase electrolysis constitutes a novel and an efficient alternative procedure. Reactions were carried out under mild conditions using very simple electrochemical apparatus. This method has several advantages, such as the absence of secondary products, low cost, selective bromination, high conversion and yields [18].

4. Preparation of Dibromomethyl, Bis(bromomethyl), Bis(dibromomethyl) Arenes

In a similar fashion as mentioned in section 2.3, dibromomethyl, bis(bromomethyl) and bis(dibromomethyl) arenes can be prepared from methyl arenes by two-phase electrolysis at 10-15 °C in a single compartment cell as shown in Fig. 5. Electrochemical bromination of alkyl aromatic compounds by two-phase electrolysis yielded the corresponding α,α -dibrominated product. The reaction was carried out using an aqueous sodium bromide (25-50 wt%) containing catalytic amount of HBr (5 wt%) as aqueous phase and chloroform containing alkyl aromatic compound as organic phase with platinum plates as electrodes at 10-15 °C. Two-phase electrolysis resulted in high yields (70-90%) of dibromomethyl, bis(bromomethyl) and bis(dibromomethyl) arenes. This method constitutes a convenient and alternate method with a yield of 60-90% even though the current efficiency is poor (25-50%) [19].

A number of alkyl aromatic and substituted alkyl aromatic compounds were conveniently subjected to dibromination at side chain. The product distributions from the reactions are listed in Table 2. The reaction proceeded under mild conditions in the presence of a less hazardous brominating agent than Br_2 , *N*-bromosuccinimide and Pyridinium tribromide and at lower temperature than the conventional methods. Although dibromine monoxide is exceptionally reactive in the side chain bromination of non-activated (entry 1) and deactivated alkyl aromatic arenes (entry 2,4) an activated compound 3,5-dimethyl phenol gave 90% nuclear brominated compound (2,4,6-tribromo-3,5-dimethyl phenol) as a sole product.

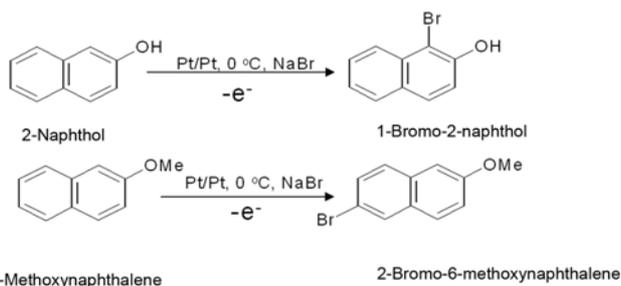
However, if phenolic group was protected as methyl ether, the product obtained was ring brominated methyl arene at the first stage. On further bromination, nuclear brominated α -bromomethyl arene was obtained as a product instead of α,α -dibromomethyl arene. Due to high deactivating nature of nitro group in the *p*-nitro toluene, current efficiency for the formation of *p*-nitro benzyl bromide was comparatively less.

5. Ring Bromination of Aromatic Compounds

Ring brominated aromatic compounds are valuable intermediates in organic synthesis and they have been used widely as industrially important products [20], and biologically active substrates as antitumor, antifungal, antibacterial, and antiviral compounds [21]. They can also undergo C-C bond formation via transmetalation reactions such as Heck, Stille, and Suzuki reactions. Most of the reagents reported for bromination are often hazardous, very toxic, expensive,

Table 2. Di bromination of alkyl aromatic compounds by two-phase electrolysis

Entry	Reactant	Product ^a	Charge passed (F/mole)	Yield (%)	Current efficiency (%)
1			20	72	20
2			17	72	24
3			20	80	20
4			19	85	21
5			12	90	30
6			24	76	15

**Fig. 6. Nuclear bromination of aromatic compounds.**

not readily available, need to be freshly prepared, require drastic conditions or prolonged reaction times and involve tedious work up. Thus a milder, selective, non-hazardous and inexpensive reagent is still in demand. A mild and efficient method was reported for the nuclear bromination of activated aromatic compounds by two-phase electrolysis using anodic oxidation of bromide ions as the bromine source (Fig. 6).

The two-phase electrochemical bromination reaction was conducted in an undivided cell. The electrolyte containing 25-50 wt% of aqueous NaBr with 5 wt% HBr acting as the upper phase was used as the bromine source. The substrate, dissolved in chloroform, acted as the lower phase. In this constant current electrolysis, two platinum sheets (10 cm²) were used as the anode and the cathode, respectively. The electrolysis was conducted galvanostatically at a

current density of 30 mA/cm². A wide range of aromatic compounds possessing electron-donating groups such as methoxy, hydroxy or amino groups have been carried out by two-phase electrolysis. The electrochemical method results in high yields (70-98%) of mono-bromo compounds and usually with high regioselectivity (>95%) for the *para* position as indicated in Table 3. After completion of electrolysis, the lower organic phase was separated, and worked up to get ring brominated product. It is believed that an electrochemically generated polarized bromine molecule combines with water giving one molecule of hypobromous acid and one molecule of HBr. The hypobromous acid is unstable due to its pronounced ionic nature, and thus in the presence of hydrobromic acid, one molecule of water is removed from hypobromous acid giving Br⁺, which attacks the electron rich aromatic ring and the product obtained under these conditions is exclusively the ring-brominated product (*p*-isomer) and no trace of other regio isomers or dibromo products was detected.

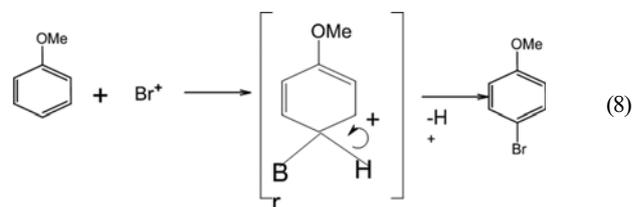


Table 3. Nuclear bromination of aromatic compounds by two-phase electrolysis

Entry	Substrate	Product ^a	Charge passed (F/mol)	Yield (%)	Current efficiency (%)
1			2.3	92	87
2			4.0	98	50
3			1.9	86	85
4			2.2	95	90
5			2.0	94	94

Although the protected aromatic amine and phenol were *para* brominated in excellent yields, aniline and phenol-like aromatic substrates furnished a mixture of *ortho*- and *para*-bromo isomers (*o*-cresol gave 30% *ortho*- and 30% *p*-bromo isomers along with 40% of starting material) after passing the theoretical charge, while highly deactivated compounds such as nitrobenzene and chlorobenzene did not undergo bromination even on prolonged reaction time. In the case of bromination of 2-naphthol, 1-bromo 2-naphthol was the sole product when the -OH group was unprotected. When protected with a methyl group, the *para*-brominated product formed exclusively (entry-2) in excellent yield.

It is notable that following electrolysis, the brominated aromatic compound was isolated simply by separation of the organic layer with the remaining aqueous solution containing bromide salt for further use as electrolyte in anodic bromination. The amount of bromide ion depleted in the anolyte (based on the amount of ring bromi-

nated product obtained) can be made up by adding 46 wt% HBr solution. Thus, completely 'spent reagent' free electroorganic synthesis could be demonstrated using two-phase electrolysis (Fig. 7).

6. Oxidation of Benzylic Alcohols by Two Phase Electrolysis

The oxidation of alcohols is widely considered as one of the most important and fundamental transformations in both laboratory and industrial synthetic chemistry, as the corresponding carbonyl compounds used as an important and versatile intermediates for the synthesis of fine chemicals [22,23]. Numerous oxidizing reagents such as chromium (VI) oxide, potassium permanganate, ruthenium tetra oxide and potassium dichromate have been employed to accomplish this transformation. Most of these reagents are, however, required in stoichiometric quantities, resulting in the formation of a vast amount of environmental wastes [24]. The selective oxidation of primary alcohols to aldehydes is crucial for the synthesis of fine chemicals such as fragrances or food additives [25]. Earlier, Tomov and Janson oxidized aromatic alcohols by electrogenerated hypobromite in an emulsion condition using a quaternary ammonium salt as a phase transfer agent [26]. As the electrolysis was conducted in emulsion phase, the voltage was high due to poor electrical conductivity of organic solvent and ultimately the process was not economic.

Recently, nitroxyl radicals, N-oxyl compound mediated electro oxidation of alcohols have also been reported in two phase electrolysis [27]. In these processes costly catalyst is used along with mediators. Electrochemical oxidation of benzylic alcohols to the corresponding benzaldehyde is achieved in excellent yields using *in-situ* generated hypobromous acid via a two-phase electrolysis in an undivided cell. This constitutes a novel and an efficient alternative procedure to traditional oxidation. Hypobromous acid is an inexpensive reagent and can be generated *in situ* by electrochemical oxidation of bromide ions in the presence of HBr. The two-phase electrolysis system consists of a 25 wt% NaBr solution containing catalytic amount of HBr (5 wt%) as the aqueous phase and chloroform containing aromatic alcohol as the organic phase. Using this sys-

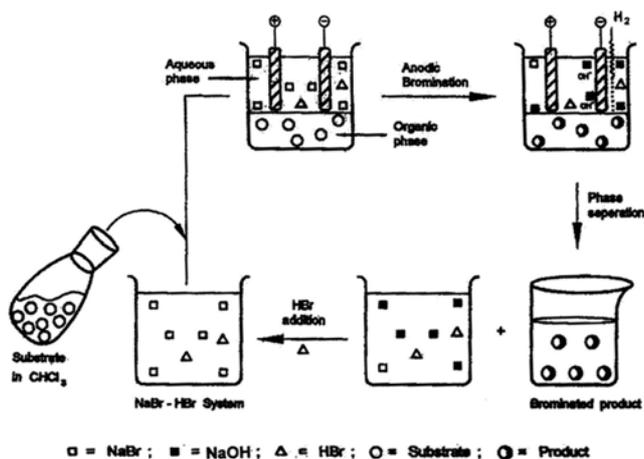


Fig. 7. Schematic diagram of spent reagent free electrochemical bromination of aromatic compounds.

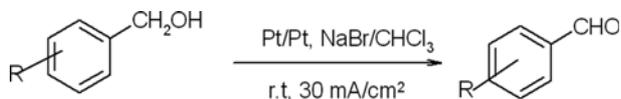


Fig. 8. Electrochemical oxidation of alcohols by two-phase electrolysis.

tem, benzylic and substituted benzylic alcohols are oxidized to the corresponding aldehydes at room temperature in a single compartment cell in high yield (Fig. 8).

The yields of the products are listed in Table 4. The products were confirmed by analyzing NMR, infrared, and mass spectroscopic data.

It is observed that a smooth oxidation of benzylic alcohol and substituted benzylic alcohols had electron donating groups such as $-CH_3$, $-OCH_3$, *t*-butyl with 2-4 F/mol of current, while the alcohols substituted with electron withdrawing groups required 4-6 F/mol. The highly deactivating $-NO_2$ substituted benzylic alcohol did not react at all. Primary aliphatic alcohols are allowed to react under these conditions, but the corresponding aldehydes were obtained in low yields. The secondary alcohol, 1-phenylethanol, was less reactive, affording the corresponding ketone in only 11% yield. This study reveals that this method can be applied for the selective oxidation of benzylic alcohols in the presence of secondary hydroxyl groups.

A possible mechanism for the oxidation, based on a literature report, is outlined in Eqs. (9)-(11) [28]. As the electrolysis proceeds, the bromide ion is oxidized at the anode to bromine which, on hydrolysis, results in the formation of hypobromous acid and HBr. The halide salt plays an important role as the supporting electrolyte as well as a source of HOBr in this reaction system. In presence of HBr, the unstable hypobromous acid forms Br^+ due to its ionic nature, which subsequently oxidizes the alcohols to the corresponding aldehyde (Fig. 9).



Considering the oxidation of benzylic alcohol to benzaldehyde as

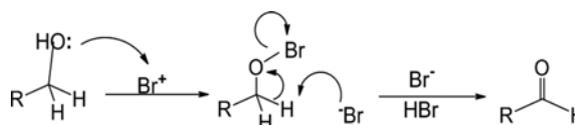
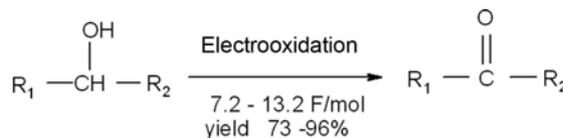


Fig. 9. Oxidation of aromatic alcohols by two-phase electrolysis.



$R_1, R_2 = \text{Aryl, KI (1.2 equivalent), NaOMe in methanol}$

Fig. 10. Electrooxidation of diarylmethanol to ketone.

a model reaction, various electrode materials were studied to determine the effectiveness of the electrode for the oxidation of bromide ions. Even though the other electrodes did not perform as well as platinum, commercially available graphite works quite well, affording a yield of 89% benzaldehyde along with 8% of recovered benzyl alcohol. The electrolyte was reused for five runs without any change in product yield.

Easy separations of the product, simple work-up process, reuse of electrolyte are the primary advantages of this two-phase electrolysis. Very recently Yoshida and co workers reported the oxidation of various diphenylmethanol to its corresponding ketone [29] in divided cell in very good yield under mild reaction conditions [Fig. 10]. The electrolysis was carried out in a 50 ml beaker equipped with a fine frit cup as the cathode compartment. A nickel coil cathode was used along with a cylindrical platinum net anode. Because of the relatively high oxidation potential, bulky structure, and somewhat poor solubility, diarylmethanol does not readily undergo direct electro oxidative transformation towards the corresponding ketone.

HOMOGENEOUS ELECTROLYSIS

1. Electrochemical Epoxidation of Styrene

Epoxides are versatile building blocks for the manufacture of a

Table 4. Electrochemical oxidation of alcohols by two-phase electrolysis system

Entry	Reactant	Product	Yield ^a (%)	Charge passed (F/Mol)	Current efficiency (%)
1			96	5.5	37
2			90	5.5	33
3			85	4.0	44
4			96	3.0	71
5			11	6	4

Table 5 α -Bromination of alkyl aryl ketones by two-phase electrolysis

Entry	Substrate	Product	Charge passed (F)	Yield (%)	Current efficiency (%)
1			4.5	83	36
2			3.8	91	50
3			5.0	81	32
4			5.0	85	31
5			5.5	84	28

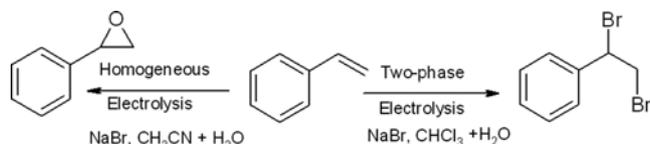
range of pharmaceuticals, natural products, and functional materials [30]. There are several methods available in the literature for the epoxidation of alkenes [31,32]. The conventional methods for epoxidation of alkenes use peracids are being replaced by H_2O_2 with reusable homogeneous catalysts that are more environment friendly. Among these, the epoxidation of styrene to styrene oxide is of particular interest from both scientific as well as commercial point of view. Though H_2O_2 is used as terminal oxidant for epoxidation, there is concern about the potential hazards associated with the storage and transportation of 30-50 wt% H_2O_2 . Electroorganic synthesis avoids the above problems as it utilizes reactive species generated by electron transfer at the electrode for following chemical reaction without any hazardous oxidizing agents. The epoxidation of styrene was attempted both in two-phase and single phase electrolytic conditions and the products obtained are entirely different [Fig. 11].

The two-phase electrolysis is conducted in 25 wt% NaBr solution containing 5 wt% HBr as aqueous phase and chloroform containing styrene as organic phase. Constant current electrolysis is followed at room temperature and at a current density of 30 mA/cm². Two platinum sheets (5 cm²) were used as electrodes and placed in the aqueous phase without touching the lower organic phase. After

passing 4 F/mol charge, 1, 2-dibromoethyl benzene was obtained as product in 98% yield [33]. Ines and coworkers obtained 23-79% yield of styrene epoxides from styrenes when the oxidation was carried out with electrochemically generated hypobromous acid (HOBr) in $\text{CH}_3\text{CN-H}_2\text{O}$ (4 : 1) containing one equivalent of NaBr (homogeneous electrolysis) [34]. In this electrochemical system HOBr is generated *in situ* at the vicinity of anode and adds efficiently to the styrene to form bromohydrin, which subsequently forms styrene epoxide by the action of cathodically generated base (OH^-) regenerating the bromide for next cycle. After completion of electrolysis CH_3CN was removed under reduced pressure and the epoxide was extracted with an organic solvent to isolate the product. Better conductivity and higher selectivity was observed when the similar experiment was carried out using an ionic liquid, 1-butyl 3-methyl imidazolium bromide (Bmim)Br instead of NaBr, and styrene epoxide is formed in 86% yield [35].

2. α -Bromination of Ketones

The α -bromination of carbonyl compounds is an important transformation in synthetic organic chemistry, as the resulting products are very much useful as an intermediate in the synthesis of biologically active compounds [36]. For example, in the preparation of naproxen (a non-steroidal anti-inflammatory agent) α -bromination of aryl group to get the product in very high yield [37]. A number of methods have been described for the bromination of ketones by employing acetyl cupric bromide [38], ammonium bromide [39], dioxane dibromide [40] and tetrabutyl ammonium tribromide [41]. All the above methods require high temperature and suitable catalysts or free radical initiators for the reaction to proceed.

**Fig. 11.** Two-phase electrolysis for epoxidation of styrene.

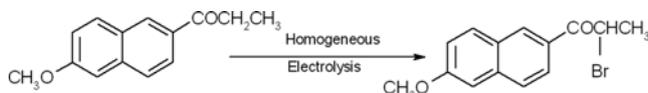


Fig. 12. Electrochemical bromination of alkyl aryl ketone.

Electrochemical bromination of alkyl aryl ketone was carried out in a single phase using $\text{CH}_3\text{CN-H}_2\text{O}$ as solvent containing 20 wt% HBr as electrolyte [42]. A wide variety of ketones underwent this transformation and α -Bromo alkyl aryl ketones were obtained in 70-95% yield as shown in Fig. 12. After completion of electrolysis acetonitrile was removed under reduced pressure and the product extracted with diethyl ether to get the product in 82% yield along with 5-10% α , α -dibromo ketone in some cases.

CONCLUSION

The nuclear and side chain bromination of alkyl aromatic compounds can be carried out in very good yield by electrochemical method. A 25-50% NaBr solution was used as an electrolyte and as a bromine source. The two-phase electrolysis has the advantages of simple product isolation, reuse of the electrolyte after replenishing the bromide concentration in aqueous phase. Benzylic alcohols can also be oxidized to the corresponding aldehydes in excellent yield without using any transition metal catalyst. Under electrochemical condition this offers an environment friendly process. Formation of epoxides and vicinal dibromides under homogeneous and biphasic electrolytic conditions is also discussed in detail in this chapter.

REFERENCES

1. T. M. Shaikh and A. Sudalai *Tetrahedron Lett.*, **46**, 5587 (2005).
2. M. Eissen and D. Lenoir, *Chem. Eng. J.*, **14**, 9830 (2008).
3. A. Chakradhar, R. Roopa, K. C. Rajanna and P. K. Saiprakash, *Synth. Commun.*, **39**, 1817 (2009).
4. R. Mestres and J. Palenzuela *Green Chem.*, **4**, 314 (2003).
5. J. B. Sperry and D. L. Wright, *Chem. Soc. Rev.*, **35**, 605 (2006).
6. J. Yoshida, K. Kataoka, R. Horcajada and A. Nagaki *Chem. Rev.*, **108**, 2265 (2008).
7. S. Suga, K. Matsumoto, K. Ueoka and J. Yoshida *J. Am. Chem. Soc.*, **128**, 7710 (2006).
8. S. R. Forsyth and D. Pletcher, *Extended abstracts of 1st International Symposium on Electro organic synthesis, Kurashiki*, **35** (1986).
9. H. Fees, H. Wendt, *J. Chem. Technol. Biotechnol.*, **30**, 297 (1980).
10. M. Morita, S. Yamamoto and Y. Matsuda, *J. Appl. Electrochem.*, **18**, 49 (1988).
11. T. Raju, K. Kulangiappar, K. Shankar and M. AnbuKulandai *Electrochim. Acta*, **51**, 356 (2005).
12. A. Muthukumar, T. Raju and V. Krishnan, *Bull. Electrochem.*, **9**, 630 (1993).
13. M. Anbu Kulandainathan, K. Kulangiappar, M. Elangovan, S. Govindu, T. Raju and V. Krishnan, *Bull. Electrochem.*, **16**, 392 (2000).
14. T. Raju, K. Kulangiappar, M. Anbu Kulandainathan, M. Revathy, U. Uma and A. Malini, *Tetrahedron Lett.*, **47**, 4581 (2006).
15. T. Ogami, K. Mori, S. Yamamura and S. Nishiyama, *Electrochim. Acta*, **49**, 4865 (2004).
16. K. Rossen, R. P. Volante and P. J. Reider *Tetrahedron Lett.*, **38**, 777 (1997).
17. N. H. Jonathan, A. Ahmed and H. S. Rodney, *US Patent*, 5,385,650. Jan 31 (1995).
18. T. Raju, K. Kulangiappar and M. Anbu Kulandainathan, *Tetrahedron Lett.*, **46**, 7047 (2005).
19. K. Kulangiappar, G. Karthick and M. Anbu Kulandainathan, *Synth. Commun.*, **39**, 2304 (2010).
20. *Ullman's encyclopedia of Industrial chemistry*, 6th Ed., Wiley-VCH, Weinheim Electronic Release (1998).
21. A. Butler and J. V. Walker, *Chem. Rev.*, **93**, 1937 (1993).
22. M. Hudluchy, *Oxidations in organic chemistry*, ACS Monograph series, American Chemical society, Washington, DC (1990).
23. S. S. Stahl, *Angew. Chem., Int. Ed.*, **43**, 3400 (2004).
24. G. Cainelli and G. Cardillo, *Chromium oxidants in organic chemistry*, Springer, Berlin (1984).
25. M. Musawir, P. N. Davey, G. Kelly and I. V. Kozhevnikov *Chem. Commun.*, **14**, 14 (2003).
26. R. E. W. Jansson and N. R. Tomov *J. Appl. Electrochem.*, **10**, 583 (1980).
27. Y. Shimizu, K. Mitsudo and H. Tanaka, *Tetrahedron Lett.*, **46**, 8975 (2005).
28. B. S. Koo, C. K. Lee and K. J. Lee, *Synth. Commun.*, **32**, 2115 (2002).
29. T. Yoshida, M. Okimoto and M. Hoshi, *Synth. Commun.*, **41**, 3134 (2011).
30. M. C. Jose, M. T. Molina and A. Shazia, *Chem. Rev.*, **104**, 2857 (2004).
31. B. S. Lane and K. Burgess, *Chem. Rev.*, **103**, 2457 (2003).
32. I. Sakia, B. Kashyap and P. Phukan, *Synth. Commun.*, **40**, 2647 (2010).
33. T. Raju and K. Kulangiappar, Unpublished results.
34. I. Massuquinini, J. M. Antunio, P. Ana, D. I. Esteves and J. M. Maria, *Comptes Rendus Chimie.*, 841 (2009).
35. T. Raju and K. Kulangiappar, Unpublished results.
36. A. M. Erian, S. M. Sherif and H. M. Gaber, *Molecules.*, **8**, 793 (2003).
37. C. Giodano, G. Castaldi and C. Giordano, JP92054657 - B2 (1992).
38. L. C. King and G. K. Ostrum, *J. Org. Chem.*, **29**, 3459 (1964).
39. A. T. Khan, P. Goswami and L. H. Choudhury, *Tetrahedron Lett.*, **47**, 2751 (2006).
40. K. Tanemura, T. Suzuki, Y. Nishida, K. Satsumabayashi and T. Horaguchi, *Chem. Lett.*, **32**, 932 (2003).
41. S. Kajigaeshi, T. Kakinami, T. Okamoto and S. Fujisaki, *Bull. Chem. Soc. Jpn.*, **60**, 1159 (1987).
42. R. Senthil Kumar, K. Kulangiappar and M. Anbu Kulandainathan, *Synth. Commun.*, **40**, 1736 (2010).