



International Journal of ChemTech Research CODEN(USA): IJCRGG ISSN : 0974-4290 Vol.6, No.1, pp 361-365, Jan-March 2014

Electro-Organic Synthesis of 2-Pyridyl Methanol At SS-316 Electrode in Basic Aqueous Medium

Anil Kumar Nainawat^{1*}, P.S. Verma² and I.K. Sharma²

¹Department of Education in Science and Mathematics, Regional Institute of Education (NCERT), Ajmer (India) - 305 004

²Centre for Advanced Studies, Department of Chemistry, University of Rajasthan, Jaipur (India) - 302 005

*Corres.author: drnainawat@gmail.com, Phone: + (91) 1412781865, + (91) 9414605854

Abstract: Electrochemical studies have been carried out for conversion of Pyridine-2-carbaldehyde into 2-Pyridyl methanol. This may provide a basis for attractive environmental friendly and sustainable synthetic procedure. The reduction process was investigated cyclic voltammetrically to explore it as an alternative synthetic route for the preparation of alcohols. On electrolysis in basic medium (pH-9) controlled current in 1.0 M Sodium acetate, 2-Pyridylmethanol was obtained as the major product, which was isolated, purified and characterized by combined application of chromatographic and spectroscopic techniques. Stainless steel (SS-316) electrodes were used as anode & cathode. The effect of pH on electrochemical reduction was also studied. **Keywords:** Pyridine-2-carbaldehyde, Stainless Steel (SS-316) Electrode, Cyclic Voltammetry, Controlled Current electrolysis.

1.1 Introduction

Electrochemical routes for organic synthesis are emerging as good alternatives to traditional laboratory as well as industrial methods (e.g. heterogeneous and homogeneous catalysis). They have potential to compete with modern methods (e.g. enzymaticcatalysis, photocatalysis). All syntheses require application of energy to accomplish the transformation of raw materials. Electrochemical synthesis involves application of a potential in the presence of active electrode surfaces. The resulting flow of current drives the oxidation or reduction and subsequent recombination of reactants. Extensive reviews of electroorganic syntheses are available [1–4]. There are several features of electroorganic synthesis that are often cited as being environmentally favorable [5]. First, electrons flowing as current may be regarded as one of the reagents. Second, reactions may take place in a low-temperature environment reducing the local consumption of energy and reducing the risk of corrosion, material failure, and accidental release. Also, reactions may occur in low volatility or no-volatility reaction media. The electrodes may be regarded as heterogeneous catalysts that are easily separated from the products. Supporting electrolyte and electrochemically active mediator species may be regenerated electrochemically and recovered.

Pyridine 2- carbaldehyde is a useful intermediate in pharmaceuticals (6) .It is used in the preparation of pralidoxime methiodide which is an antidote for poisoning by organophosphate acetyl-cholinesterase inhibitor, and in production of bisacodyl, a laxative (6). Its reduction product 2-pyridyl methanol too is a very important intermediate in pharmaceutical industry. (6) In this paper, we are reporting the electroorganic synthesis of 2-pyridyl methanol by the reduction of Pyridine-2-carbaldehyde galvanostatically using stainless steel (SS- 316) electrode in basic medium.

1.2 Material and methods

All the chemicals used were of analytical grade and the solutions were prepared in triply distilled water. All experiments were carried out at room temperature. Prior to the electro-organic synthesis, the optimum conditions of the reaction were worked out by utilizing the concepts of organic reaction mechanism along with the appropriate interpretation of signals obtained from cyclic voltammetry in combination with spectroscopy. Cyclic voltammograms obtained in acidic, neutral and basic conditions were of dissimilar nature, which clearly indicates formation of different electrolysis products under different condition of pH. At low pH values, reduction of Pyridine-2-carbaldehyde exhibits two irreversible single electron waves and with the increase in the pH of the medium these two waves merge to form one two-electron reduction wave.

In acidic medium pinacol is obtained but under these conditions, stainless steel electrode cannot be used hence no attempt was made to synthesize this product. The present method therefore offered single product viz. Pyridyl-2-methanol in alkaline conditions. The attractive features of the technique are single product (Pyridyl-2methanol), economical electrode stainless steel (SS-316), and last but not the least ecofriendly conditions. Cyclic voltammograms were recorded at the scan rate of 100 mV/s using a computer interfaced instrument ECDA-001 supplied by Con-serv Enterprises, Mumbai. The cyclic voltammogramic studies were carried out using glassy carbon as working electrode, Ag/AgCl as reference and platinum electrode as counter electrode. The results thus obtained were utilized to decide the optimum reaction conditions for the reduction. The electroorganic synthesis was then carried out using a CDPE (Centre for Development of Physics Education, U.O.R. Jaipur) make Galvanostat at Stainless steel electrode (SS-316). The reaction product was isolated, purified and characterized by combined application of chromatographic technique and spectroscopy.

1.3 Results and Discussion

The carbonyl group is an electrophoric group offering interesting synthetic possibilities [7-8]. The reduction of a large number of organic compounds including carbonyl compounds has been carried out electrochemically using stainless steel electrode in aqueous media at controlled potential [9-10] and controlled current [11-12] in our laboratory. The reduction of carbonyl compounds in aqueous solutions is pH dependent. At low pH (i.e. pH-4) their cyclic voltammogram shows two irreversible single electron waves [13], indicating formation of two products. Electrolysis on the plateau of the first wave usually affords the pinacol while reduction on the second plateau produces the alcohol [14]. The product formation can be accounted for by the suggested mechanism (in acidic medium).



With increase in the pH of the medium the two waves merge to form one two-electron reduction wave [15]. Under these conditions the primary product is the corresponding alcohol as clarified in the proposed mechanism (in basic medium).



The effect of pH on reduction of Pyridine-2-carbaldehyde has been summarized in the collective cyclic voltammograms taken at different pH and same scan rate of 100 mV/s in aqueous medium (Fig.1). The voltammographic curves of 0.5 mM Pyridine-2-carbaldehyde in aqueous medium, 2.5 M Potassium Chloride as supporting electrolyte and BR buffer of different medium (pH = 4.0, 7.0 and 9.0) at glassy carbon electrode using Ag/AgCl as reference electrode are taken.

The conventional H-type cell with two limbs separated by G-4 disc was used for electrolysis. The supporting electrolyte sodium acetate (1 M) was filled equally in both the limbs. The Pyridine-2-carbaldehyde (1.40 g) was dissolved in the alcohol and placed in the cathodic chamber. The stainless steel (SS-316) electrode having an area 2×3 cm² was used as cathode as well as anode. The constant current (1 A) was passed through the electrolyte for 2 hours with the help of CDPE make Galvanostat.

The workup involved extracting the aqueous solutions three times with methylene chloride (50 mL each). The methylene chloride extract from the reaction was combined and washed with an aqueous solution of saturated

NaCl. The organic extracts were then dried over anhydrous Na_2SO_4 after the separation and then the product formed was identified.

The separation of the electrolysis product was carried out with the help of semi preparative HPLC (Shimadzu, Japan) and the identification was made with FTIR (Shimadzu, Japan), GC-MS spectrophotometer (Thermofinnigan Trace-GC) and NMR (JEOL, Japan, 300 MHz) techniques. The results are tabulated in Table 1.

Fig. 1: Cyclic Voltammograms showing effect of pH



PYRIDINE 2-CARBALDEHYDE

Table 1.

Name of substrate	Yield (%)	Yield	IR Data (cm ⁻¹)	Mass Spectra	NMR Data
		(in g)		m/z	(δ-value)
Pyridine-2- carbaldehyde	87.9	1.23	3417,	109, 108,	7.36-8.50 (m,4H)
			1605-1480	31, 78	4.35 (s,2H),
			3000-3100		4.43 (s,1H)

The FTIR data indicates prominent absorption bands at (i) 3080-3010 cm⁻¹ (ii) 1600-1430 cm⁻¹(s) due to C=C and C=N stretching and a sharp peak at 1680 cm⁻¹ due to C=0 stretching of carbonyl compounds were observed in the starting material, the latter were not observed in the FTIR of the product. A band at 3417 cm⁻¹ observed in the FTIR of the product which is due to -OH stretching. This indicates transformation of CO group in to OH group. Appearance of a singlet at 4.43 ppm in the NMR spectrum of the product and assigned to OH group

further confirms the aforesaid transformation. The fragmentation pattern of the product in its mass spectrum indicates the presence of CH_2OH unit in the product (m/z= 31).

The boiling point of the product was obtained as 220-221 ⁰ C, which is in good agreement with the reported value for 2-pyridyl methanol.

1.4 Conclusions

Electrochemical reduction of the carbonyl compounds at constant current thus provides an attractive synthetic route for synthesis of alcohols which are building blocks/synthons for pharmaceutical drugs. The attractive feature of the technique are single product (Pyridyl-2-methanol), economical stainless steel (SS-316) electrode, and last but not the least ecofriendly conditions.

Acknowledgements

Authors wish to thank to the Head, Department of Chemistry and Principal, Regional Institute of Education, Ajmer for their support and kind co-operation.

References

- 1. D. Degner, Top. Curr. Chem. (1988) 148, 1.
- D. Degner, Techniques of Electroorganic Synthesis, Part III, Wiley, New York (1985) Ch. 32, pp. 251– 265,
- 3. A.J. Fry, Synthetic Organic Electrochemistry, Harper & Row, New York, 1972.
- 4. 4. J. Utley, Chem. Soc. Rev. (1997) 26,157.
- 5. E. Steckhan, T. Arns, W.R. Heineman, G. Hilt, D. Hoorman, J. Jorissen, L. Krone, B. Lewall, H. Putter, Chemosphere (2001) 43, 63.
- 6. Ullamanns Encyclopedia of Industrial Chemistry, VCH (1993) Vol. A22, p.421.
- 7. F.D. Popp, H.P. Schultz, Chem. Rev. (1962) 62, 19.
- 8. P. Zuman, Collect. Czech. Chem. Commun. (1968) 33, 2548.
- 9. Nidhi Singhal, I.K. Sharma, P.S. Verma, Trans. SAEST (1997) 32,77.
- Sheesh R. Yadav, Rakesh Yadav, Alka Sharma, I.K. Sharma, P.S. Verma, Bull. Electrochem. (2002) 18 (2), 87.
- 11. Anil Kumar Nainawat, Nemicand Kharia, Alka Sharma and I.K. Sharma, Bull. Electrochem. (2006) 22 (7) ,297.
- 12. Meenu Vijay, Nemicand Kharia, Alka Sharma, I.K. Sharma and P.S. Verma, J. Ind. Chem.Soc. (2007) 84 (5), 493.
- 13. M. Ashworth, Coll. Czech. Chem. Commun. (1948) 13,229.
- 14. S. Swann, J. Trans. Electrochem. Soc. (1944) 85,231.
- 15. P. Elving, J. T. Leone, J. Am. Chem. Soc. (1958) 80, 1021.
