J. Indian Chem. Soc.,
Vol. 86, November 2009, pp. 1129-1142

REVIEW

Electroorganic synthesis : A novel route of green synthesis

Sanjeev Kumar, Laxmi Kant Sharma and R. K. P. Singh*

Electrochemical Laboratory of Green Synthesis, Department of Chemistry, University of Allahabad, Allahabad-211 002, Uttar Pradesh, India

E-mail : rkp.singh@rediffmail.com *Fax* : 91-532-2461157

Manuscript received 17 April 2009, accepted 3 July 2009

Abstract : Electroorganic synthesis of alkanes, alkenes and esters by anodic decarboxylation of potassium salt of palmitic acid, stearic acid, lauric acid and myristic acid, amines by reduction of aromatic nitro compounds, pinacols by reduction of carbonyl compounds, aromatic dimmers by oxidation of aromatic amines, 1,3,4-oxadiazole derivatives by electrocyclization of semicarbazone and acylthiosemicarbazone, aldol condensation of aldehydes, and acetamidation of aromatic compounds were carried out at platinum plate in undivided electrochemical cell at desired potential using simple solvent and supporting electrolyte. All the reactions were carried out at room temperature by using small amount of electricity without involvement of toxic chemicals.

Keywords : Electroorganic synthesis, controlled potential electrolysis, supporting electrolyte, reference electrode, platinum electrodes, green chemistry.

Introduction

The application of electrochemistry in the study of organic compounds has more than 150 years of history. The well known Kolbe electrolysis[1] published in 1849 was the first finding in this field. The majority of electrochemical studies unfortunately have been carried out in the area of pure electrochemistry. In 1952, anodic oxidation of furan and a series of synthetic reactions using the oxidation of furan as the key reaction were reported[2]. Now-a-day's interest is increasing for clean synthesis of fine chemicals by using electrochemistry. Traditionally, synthesis of molecules involve use of chemicals which are expensive and hazardous and also put the risk both on human beings and to the environment. Avoiding hazardous reagents and byproducts, a variety of important organic compounds were synthesised in good yield using simple electrochemical technique. By using this technique, it is possible to carryout many reactions more efficiently than conventional heating technique.

In an organic reaction, the activation of substrate molecule has generally been performed by donation of photo energy or thermal energy from outside the reaction system. On the other hand, in an electroorganic reaction the formation of an active species from a substrate is achieved by the transfer of electron between the substrate and an electrode[3-5].

Although, the activation of substrate in a usual organic reaction is sometimes carried out by using a method which involves electron transfer between the substrate and an electron donor or acceptor existing in the reaction system but the reactivity of the active species formed here is not the same as that formed by the electroorganic method, since the electron donor or acceptor in the solution are completely absent in the latter method.

Since the formation of the active species takes place at the surface of the solid electrode, known as interface, this special environment donate unique selectivities to the active species.

On the basis of these essential characteristics of the electroorganic reaction, the following are the merits of the electroorganic synthesis

(i) In the general organic reaction the activation of a substrate molecule is generally been performed by donation of photo energy or thermal energy from outside the reaction.

On the other hand, in an electroorganic reaction the formation of an active species from a substrate is achieved by the transfer of electron between the substrate and an electrode i.e. very small amount of electricity is used instead of reagents.

(ii) The electroorganic reaction is essentially non-pollu-

ting i.e. ecofriendly and achievable at room temperature.

(iii) Since the electrode potential can be controlled over a wide range, a wide variety of electroorganic reactions could be designed.

(iv) Since the structures and reactivity of the active species are different from those formed in usual chemical reactions, a variety of novel reactions can be realised.

(v) Since the polarity of a substrate is inverted by the transfer of electrons, the reaction between electrophile and electrophile, or nucleophile and nucleophile becomes possible.

(vi) The reaction environment can be altered by the modification of the electrode surface. Hence the control of the stereoselectivity or chemoselectivity may be possible by using modified electrode.

(vii) The potential of an electroorganic reaction may be enhanced by using a mediator.

(viii) Some types of reactions are completed only on a catalytic amount of electricity.

(ix) The energy efficiency is usually high.

(x) The reaction rate is controlled easily.

Experimental conditions

The important experimental details involved in electroorganic synthesis such as electrode material, temperature control, type of reaction, reference electrode, solvents and supporting electrolyte are discussed here.

(i) Electrochemical cell : The electroorganic reactions were carried out in the electrochemical cell. A variety of traditional electrochemical cells are available and several others are constructed as per requirement time to time. Basic component which are present in all electrochemical cells are a well shaped pot of suitable capacity, cathode, anode and proper connectivity arrangements. An example of four mouth electrochemical cell designed in our laboratory for the electrooganic synthesis is represented in the Fig. 1.

Among the four mouths, two mouths are used for the cathode and anode while third mouth is used for insertion of reference electrode and fourth for the addition of reagent or solvent during electrolysis and also for collection of gaseous product. A magnetic stirrer was used whenever necessary for stirring of the reaction mixture for avoiding the deposition of viscous product on the electrodes.

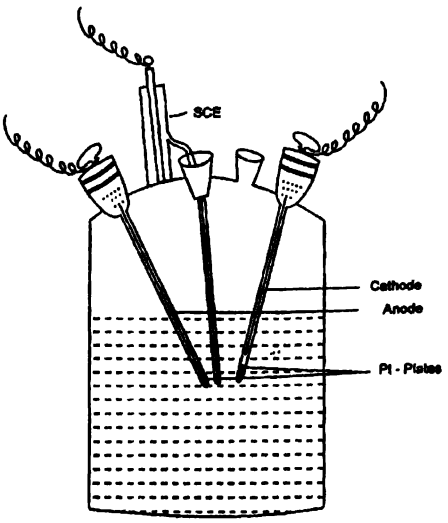


Fig. 1

(ii) Solvent : The solvents are very important in electroorganic reactions as they provide medium for the reactants. Selection of the solvents for a particular reaction depends on its physical and chemical property, solubility of reactants and supporting electrolytes in it and nature of the reactions to be carried out[6-9].

Following characteristics are required for the solvents used in the electroorganic reactions :

(a) Good solubility of supporting electrolytes and substrates in the solvent, (b) high electrochemical stability, (c) high electroconductivity, (d) suitable chemical reactivity, (e) chemical inertness towards the substrate.

The solvents preferred for oxidation reactions are mainly CH_3OH, CH_3COOH, CH_3CN, CH_2Cl_2, CH_3NO_2, tetramethylene sulphone, pyridine, tetrahydrofuran, $CH_3OCH_2CH_2OCH_3$ and propylene carbonate whereas CH_3CN, dimethylformamide, $(CH_3)_2NCOCH_3$, $(CH_3)_2SO$, hexamethylphosphoramide, *N*-methylpyrrolidone, tetrahydrofuran, dioxane and propylene carbonate for reduction reactions[10-15].

Acetonitrile shows the wider effective potential range and is especially useful because of its resistance to oxidation and its low reactivity towards ion radicals. DMF is much easier to oxidize and is therefore not very useful for anodic reactions. Although it is the best choice of solvent for reduction.

The electrolytic conductivity will always be neces-

sary, hence the dielectric constant of a solvent plays an important role. In our studies we have used acetonitrile, DMF, water, methanol and acetic acid as solvent in different types of reactions having sufficient solubility of electrolytes.

(iii) Supporting electrolyte : The supporting electrolyte is essential for the electroorganic reaction. The following properties are important for the selection of the supporting electrolyte[3-5]. (i) Solubility in the solvent commonly used for electrolysis, (ii) electrochemical and chemical inertness, (iii) no interaction with reaction intermediate.

A solvent such as water, methanol, CH_3CN or DMF will dissolve a variety of inorganic supporting electrolyte while only organic supporting electrolytes are used for most of organic solvents. The anion part of commonly used supporting electrolyte is X^- (halide anion), ClO_4^-, BF_4^-, PF_6, OTs^- or RO^- where as the cation part is M^+ (alkali metal cation) or R_4N^+.

Although its concentration is not limited to certain range, a high concentration often makes the oxidation or reduction of a substrate easier. KNO_3, KCl, $LiClO_4$, CH_3COONa and CH_3ONa were used during our study.

(iv) Electrode material : The materials used for the construction of the anode are generally limited to those which are stable towards anodic oxidation. Platinum and carbon (graphite) are the most typical materials for the anode. The material used for the anode, often influences the reaction. A typical example is the anodic oxidation of a carboxylate anion in which a platinum anode gives the normal Kolbe[1] dimer whereas a product resulting from the formation of a carbonium ion intermediate is obtained by using a graphite anode. Glassy carbon however, often gives products that are the same as those obtained using a platinum anode. The chemical interaction of the cathode with the active species generated from the substrate at the cathode is particularly important factor in the selection of the material for the cathode. We have used flattened Pt-sheets as working and counter electrodes in our studies.

(v) Reference electrode : The reference electrode is necessary for the determination of oxidation and reduction potentials of a substrate and also for controlled potential electrolysis. The electrochemical oxidation takes place at anode and reduction takes place at cathode. The electrode at which particular reaction takes place is known as working electrode.

Potential of working electrode is determined during the electrochemical reactions but we know that it is impossible to determine the potential of single electrode. It is only the potential difference between the two electrodes that can be measured by combining them to give a complete cell. By arbitrarily fixing potential of one electrode as zero, it is possible to assign numerical values to potentials of the various electrodes. Only potential difference between two electrode can be determined, therefore a reference electrode is connected with the working electrode and potential difference between the working and reference electrode is measured and is known as electrode potential. Common reference electrode used in electrochemical reactions are standard hydrogen electrode and saturated calomel electrode (SCE). In our studies we have used SCE.

(vi) Temperature : One of the most remarkable features of the electroorganic reaction is that it is generally achievable at room temperature. As a matter of course, the reaction temperature is not limited to room temperature. It is often necessary to cool the cell externally due to heat evolution caused by the passage of electricity. The electrode potentials and diffusion coefficient[16] are affected by variation in temperature. Rigorously valid comparisons between potential measurements at different temperature cannot be made.

(vii) Electrode potential : The electrode potential has to be determined on the basis of the oxidation or reduction potential of the substrate which is measurable by using cyclic voltammeter. The electrode potential is one of the most important factors in controlling the reaction. Since it is not controlled under constant current condition, controlled potential condition are often necessary to carryout the reactions with high selectivity.

When a substrate has two functional groups and the oxidation or reduction potential of both the functional groups are reasonably close, the controlled current reaction does not lead to the intramolecular reaction between both functional group. On the other hand, the controlled-potential reaction carried out at the potential where only one of the two functional groups are oxidised or reduced, will give a satisfactory result.

(viii) Amount of electricity passed through the cell : The amount of electricity corresponds to the amount of one of the reagents in the usual chemical reaction. The theoretical amount of electricity can be calculated on the basis of the number of electrons which are required to promote the reaction. The unit usually used is the cou-

lomb or faraday per mole ($Fmol^{-1}$). Since the electricity corresponds to a reagent, the yield is calculated on two different basis. One is the usual material yield and the other is current yield (or current efficiency) calculated on the basis of the amount of electricity :

Current yield (%) = $P/T \times 100$,

where P is the amount of product (mol) obtained at a given stage when a certain amount of electricity has passed and T is the theoretical amount of product (mol) obtained after passage of the same amount of electricity.

Electrochemistry is widely used in industry for example in effluent treatment, corrosion prevention and electroplating as well as electrochemical synthesis. Now-a-day's, interest is increasing for clean synthesis of fine chemical using electrochemistry. The basis of electrochemical synthesis is the electrochemical cell of which there are many types, both batch and continuous flow, with a multitude of electrode variation using lead, cadmium, zinc and carbon electrodes.

Electricity can be used in oxidation and reductions instead of reagents. When iodine is reduced to hydroiodic acid in this way[1] no waste product was formed. Naphthalene can be oxidized to naphthoquinone with 80% selectivity using small amount of cerium salt.

Substituted aromatic compounds can be oxidized to the corresponding phenols electrically with a platinum electrode in trifluoroacetic acid, triethylamine and methylene chlorides. Ketones can be converted to alcohols in up to 98% yield by electrocatalytic hydrogenation using rhodium modified electrodes.

Electrochemistry is used in large scale in the production of organic and inorganic compound. Reduction of carboxylic acids, nitro compounds and nitriles has been widely reported. Oxidation of aromatics and methyl aromatics has also been studied. Other important inorganic compounds like chlorine and sodium hydroxide etc. are manufactured using electrochemical technology. Electrochemical treatment processes can provide valuable contribution to the protection of environment through the minimization of waste and toxic material in the effluents.

Traditionally synthesis of molecules involves use of chemicals, which are hazardous and also put a risk both the human being and environment. Also tightening and more universal legislation over the use of hazardous chemicals may indirectly hindered or prevent manufacturing of many important chemical products. Green chemistry is applied to chemical processes can be environmentally benign (in terms of reduction of energy, auxiliaries, waste, etc.) and should lead to simplification of processes in terms of chemicals used and steps involved.

There is a great need for such type of work. Present work is intended to the organic reactions in aqueous and non-aqueous systems, especially in non-aqueous system. It is arranged systematically from the starting upto now. In reviewing the electrochemical reactions, an attempt have been made to discuss the conclusion with various parameters used. The contents are based on a literature search carried through 1968.

Experimental

Reaction mixture : A reaction mixture was prepared by mixing the solution of reactant with the electrolyte of the respective strength for the purpose of electrolysis. 2.0 mL phenol ($pK_a = 9.98$) was added in the solution as a proton donor wherever it is required.

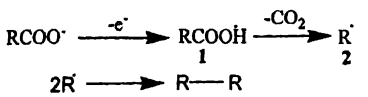
Electrolysis : The electrolysis were carried out at controlled potential in the electrochemical cell. For this constant potential electrolysis we have used conventional three electrode cell assembly with platinum (flattened sheet of dimension 1.0 cm × 0.5 cm) as working as well as counter electrode and saturated calomel electrode (SCE) as reference electrode.

Anodic decarboxylation :

The reaction that forms the dimer of the alkyl radical will be referred here as the Kolbe reaction. It is outlined as follows :

$$C_nH_{2n+1}COO^- \longrightarrow C_{2n}H_{4n+2} + 2CO_2$$

Good reviews of the Kolbe[1] reaction are available. Weedon has discussed the optimal experimental procedures for the Kolbe reaction. Best yields (50–95%) of dimer are obtained when the carboxylic acid containing 2–18 carbon atoms are oxidized at low voltage at a platinum anode in methanol or dimethylformamide. Under these conditions, the carboxylate anion suffers 1-electron oxidation to an aceloxy radical **1** which losses CO_2 to afford radical **2**, which then dimerises. However, there are some special features involved in this dimerisation.



Reaction mechanism and possible products :

Several mechanisms have been advanced to account

for Kolbe dimer formation. The ion-discharge theory of Brown and Walker[17] is shown as follows :

$$2C_nH_{2n+1}COO^- \xrightarrow{-2e^-} 2C_nH_{2n+1}COO^{\cdot} \quad \text{adds}$$

$$C_nH_{2n+1}COO^{\cdot} \longrightarrow \dot{C}_nH_{2n+1} + CO_2$$

$$2\dot{C}_nH_{2n+1} \longrightarrow C_{2n}H_{4n+2} \quad \text{Dimer}$$

Several possible products due to free-radical[18] is as follows :

$$2\dot{C}_nH_{2n+1} \longrightarrow C_{2n}H_{4n+2} \quad \text{Dimer}$$

$$2\dot{C}_nH_{2n+1} \longrightarrow C_nH_{2n+2} + C_nH_{2n} \quad \text{Disproportionation}$$

$$2\dot{C}_nH_{2n+1} + C_nH_{2n+1}COO^{\cdot} \longrightarrow C_nH_{2n+1}COOC_nH_{2n+1} \quad \text{Ester}$$

$$\underset{\text{Alkene}}{H_{2n-2}C_{n-1}{=}CH_2} + C_nH_{2n+1}COO^{\cdot} + C_nH_{2n+1} \longrightarrow \begin{array}{l} H_{2n-2}C_{n-1}{-}CH_2 \\ \quad\;\; | \qquad\quad | \\ H_{2n+1}C_n \quad OOCC_nH_{2n+1} \end{array} \quad \text{Branched Ester}$$

$$\underset{3}{\begin{array}{l} H_{28}C_{14}{-}CH_2 \\ \quad\;\; | \qquad\quad | \\ H_{31}C_{15} \quad OOCC_{15}H_{31} \end{array}} \qquad \underset{4}{\begin{array}{l} H_{20}C_{10}{-}CH_2 \\ \quad\;\; | \qquad\quad | \\ H_{20}C_{10} \quad OOCC_{11}H_{23} \end{array}}$$

The product no. **3** and **4** are obtained as new products in Kolbe reaction performed by us. This is the unique feature of our studies. The m/e values for product no. **3** and **4** are 677 and 508 respectively, which confirms the formation of above mentioned new products.

The electrolysis of potassium salt of palmitic acid, stearic acid, lauric acid and myristic acid were carried out several times at low and high potential range of 1.2 to 2.0 V[19]. It was observed from the recorded data that rate of reaction increases as the anodic potential increases upto 1.85 V and after that rate of reaction decreases and is completely checked at the potential 2.0 V. Therefore it was inferred that the potential 1.85 V is specific potential in overall reaction. The observations are depicted in the Table 1. 0.10–0.20 $Fmol^{-1}$ of electricity was passed for the electrolysis, which is very small.

Reduction of aromatic nitro compounds (synthesis of amines) :

A more complex electrochemical behaviour is shown by the nitro group because of the multiple bonds. The path of the reaction of single bond and multiple bond is completely different and bond breaking takes place in first whereas the primary event is addition of an electron to an antibonding orbital of the substrate followed by bond breaking in the later.

The nitro functional group readily undergoes reduction in protic as well as in the aprotic solvents[3]. This reaction in aqueous systems has been of interest as a basis for an analytical method in aprotic systems. The electroreduction of nitroaromatics has received considerable attention because it provides a convergent route to stable anion radicals[20]. The reduction of nitro-aliphatic has been studied which gives a much less stable radicals. There is no result of anodic oxidation of nitro compounds other than nitroaromatics. This involves removal of an electron from the highest filled molecular orbital of the molecule which is not strongly attracted by a nitro substituent.

Reduction of nitrobenzene in acidic solution gives aniline by reduction of phenylhydroxylamine before it can undergo rearrangement[21].

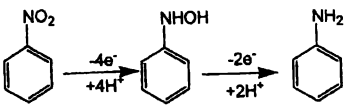


Table 1

Sl. no.	Reactant	Product	Strength of reactant (*M*)	Potential (mV)	Current (mA)
1.	Potassium palmitate	Alkane, alkene, straight chain esters and branched chain esters	0.1	1850	350
2.	Potassium laurate	do	0.1	1400	330
3.	Potassium myristate	do	0.1	1500	370
4.	Potassium stearate	do	0.1	1500	400

The nitrobenzene radical anion is quite stable in solvents of low proton availability and can be readily characterized by controlled potential electrolysis in an aprotic solvent[22] or even aqueous alkali[23]. In aprotic solvents a sequence of steps involving reduction of the radical anion to a dianion, proton abstraction by the later from its surroundings, and the ejection of hydroxide ion to form nitrosobenzene are all fast. Nitrosobenzene is easier to reduce than nitrobenzene and hence it undergoes immediate 2-electron reduction, accounting for the overall 3-electron process in the next step.

In our studies the electrochemical reduction of some nitroaromatics viz. nitrobenzene, 3-nitrobenzoic acid, *m*-dinitrobenzene, *p-N,N*-dimethylaminobenzaldehyde-2,4-dinitrophenylhydrazone (Schiff base), 4-chloronitrobenzene, 2,4-dinitrobenzoic acid and 4-nitrophenol have been carried out at controlled potential[24,25] in DMF-water solvent using phenol as a proton donor. The products formed during electrolysis on the surface of Pt-cathode is continually diffused and dissolved in the bulk. As the reaction proceeds, the solution gets darkened. After extracting the product from the reaction mixture, it was analysed and characterised for particular functional group.

Approximately the same mechanistic pathway and same product is obtained by chemical reduction[11] of nitroaromatics but on account of the merits discussed above it is a good method.

The chemical reduction of nitro group requires a number of chemicals including strong acid or base, which can be hazardous to environment and also the product obtained by chemical reduction method is not in pure state. The electrochemical method requires only two platinum electrodes, a very small amount of phenol and DMF as solvent. The reduction takes place at room temperature and there is no danger in the handling of reagents. The observations are depicted in the Table 2. 0.15–0.50 $Fmol^{-1}$ of electricity was passed for the electrolysis which is very small in comparison to energy used in other conventional methods.

Reduction of carbonyl compounds (Synthesis of pinacols) :

The electrochemical behaviour of functional groups containing multiple bonds such as carbonyl or nitro groups tends to be more complex than the systems as the cleavage of single bonds between carbon-oxygen, carbon-nitrogen, carbon-sulfur and other single bonds. A wider variety of reaction pathways are available[26,27] and the fundamental electrochemical process is different. The electron transfer is generally accompanied by bond breakage in the case of single bond, whereas with multiple bonded functional groups the primary event is addition of an electron to an antibonding orbital of the substrate. If one understands the mechanism of an electrochemical reaction, it is easier to plan new applications of it, the most important and best-studied functional groups will be examined. They have been selected because they illustrate the fact that the multiple-bonded groups frequently exhibit a diversity of reactions depending on the experimental conditions under which the electrolysis is carried out. We will explore the reasons. Armed with an understanding of the essential principles, a scholar is in a position to plan new chemistry of these and other functional groups and to understand the behaviour of more complex system such as heterocycles or polyfunctional molecules.

Considering the carbonyl group, now it is a question why an aldehyde or ketone is converted into an alcohol and not into a pinacol under certain conditions after all, there are many good conventional reagents for that particular conversion. The principles, which govern whether a pinacol or alcohol is formed when the carbonyl compound is electrolysed are, completely general and can be applied to other more complex systems. The division of the system may be clasified on the basis of conjugation. The initial electrochemical step in the reduction of both kinds of compound is addition of an electron to the lowest unfilled orbital of the electrophore to form a radical, whose subsequent fate depends on such experimental variables as electrode potential, pH and solvent. The chemistry of conjugated system is more diverse because they can react at more than one site. It is easier to undertake this problem after considering a simpler functional groups.

Systems : Aqueous and non-aqueous :

Carbonyl compounds whether aldehydes or ketones, aromatic or aliphatic, saturated or unsaturated are reducible in protic and in the aprotic solvents and produce generally the alcohols[28].

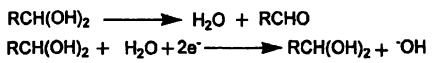
Aqueous system :

In aqueous systems, an equilibrium exists between aldeyhde and the hydrated form, a gem glycol, which is unreactive. This equilibrium is most important for the short chain aliphatic aldehydes. The electrode reaction is preceded by a chemical step which causes the process not to be diffusion controlled. The existence of unreactive

Table 2

Sl. no.	Reactant	Product	Strength of reactant (*M*)	Potential (mV)	Current (mA)	Yield (%)
1.	Nitrobenzene	Aniline	0.1	1960	300	60
2.	3-Nitrobenzoic acid	3-Aminobenzoic acid	0.1	1970	270	50
3.	*m*-Dinitrobenzene	2,4-Phenylenediamine	0.1	1450	120	55
4.	*p-N,N*-Dimethyl-phenyl-2,4-dinitro-phenyl hydrazone	*p-N,N*-Dimethylphenyl-2,4-diaminophenyl hydrazone	0.1	1500	130	55
5.	4-Chloronitrobenzene	4-Chloroaniline	0.1	1610	290	80
6.	2,4-Dinitrobenzoic acid	2,4-Diaminobenzoic acid	0.1	1820	320	70
7.	4-Nitrophenol	4-Aminophenol	0.1	1620	150	75

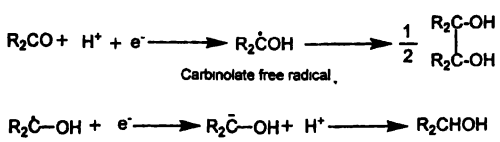
hydrated forms of aromatic aldehydes has also been suggested[29] .



The half wave potentials for reduction of aliphatic aldehydes show pH dependence in the range of 1.5 to 1.8 V vs SCE.

Reduction of aromatic ketones in aqueous systems has been examined by Elving and Leone[30] using large scale controlled potential electrolysis. In acidic solutions, a one-electron transfer reaction takes place.

The initial reaction in acidic solutions is thought to involve the formation of the carbinolate free radical and then reduction of the carbinolate free radical to carbinol.



The ultimate product of large scale electrolysis in the potential range for one electon is the pinacol because the potential is insufficiently cathodic to cause rapid addition of the second electron. The major product is the carbinol in the case of two electrons.

Non-aqueous systems :

At first the reduction of benzaldehyde, acetophenone and ferrocenaldehyde in buffered anhydrous ethanol has been described by Laviron and Lucy[31]. The results differ slightly from those obtained in aqueous solutions. The acidic solution gives one electron process, which is attributed to reduction of protonated and neutral aldehydes or ketones respectively. The result in both cases is carbinolate free radical which dimerizes. In basic solutions the process involving a total of two electrons to form the carbinol. In still more basic solution, the carbinolate anion radical must be protonated to be easily reduced as in aqueous solution, due to the onset of background reductions.

Reduction of aromatic aldehydes and ketones in DMF, using large scale electrolysis has been studied by several groups. In most cases the reaction occurs by two electron way and is similar to the behaviour in alkaline aqueous systems.

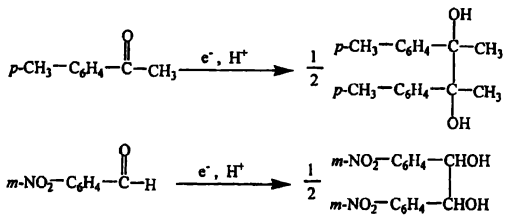
The electrochemical reduction of carbonyl compounds in aqueous-ethanol system is pH dependent and takes place with the intermediacy of corresponding free radical carbinolate anion in the alkaline region and the radical carbinolate is formed in the acidic medium. The reduction to the carbinol of the resultant free radical and its ion possibly occurs before dimerisation[32].

But as per our experiment in non-aqueous weakly acidic medium, no such pH-dependency is seen. In this experiment, the dimethylformamide (DMF) and weak acid (phenol) provides the good system[33] and phenol serves as a proton donor.

It is generally accepted that the behaviour of carbonyl compounds, in aqueous or non-aqueous systems, is determined by the availability of protons. In water and alcohol this can be measured by pH and controlled by buffers. In aprotic solvents, it can be controlled by addition of proton donors[34].

We have studied the reduction of some carbonyl compounds specially aryl ketone and arylaldehyde viz. *p*-methylacetophenone, *m*-nitrobenzaldehyde, *p*-dimethylaminobenzaldehyde, *p*-hydroxybenzaldehyde, anisylaldehyde, 4-chlorobenzaldehyde and acetophenone which give pinacols at the platinum electrode on controlled potential

electrolysis[35,36]. At definite potential the electrode surface is covered by dark brownish layer of the reduction product and that product is continually diffused in the bulk which is visible. 1.3–2.5 $Fmol^{-1}$ of electricity was passed for the electrolysis which is very small in comparison to energy used in other conventional methods. The observations are depicted in Table 3.



depends upon the position of the ring which bears the highest degree of positive charge in the radical cation. He suggested that radical cation bearing the highest charge at an unsubstituted carbon will be prone to biaryl formation. Dimerisation processes are not normally observed during the oxidation of hydrocarbon in the solvent such as acetonitrile, which can attack the benzyl cation formed to afford a substituted acetamide. Dimerisation can however be observed even in moderately nucleophilic solvent if the starting material is more nucleophilic than the solvent.

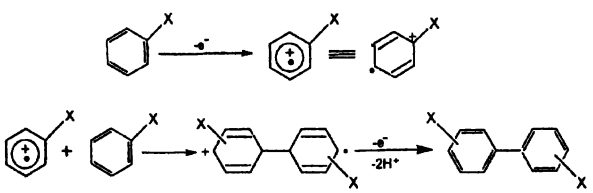
Therefore the biaryl formation is very important with aromatic amines because of the high nucleophilicity of the ring. Triarylamines in which all three of the rings bear *para* substituents form stable radical cations. Effi-

Table 3

Sl. no.	Reactant	Product	Strength of reactant (*M*)	Potential (mV)	Current (mA)	Yield (%)
1.	*p*-Methyl-acetophenone	2,3-Bis(*p*-tolyl)-2,3-butanediol	0.20	1700	110	90
2.	*m*-Nitrobenzaldehyde	1,2-Di(*m*-nitro)phenyl-1,2-ethanediol	0.20	1300	130	80
3.	*p*-Dimethylamino-benzaldehyde	1,2-Bis(*p*-dimethyl-aminophenyl)-1,2-ethanediol	0.20	1700	120	90
4.	*p*-Hydroxy-benzaldehyde	1,2-Di(*p*-hydroxy phenyl)-1,2-ethanediol	0.20	1800	150	90
5.	4-Anisylaldehyde	1,2-Di(*p*-anisyl)-1,2-ethanediol	0.26	1850	100	95
6.	4-Chlorobenzaldehyde	1,2-Di(*p*-chlorophenyl)-1,2-ethanediol	0.25	1820	170	95
7.	Acetophenone	2,3-Butanediol	0.25	1750	180	90

Oxidation of aromatic amines :

The nuclear dimerisation is a common reaction where the medium does not contain an added nucleophile e.g. during oxidation of a hydrocarbon in a solvent such as dichloromethane containing a non-nucleophilic salt such as a tetra alkylammoniumtetra-fluoroborate. Under these conditions the hydrocarbon itself can act as a nucleophile towards cationic intermediates in the oxidation[37].



These products are formed through attack on the radical cation. Nyberg[38] has suggested that whether a given substrate undergoes such nuclear dimerisation or not, cient coupling takes place when one or more *para*-positions are free[39,40]. The aromatic amines e.g. *o*-anisidine, *p*-anisidine, diphenylamine and *o*-toluidine are susceptible to oxidation and the oxidative conversion into dimers takes place at the platinum anode.

Anodic oxidation of some aromatic amines viz. aniline, 1-naphthylamine, *o*-anisidine, *p*-anisidine, diphenylamine and *o*-toluidine have been studied. Controlled potential[1,2] electrolysis was carried out for this electrochemical oxidation. The product is formed at the anode in a potential range between 0.80 to 1.24 V. The colour of bulk becomes dark due to the formation of product with time. The product is extracted from the reaction mixture and then analysed by chemical as well as spectral analysis. The reaction is an important example of synthesis of high molecular weight amines. The reaction also shows the polymerisation through oxidation.

Anisidine has one free *p*-position, hence the products

4,4′-diamino-3,5′-dimethoxybiphenyl and *o,o′*-dimethoxyazobenzene are obtained in approximately equal ratio. Since *p*-anisidine has no free *p*-position, therefore the major product of the oxidation is *p,p′*-dimethoxyazobenzene. Diphenylamine has two free *p*-positions, hence the product *p,p′*-(*N,N′*-diphenyl)diaminobiphenyl is formed together with tetraphenylhydrazine. The products 4,4′-diamino-3,5′-dimethylbiphenyl and *o,o′*-dimethylazobenzene are obtained in the oxidation of *o*-toluidine. Since it has a one free *para*-position, both the products are formed in approximately equal amount.

In aqueous media it is possible to degrade the diarylamine to aniline on hydrolysing by repetition of the process. Diarylamine with at least one free *para*-position are also converted to benzidine on oxidation[41]. Thus benzidine is an additional oxidation product due to the intermediate formation of aniline, as a degradation product in the oxidation of diarylamine.

The products were extracted from the reaction solution to the chloroform layer by the general solvent extraction method after diluting the reaction solution with double distilled wtater. Two immiscible layers of above solvents were shaken in seperatory funnel and allowed to settle. After some time chloroform layer containing the desired product was removed[42]. Approximately 0.15 F mol^{-1} of electricity was passed for the electrolysis which is very small. The observations are depicted in the Table 4.

Electroinduced aldol condensation :

The electrochemical synthesis of aldol and α,β-unsaturated compounds in non aqueous system is not dependent on pH and take place through free radicals[43]. Aldol condensation takes place in the presence of strong base, unlike this, electro induced aldol condensation which does not require acidic or alkaline medium, even the subsequent dehydration, also take place in neutral medium.

In our study, we have discussed the aldol condensation of some aldehydes viz. acetaldehyde with acetaldehyde, propanal with propanal, benzaldehyde with acetaldehyde, benzaldehyde with propanal, anisylaldehyde with acetaldehyde, anisylaldehyde with propanal, *p*-hydroxybenzaldehyde with acetaldehyde, *p*-hydroxybenzaldehyde with propanal i.e. both general and crossed aldol condensation were studied. All the electrolysis were carried out at controlled potential using three electrode cell assembly with platinum working as well as counter electrodes and saturated calomel electrode as reference electrode[44].

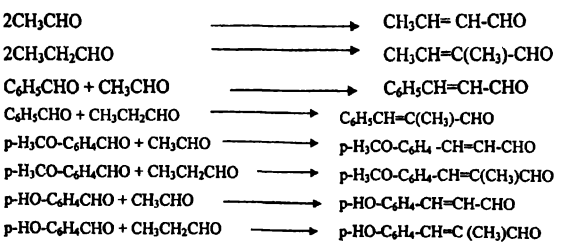


Table 4

Sl. no.	Reactant	Product	Strength of reactant (*M*)	Potential (mV)	Current (mA)	Yield (%)
1.	Aniline	Benzidine, *p*-aminodiphenylamine	0.1	930	560	86
2.	1-Naphthylamine	Dimer	0.1	800	450	92
3.	*o*-Anisidine	4,4′-Diamino-3,5′-dimethoxybiphenyl, *o,o′*-dimethoxyazobenzene	0.1	1000	610	90
4.	*p*-Anisidine	*p,p′*-Dimethoxyazobenzene, 2,6′-diamino-3,5′-dimethoxybiphenyl	0.1	930	420	80
5.	Diphenylamine	*p,p′*-(*N,N′*-Diphenyl)diaminobiphenyl, tetraphenylhydrazine, benzidine, *p,p′*-(*N,N′*-diphenyl)diaminobis-(biphenyl)amine	0.1	1240	410	85
6.	*o*-Toluidine	4,4′-Diamino-3,5′-dimethylbiphenyl, *o,o′*-dimethylazobenzene	0.1	1050	340	90

At the definite potential electrode surface is covered by coloured material which is continually diffused in the bulk.

It is obvious from the studies that the electroinduced aldol formation provides a good method of electroorganic synthesis of aldol or α,β-unsaturated aldehydes and it is a simple and ecofriendly synthetic method.

Controlled potential electrolysis was carried out similar to the above reaction. In this system the reaction takes place at the room temperature and a potential range of 1.55–2.20 V, but the specific potential for the reaction is found to be approximately 2.00 V. 0.1–1 $Fmol^{-1}$ of electricity was used for the electrolysis. The observations are depicted in the Table 5.

comparison to this substituting group. Although it is not necessary that all anodic reactions are initiated by oxidation of the aromatic substrate.

Now it is generally accepted that most of the oxidation of aromatic hydrocarbons involves removal of one electron from the hydrocarbon to afford a radical cation. The structure of the radical cation and the environment in which it is created both influence its subsequent reactions. Here we would expect that the nuclear substitution and addition to be most favoured in the presence of good nucleophiles and where the ring is not highly alkylated. This is due to the less stable benzylic type carbocation by hyperconjugation i.e. the alkyl substituents enhance the

Table 5

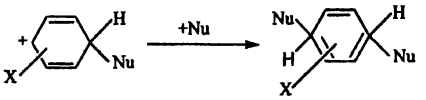
Sl. no.	Reactant	Product	Strength of reactant (*M*)	Potential (mV)	Current (mA)	Yield (%)
1.	Acetaldehyde	Crotonaldehyde	0.30	1580	230	55
2.	Propanal	3-Methylpent-2-ene-l-al	0.30	1550	310	55
3	Benzaldehyde with acetaldehyde	Cinnamaldehyde	0.30	1580	330	60
4.	Benzaldehyde with propanal	2-Methyl cinnamaldehyde	0.30	1600	340	60
5.	*p*-Anisylaldehyde with acetaldehyde	*p*-Methoxy cinnamaldehyde	0.30	2010	310	80
6.	*p*-Anisylaldehyde with propanal	2-Methyl-*p*-methoxy cinnamaldehyde	0.30	2150	780	80
7.	*p*-Hydroxybenzaldehyde with acetaldehyde	*p*-Hydroxy cinnamaldehyde	0.30	2050	820	80
8.	*p*-Hydroxybenzaldehyde with propanal	2-Methyl-*p*-hydroxy cinnamaldehyde	0.30	2150	840	80
9.	*p*-Bromobenzaldehyde with propanal	*p*-Bromo cinnamaldehyde	0.30	2100	790	80

Nuclear acetamidation of aromatic compounds :

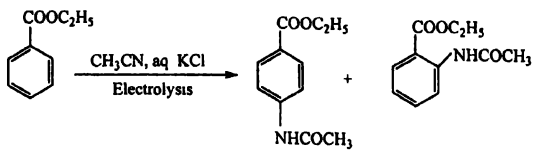
The nuclear acetamidation of aromatic compounds does not require any specific reagent, catalyst or acid and base. It takes place through the free radicals in the solution.

Very important point of this electrochemical study is that which component of this reaction solution is actually undergoing electron transfer. Infact all nuclear substitutions, were thought to involve attack on hydrocarbon by an electrochemically generated reagent. The voltammetric data shows that the primary electrochemical step in the nuclear substitution is the oxidation of the hydrocarbon[45,46], since the benzene ring is easily oxidised in stability of benzylic carbocation or radical formed in the initial stage, where the attacking centre becomes alkylated group.

Now the nucleophile is another reactant which can attack the ring to afford a cationic intermediate which most commonly loses a proton after a second electron transfer to regenerate the aromatic ring and afford a nuclear substitution product but in special cases it may suffer attack by a second molecule of nucleophile to afford an addition product.



In the present study we have discussed nuclear acetamidation of aromatic compounds viz. ethylbenzoate, acetophenone, benzoic acid, benzene, naphthalene, *p*-xylene, 3,4-dimethoxy phenylaceticacid and methyl-*p*-hydroxy benzoate[47]. The reaction is an important example of nuclear oxidation which is not easily possible by the conventional chemical synthetic methods. The nuclear acetamidation is a substitution of acetamido group on benzene nucleus through the nuclear oxidation. Therefore the reaction is a result of oxidative nuclear substitution. For this controlled potential electrolysis was carried out similar to the above reaction.



In this system the reaction takes place at the room temperature in a potential range of 1.80 to 2.80 V, but the specific potential for the reaction from various observations is found to be approximately 2.5 V vs Hg/Hg^{2+}. Total 0.5–3.0 $Fmol^{-1}$ of electricity was passed for the electrolysis which is very small in comparison to energy used in other conventional methods. The observations are depicted in the Table 6.

The product was extracted from the reaction mixture to chloroform layer by simple solvent extraction method after diluting the reaction solution with double distilled water. The two immiscible layers of above solvent were shaken in seperatory funnel and allowed to settle. After some time the chloroform layer containing desired product was removed.

Synthesis of 5-substituted-2-amino (substituted amino)-1,3,4-oxadiazoles :

Substituted 1,3,4-oxadiazoles are of considerable pharmaceutical and material interest, which is documented by steadily increasing number of publications and patents. A large number of 1,3,4-oxadiazoles have been discussed in the various literatures because of great anti-microbial, anti-fungal, anti-inflammatory, hypotensive, muscle relaxant and antimitotic activity but all the methods require dangerous reagents specially bromine, the handling of which is very sensitive and various other chemicals which produce environmental hazards.

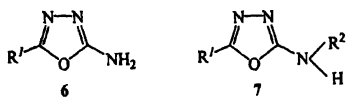
In the series of various other chemical reactions of oxidation, reduction and substitution, we made an effort as a trial method for the oxidation of semicarbazone **10** and acylthiosemicarbazone **13** for the preparation of 1,3,4-oxadiazoles[48] and this is surprising that we got success in the oxidation of semicarbazone **10** and acylthiosemicarbazone **13**.

Table 6

Sl. no.	Reactant	Product	Strength of reactant (*M*)	Potential (mV)	Current (mA)	Yield (%)
1.	Ethylbenzoate	4-Acetamidoethylacetate, 2-acetamidoethylacetate	0.1	2500	183	90
2.	Acetophenone	4-Acetamidoacetophenone, 4-acetamidoacetophenone	0.1	2500	253	80
3.	Benzoic acid	4-Acetamidobenzoicacid, 2-acetamidobenzoicacid	0.1	2.51	210	185
4.	Benzene	*N*-Phenylacetamide	0.1	2.80	223	190
5.	Naphthalene	*N*-Acetylnaphthylamine	0.1	2.50	195	96
6.	*p*-Xylene	2,5-Dimethylacetanilide	0.1	2.50	333	97
7.	3,4-Dimethoxy-phenylacetic acid	3-(*N*-Acetyl)amino-4,5-dimethoxyphenyl-acetic acid 2-(*N*-acetyl)amino-4,5-dimethoxyphenylacetic acid	0.1	2.21	397	80
8.	Methyl-*p*-hydroxy-benzoate	Methyl-3-(*N*-acetyl)amino-4-hydroxybenzoate, methyl-2-(*N*-acetyl)amino-4-hydroxybenzoate	0.1	2.63	318	85

The electroorganic synthesis of oxadiazole derivatives have been carried out by electrochemical cyclization of thiosemicarbazone **10** of aldehydes **8** and semicarbzide **9**, acylthiosemicarbazone **13** of acylhydrazene **11** and isothiocyanates **12**.

The oxadiazole ring systems have a long history of application in pharmaceutical and agrochemical industries due to their activity.

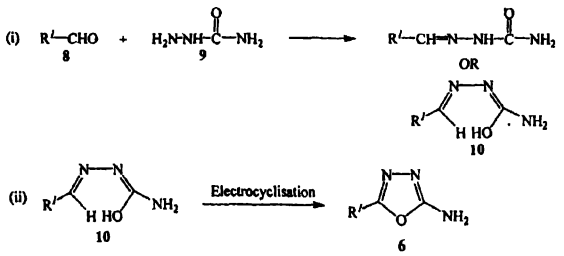


Literature synthesis[49,50] of oxadiazoles **6** and **7** include bromine oxidation of semicarbazide derivative and the cyclodesulfurisation of acylthiosemicarbazide derivative in solution using I_2/NaOH or 1,3-dicyclohexylcarbodimide (DCC)[51-54] as well as mercury(II) acetate [$Hg(OAc)_2$] or yellow mercury(II) oxide HgO[55,56]. All these methods are usually carried out in diffferent synthetic steps and requires very dangerous reagent such as bromine or other compound of mercury. Not only the handling, these reagents are also very hazardous to environment. From first step to the last stage of the reaction including extraction and purification of the products from the mixture demands great precautions.

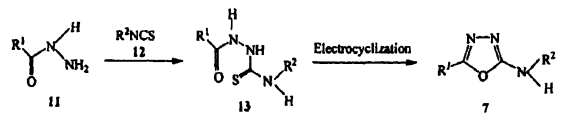
Our objective was to find out a new simple synthetic method for the preparation of 1,3,4-oxadiazoles in which the use of above said reagents could be minimised by amount and number both. Keeping these objectives in mind we have synthesized a large number of 5-substituted-2-aminooxadiazoles **6** by electroorganic cyclization of semicarbazone **10**. This electrochemical cyclization gives the oxadiazoles of the type **6** only (Scheme 1), without requirement of any hazardous reagents. We have used a general solvent acetonitrile and an electrolyte lithium perchlorate ($LiClO_4$) that can be handled very easily without major precautions.

The oxadiazoles **7** cannot be prepared directly from the oxidative cyclization of semicarbazone **10**. For this we have designed new path for the preparation of **7** in which some compounds were prepared through chemical method before oxidative cyclization on electrode.

The oxadiazoles **7** were now synthesised by the electrocyclization of acylthiosemicarbazone **13** without use of any above mentioned reagents (Scheme 2). Although the method of synthesis of oxadiazoles **7** in Scheme 2 requires one more step for the preparation of acylthiosemicarbazone **13** from acylhydrazines **11** and isothiocyanates **12** but there is no need of extra reagents.



Scheme 1. Electrocyclization of semicarbazone for the synthesis of oxadiazoles **6**.



Scheme 2. Electrocyclization of acylthiosemicarbazone for synthesis of oxadiazoles **7**.

Experimental

Preparation of reaction mixture :

For constant potential electrolysis a reaction mixture was prepared by dissolving appropriate amount of substrate and supporting electrolyte in acetonitrile viz. *Preparation of reaction mixture for electrocyclisation of semicarbazone* : Semicarbazone **10** (1.0 g) was dissolved in acetonitrile (100 mL) and $LiClO_4$ (0.106 g) was dissolved in the above solution maintaining the strength of supporting electrolyte 0.01 *M*. *Preparation of reaction mixture for electrocyclisation of acylthiosemicarbazone* : Acylthiosemicarbazone **13** (0.80 g) was dissolved in acetonitrile (100 mL) and $LiClO_4$ (0.016 g) was dissolved in the above solution maintaining the strength of supporting electrolyte 0.01 *M*.

All the products were separated by using the column chromatography and purified before the analysis. The number of products are also verified by thin layer chromatography (TLC). Approximately 4 $Fmol^{-1}$ of electricity was passed for the electrolysis which is very small in comparison to energy used in other conventional methods. The observations are depicted in the Table 7.

Table 7

Sl. no.	R^1	R^2	Strength of reactant (*M*)	Potential (mV)	Current (mA)	Yield (%)
1.	C_6H_5	H	0.1	1440	400	90
2.	4-Cl-C_6H_4	H	0.1	1430	600	80
3.	4-OCH_3-C_6H_4	H	0.1	1420	500	95
4.	3-NO_2-C_6H_4	H	0.1	1430	800	90
5.	4-OH-C_6H_4	H	0.1	1420	500	85
6.	CH_3	H	0.1	1430	300	90
7.	C_6H_5	C_6H_5	0.1	1470	500	80
8.	CH_3	C_6H_5	0.1	1260	800	95
9.	CH_3	2-OCH_3-C_6H_4	0.1	1300	900	90
10.	C_6H_5	2-OCH_3-C_6H_4	0.1	1430	400	95
11.	CH_3	4-OCH_3-C_6H_4	0.1	1300	700	95
12.	C_6H_5	4-OCH_3-C_6H_4	0.1	1320	700	95
13.	CH_3	CH_3-C_6H_4	0.1	1280	700	95
14.	C_6H_5	CH_3-C_6H_4	0.1	1280	700	90

Conclusion :

The use of electrochemistry in various processes is increasing day by day. A number of applications like effluent treatment, corrosion prevention, electroplating, electrochemical synthesis of large number of organic and inorganic compounds are the important uses by this technique. Now-a-day's interest is increasing for clean synthesis of fine chemicals using environmentally benign processess. Among these electroorganic synthesis finds application in various types of reactions such as oxidation, reduction, substitution and cyclization. In all the reactions it is observed that the yield is very good with use of very small amount of energy. Hence it is concluded that this technique will prove to be a very good ecofriendly method in organic synthesis and a valuable contribution in the field of green chemistry.

Acknowledgement

We are grateful to Head of the Chemistry Department, Professor M. C. Chattopadhyaya for providing necessary laboratory facilities and for his keen inspiration to write this review article. Thanks are also due to UGC, New Delhi and CST, Lucknow for providing financial assistance.

References

1. H. Kolbe, *Anal. Chem.*, 1849, **69**, 257.
2. N. C. Kaas, F. Limborg and K. Glens, *Acta Chem. Scand.*, 1952, **6**, 531.
3. C. K. Mann, in "Electroanalytical Chemistry", ed. A. J. Bard, Dekker, New York, 1969, **3**, 57.
4. Albert J. Fry, "Synthetic Organic Electrochemistry", 2nd ed., Wiley Interscience Publication, New York, 1989, 71.
5. T. Shono, Y. Matsumura, K. Uchida and H Kobayashi, *J. Org. Chem.*, 1985, **50**, 3243.
6. J. F. Coetzee and J. J. Campion, *J. Am. Chem. Soc.*, 1967, **89**, 2513.
7. J. F. Coetzee, J. M. Sinon and R. J. Bertozzi, *Anal. Chem.*, 1969, **41**, 766.
8. I. M. Kolthoff and F. G. Thomas, *J. Phys. Chem.*, 1965, **69**, 3049.
9. H. M. Koepp, H. Wendt and H. Strehlow, *Z. Elektrochem.*, 1960, **64**, 483.
10. J. F. Coetzee, D. K. McGuire and J. L. Hedrick, *J. Phys. Chem.*, 1963, **67**, 1814.
11. A. Cizak and P. J. Elving, *J. Electrochem. Soc.*, 1963, **100**, 160.
12. G. Kortun and J. O'M. Bockris, "Test Book on Electrochemistry", New York, 1957, **1**, 186.
13. J. M. Kolthoff and J. Lingane, "J. Polarography", 2nd ed., Wiley Interscience Publication, New York, 1952.
14. D. M. Mohilner, "Electroanalytical Chemistry", Dekker, New York, 1966, **1**, 241.
15. C. K. Mann, in "Electroanalytical Chemistry", ed. A. J. Bard, Dekker, New York, 1969, **3**, 57.
16. F. Fichter, *Trans. Am. Electrochem. Soc.*, 1924, **45**, 131.
17. Albert J. Fry, "Synthetic Organic Electrochemistry", 2nd ed., Wiley Interscience Publication, New York, 1989, 238.

18. S. Kumar, A. Kumar and R. K. P. Singh, *Proc. Nat. Acad. Sci. India*, 2005, **75A (IV)**, 223.

19. L. Christensen and P. E. Iversen, *Acta Chem. Scand.*, 1979, **33B**, 352.

20. S. Swann (Jr.) and A. Weissberger, "Technique of Organic Chemistry", 2nd ed., Wiley Interscience Publication, New York, 1956, **2**, 385.

21. G. A. Russel, E. J. Smentowski, E. J. Geds, K.-Y. Chang, Jreynolds and G. Kaupp, *J. Am. Chem. Soc.*, 1967, **89**, 3821.

22. C. L. Perrin, *Proc. Org. Chem.*, 1965, **3**, 165.

23. K. L. Yadava, A. Kumar, S. Kumar and R. K. P. Singh, *J. Electrochem. Soc.*, 2003, **52**, 114.

24. S. Kumar, P. Yadav and R. K. P. Singh, *Transactions of the SAEST*, 2006, **41**, 5.

25. S. Kumar and R. K. P. Singh, *J. Indian Chem. Soc.*, 2005, **82**, 934.

26. Albert J. Fry, "Synthetic Organic Electrochemistry", 2nd ed., Wiley Interscience Publication, New York, 1988, 173.

27. M. Fedoronko, E. Fulleova and K. Linek, *Coll. Czech. Chem. Commun.*, 1971, **36**, 114.

28. I. M. Kolthoff and J. J. Lingane, "Polarography", 2nd ed., Willey Interscience Publication, New York, 1952, 652.

29. N. H. Furman and D. R. Norton, *Anal. Chem.*, 1954, **26**, 1111.

30. P. J. Elving and J. T. Leone, *J. Am. Chem. Soc.*, 1958, **80**, 1021.

31. E. Laviron and J. C. Lucy, *Bull. Soc. Chim. Fr.*, 1966, 2202.

32. S. R. Yadav, P. Goyal, A. Sharma, P. S. Verma and I. K. Sharma, *J. Indian Chem. Soc.*, 2002, **79**, 695.

33. P. H. Given and M. E. Peover, *J. Am. Chem. Soc.*, 1960, **82**, 385.

34. F. Michielli and P. J. Elving, *J. Am. Chem. Soc.*, 1989, **90**, 1688.

35. K. L. Yadava, S. Kumar, A. Kumar and R. K. P. Singh, *J. Indian Chem. Soc.*, 2004, **81**, 595.

36. L. K. Sharma, S. Kumar and R. K. P. Singh, *Transactions of the SAEST*, 2006, **41**, 48.

37. Albert J. Fry, "Synthetic Organic Electrochemistry", 2nd ed., Wiley Interscience Publication, New York, 1989, 258.

38. K. Nyberg, *Acta Chem. Scand.*, 1971, **25**, 2499.

39. R. F. Nelson and R. N. Adams, *J. Am. Chem. Soc.*, 1968, **90**, 3925.

40. E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy and R. N. Adams, *J. Am. Chem. Soc.*, 1966, **88**, 3498.

41. R. Reynolds, L. Line and R. F. Nelson, *J. Am. Chem. Soc.*, 1974, **96**, 1087.

42. K. L. Yadava, A. Kumar, S. Kumar and R. K. P. Singh, *Transactions of the SAEST*, 2005, **40**, 106.

43. T. Shono, "Electroorganic Synthesis", Academic Press, Inc., London, 1991, 140.

44. S. Kumar, L. K. Sharma and R. K. P. Singh, *J. Indian Chem. Soc.*, 2006, **83**, 1160.

45. R. P. Linstead, B. R. Shephord and B. C. L. Weedon, *J. Chem. Soc.*, 1952, 3624.

46. M. Leung, J. Herz and H. W. Salzberg, *J. Org. Chem.*, 1965, **30**, 310.

47. L. K. Sharma, S. Kumar, P. Yadav and R. K. P. Singh, *Indian J. Chem., Sect. B*, 2008, **47**, 1277.

48. L. K. Sharma, S. Kumar, S. Singh and R. K. P. Singh, *Electrokhimiya*, 2009 (in Press).

49. J. Hill, in "Comprehensive Heterocyclic Chemistry", ed. K. T. Potts, Pergamon Press, Oxford, 1984, **6**, 427.

50. A. Hetzheim and K. Moeckel, *Adv. Heterocyclic Chem.*, 1966, **7**, 183.

51. (a) O. M. Aboulwafa and O. M. M. E. Omar, *Sulfur Lett.*, 1992, **14**, 181; (b) F. A. Omar, N. M. Mahfouz and M. A. Rahman, *Eur. J. Med. Chem.*, 1996, **31**, 819.

52. S. M. Golovlyova, Y. A. Moskvichev, E. M. Alov, D. B. Kobylinskey and V. V. Ermolaeva, *Chem. Heterocycl. Compd.*, 2001, **37**, 1102.

53. F. M. Liu, B. L. Wang and Z. F. Zhang, *Youji Huaxue*, 2001, **21**, 1126.

54. R. S. Gani, R. S. Pujar and G. S. Gadaginamath, *Indian J. Heterocycl. Chem.*, 2002, **12**, 25.

55. X. Wang, Z. Li and J. Yang, *Synth. Commun.*, 2002, **32**, 1097.

56. H. M. Faidallah, E. M. Sharshira, S. A. Basaif and A. E. A-Ba-Oum, *Phos. Sulf. Sil. Rel. Elem.*, 2002, **177**, 67.