



Electro-organic Nuclear Oxidation: Methoxylation of Aromatic Compounds at Platinum Electrode

SANJEEV KUMAR

Department of Chemistry, Iswar Saran Degree College
(University of Allahabad) Allahabad-211004, India

sanjivks77@gmail.com

Received 12 August 2010; Accepted 1 November 2010

Abstract: The anodic oxidation of aromatic compounds was carried out at controlled potential in the non aqueous methanol-KOH system for the purpose of investigating this type of anodic reaction as a new possible synthetic method. The electroorganic nuclear oxidation was carried out at controlled potential electrolysis in a conventional three electrode cell assembly with platinum plate working as well as counter electrode and saturated calomel electrode as reference electrode. Controlled potential electrolysis was carried out in the solvent methanol and the supporting electrolyte in caustic potash. All the spectral and analytical data were found in good agreement with the synthesized compounds.

Keywords: Electrooxidation, Controlled potential electrolysis, Platinum electrode, Green chemistry.

Introduction

The first report of anodic methoxylation was that of Clauson-Kass¹ on methoxylation of furan and its derivatives. It involved electrolysis of furan at a platinum anode and a nickel cathode in a methanolic solution containing ammonium bromide. Hydrogen and ammonia were formed at cathode and bromine at the anode. Bromine reacts with furan and methanol to form 2,5-dimethoxydihydrogen and hydrogen bromide which reacts with ammonia to regenerate the ammonium bromide. In context of the green chemistry, in the present work a new electrochemical synthetic method has been developed for the methoxylation of aromatic compounds on the basis of general reagents, apparatus at room temperature. The development of eco-friendly synthetic methods would be most welcome. In this respect, organic synthesis involving multi-component reactions under reagents free conditions is a basic protocol because multi-step conventional synthesis produces considerable amounts of environmentally unfavorable wastes, mainly due to a series of complex isolation procedures often involving expensive, toxic and hazardous solvents and reagents after each step.

The application of electricity as a non conventional energy source for activation of reactions in the suitable solvents has now gained popularity over the usual homogeneous and heterogeneous reactions, as it provides chemical processes with special attributes, such as enhanced reaction rates, better selectivity, higher yield of pure products and several eco-friendly advantages²⁻⁴. These reactions do not require oxidizing reagents and can be performed at ordinary room temperature. The results of our studies on the anodic oxidation of some aromatic compounds have been reported in the present communication.

Experimental

Column chromatography was carried out by using Merck silica gel 60 to check the purity of synthesized compounds. The purity of the synthesized compounds were ascertained by TLC on pre-coated Silica gel plates in various solvent systems using iodine vapours and UV light as detecting agent. Infra red spectra were recorded on a Shimadzu 8201 PC IR spectrophotometer in KBr pellets and reported in cm^{-1} . ^1H NMR and ^{13}C NMR spectra were measured on Bruker DRX 300 MHz FT spectrometer instruments using DMSO-d_6 as solvent with TMS and CDCl_3 as internal standards (chemical shift in δ ppm). Carbon multiplicities were assigned by DEPT techniques. The structures of the newly synthesized compounds were assigned on the basis of elemental analysis and were recorded on a Elementar Vario EL III. Carbon, hydrogen and nitrogen analyses were within $\pm 0.4\%$ of the theoretical values. Mass spectra were taken out on a JEOL SX 102/DA-6600 mass spectrometer. All the chemicals used were of synthetic and AR grade and was procured from Agros-Organics, USA, S.D. Fine Chem. Ltd., Mumbai and Merck, Mumbai, India.

Reaction mixture

25 mL of 0.1 M aqueous solution of KOH was added with 25 mL solution of the reactant of the strength given in the Table 1 to prepare the reaction mixture for the electrolysis.

Table 1. Experimental conditions for the electrolysis

S. No.	Reactant	Solvent/Methoxylating agent	Strength of the solution, M
1	Acetophenone	$\text{CH}_3\text{OH}/\text{KOH}$	0.17
2	Ethyl benzoate	$\text{CH}_3\text{OH}/\text{KOH}$	0.11
3	<i>p</i> -Methyl acetophenone	$\text{CH}_3\text{OH}/\text{KOH}$	0.09
4	<i>p</i> -Xylene	$\text{CH}_3\text{OH}/\text{KOH}$	0.15
5	Methyl benzoate	$\text{CH}_3\text{OH}/\text{KOH}$	0.11

Electrolysis

Preparative scale controlled potential electrolysis⁵⁻¹⁰ was performed at room temperature in 250 mL three-electrode cell assembly with platinum plate as working as well as counter electrode and saturated calomel electrode as reference electrode. Magnetic stirrer was used for the proper mixing of reaction mixture. All the electrolysis experiments were carried out at their corresponding oxidation potentials and were completed in 2 h. After which no oxidation product was seen to diffuse in the bulk. The current potential data was recorded with the help of a potentiostat at the interval of 15 min and has been depicted in Table 2.

In each case after the termination of the reaction, methanol was evaporated from the reaction mixture with the help of rotatory evaporator and the products obtained were entirely different from that of reactants, which were analyzed by chemical and spectral analysis. It is evident from the Table 2 that the yield is greater than 85%. Approximately 7.0-9.0 F mol^{-1} of electricity was passed for the electrolysis which is very small in comparison to energy used in other conventional chemical methods.

Table 2. Current and potential data recorded by the potentiostat

Time, h	Current in milliampere, mA				
	Acetophenone	Ethyl benzoate	<i>p</i> -Methyl acetophenone	<i>p</i> -Xylene	Methyl benzoate
0.00-0.15	1120	920	890	1110	1230
0.15-0.30	1110	880	860	985	1200
0.30-0.45	1109	850	820	960	1176
0.45-1.00	1107	810	785	942	1150
1.00-1.15	1106	785	760	930	1120
1.15-1.30	1105	750	745	905	1083
1.30-1.45	1104	710	720	870	1065
1.45-2.00	1104	660	700	855	1045
Applied Potential	1.90 V	1.80 V	1.70 V	1.95 V	2.10 V
Yield	86%	92%	95%	85%	88%

Analytical and spectral characterization data m-methoxy acetophenone (1)

IR (KBr, cm^{-1}): 3045 (C-H aromatic), 2855 (aliphatic C-H), 2815 (OCH_3), 1720 ($\text{C}=\text{O}$), 1470 ($\text{C}=\text{C}$ aromatic), 1282 (Ar-O), 980, 890, 750, 595 (substituted benzene), ^1H NMR (DMSO, d_6 , δ/ppm): 8.76 (s, 1H, Ar-H), 7.91 (d, 1H, $J = 5.6$ Hz, Ar-H), 7.30 (d, 1H, $J = 5.6$ Hz, Ar-H), 6.94-7.14 (dd, 1H, $J = 2.6$ and 5.6 Hz, Ar-H), 3.22 (s, 3H, OCH_3), 1.48 (s, 3H, CH_3), ^{13}C NMR (DMSO, d_6 , δ/ppm): 159.5 (C_3), 144.1 (C_1), 129.1 (C_5), 120.4 (C_6), 116.9 (C_4), 113.7 (C_2), 54.5 (OCH_3), 20.6 (CH_3). MS m/z : 150 (M^+), 151 ($\text{M}^+ + 1$, 100%). Anal. calcd. for $\text{C}_9\text{H}_{10}\text{O}_2$: C, 72.0; H, 6.67. Found: C, 71.32; H, 6.45.

Ethyl-m-methoxy benzoate (2)

IR (KBr, cm^{-1}): 3042 (C-H aromatic), 2855 (aliphatic C-H), 2815 (OCH_3), 1722 ($\text{C}=\text{O}$), 1473 ($\text{C}=\text{C}$ aromatic), 1280 (Ar-O), 980, 890, 750, 595 (substituted benzene), ^1H NMR (DMSO, d_6 , δ/ppm): 8.77 (s, 1H, Ar-H), 7.90 (d, 1H, $J = 5.6$ Hz, Ar-H), 7.30 (d, 1H, $J = 5.6$ Hz, Ar-H), 6.94-7.14 (dd, 1H, $J = 2.6$ and 5.6 Hz, Ar-H), 4.07 (q, 2H, $J = 7.3$ Hz, CH_2CH_3), 3.24 (s, 3H, OCH_3), 1.33 (t, 3H, $J = 7.3$ Hz, CH_2CH_3), ^{13}C NMR (DMSO, d_6 , δ/ppm): 159.8 (C_3), 131.5 (C_1), 129.4 (C_5), 122.0 (C_6), 118.9 (C_4), 115.3 (C_2), 54.5 (OCH_3), 35.5 (CH_2), 17.9 (CH_3). MS m/z : 180 (M^+), 181 ($\text{M}^+ + 1$, 100%). Anal. calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3$: C, 66.73; H, 5.56. Found: C, 66.32; H, 5.35.

3-Methoxy-4-methyl acetophenone (3)

IR (KBr, cm^{-1}): 3045 (C-H aromatic), 2855 (aliphatic C-H), 2820 (OCH_3), 1725 ($\text{C}=\text{O}$), 1475 ($\text{C}=\text{C}$ aromatic), 1275 (Ar-O), 985, 890, 755, 597 (substituted benzene), ^1H NMR (DMSO, d_6 , δ/ppm): 8.75 (s, 1H, Ar-H), 7.56 (d, 1H, $J = 5.6$ Hz, Ar-H), 7.22 (d, 1H, $J = 5.6$ Hz, Ar-H), 3.22 (s, 3H, OCH_3), 1.95 (s, 3H, OCH_3), 1.12 (s, 3H, Ar- CH_3), ^{13}C NMR (DMSO, d_6 , δ/ppm): 160.2 (C_3), 134.4 (C_1), 129.8 (C_5), 126.2 (C_4), 120.4 (C_6), 113.6 (C_2), 54.5 (OCH_3), 21.18 (Ar- CH_3), 20.6 (COCH_3). MS m/z : 164 (M^+), 165 ($\text{M}^+ + 1$, 100%). Anal. calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 73.17; H, 7.31. Found: C, 72.46; H, 7.02.

Methyl-2,5-dimethylphenyl ether (4)

IR (KBr, cm^{-1}): 3035 (C-H aromatic), 2855 (aliphatic C-H), 2820 (OCH_3), 1465 ($\text{C}=\text{C}$ aromatic), 1275 (Ar-O), 985, 865, 810, 730 (substituted benzene), ^1H NMR (DMSO, d_6 , δ/ppm):

8.78 (s, 1H, Ar-H), 7.59 (d, 1H, $J = 5.6$ Hz, Ar-H), 7.26 (d, 1H, $J = 5.6$ Hz, Ar-H), 3.21 (s, 3H, OCH₃), 1.12 (s, 6H, ArCH₃), ¹³C NMR (DMSO, d₆, δ/ppm): 160.7 (C₂), 135.9 (C₄), 130.4 (C₆), 121.5 (C₅), 120.5 (C₁), 114.7 (C₃), 54.5 (OCH₃), 21.18 (ArCH₃). MS m/z : 136 (M⁺), 137 (M⁺ + 1, 100%). Anal. calcd. for C₉H₁₂O: C, 79.41; H, 8.82. Found: C, 78.85; H, 8.57.

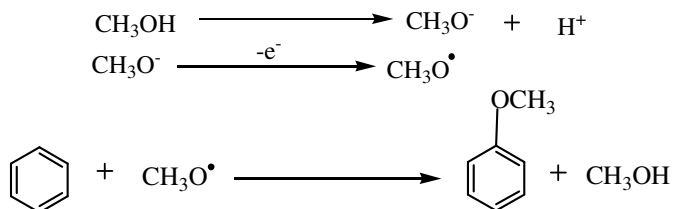
Methyl-*m*-methoxy benzoate (5)

IR (KBr, cm⁻¹): 3042 (C-H aromatic), 2855 (aliphatic C-H), 2815 (OCH₃), 1722 (C=O), 1473 (C=C aromatic), 1280 (Ar-O), 980, 890, 7505, 595 (substituted benzene), ¹H NMR (DMSO, d₆, δ/ppm): 8.77 (s, 1H, Ar-H), 7.92 (d, 1H, $J = 5.6$ Hz, Ar-H), 7.37 (d, 1H, $J = 5.6$ Hz, Ar-H), 6.94-7.14 (dd, 1H, $J = 2.6$ and 5.6 Hz, Ar-H), 3.24 (s, 3H, OCH₃), 1.12 (s, 3H, CH₃), ¹³C NMR (DMSO, d₆, δ/ppm): 159.5 (C₃), 131.4 (C₁), 129.1 (C₅), 122.4 (C₆), 118.9 (C₄), 115.7 (C₂), 54.5 (OCH₃), 21.18 (ArCH₃), 17.9 (CH₃). MS m/z : 160 (M⁺), 161 (M⁺ + 1, 100%). Anal. calcd. for C₉H₁₀O₃: C, 67.5; H, 6.25. Found: C, 66.92; H, 6.05.

Results and Discussion

All the previous methods were usually carried out in different synthetic steps and requires very dangerous reagent such as bromine. Not only the handling of these reagents is difficult but also very hazardous to the environment. Nuclear methoxylation of substrates possessing high oxidation potential was achieved with difficulty^{11,12}, whereas easily oxidizable substrates such as 1,4-dimethoxy benzene were transformed to the corresponding quinone bisacetals by anodic oxidation in higher yields¹³⁻¹⁵.

Anodic oxidation of system that contains organic compounds frequently leads to reaction in which groups derived from the solvent or an electrolyte are substituted in the organic molecule. The anodic substitution occurs as a result of the discharge of an anion to form a radical which attacks the substrate in a homogeneous radical reaction². The reaction scheme that involves direct electrode attack on the substrate with subsequent ionic steps responsible for the formation of substituted product. Therefore a mechanism is preferable^{16,17}, involving initial attack on the solvent or supporting electrolyte, which is given as Scheme 1.

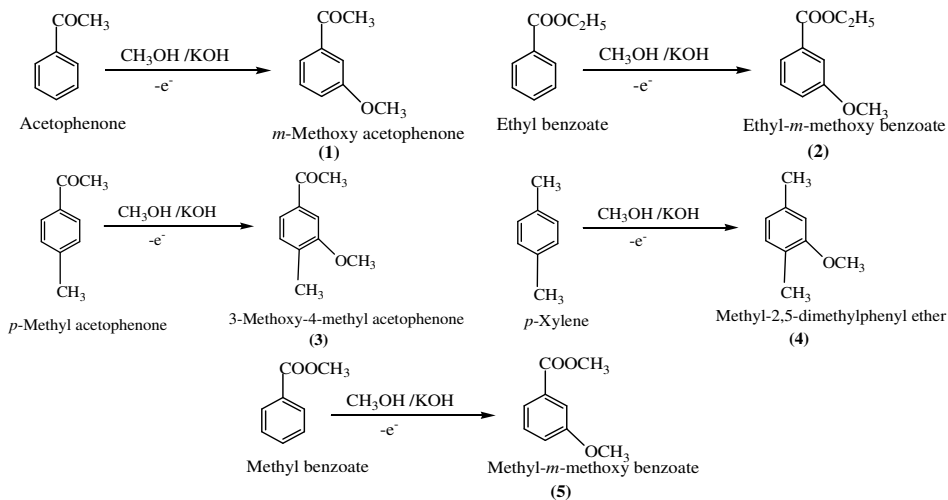


Scheme 1

The position of substitution in this free radical is similar to the substitution in the conventional organic chemical reaction. The relative reactivity's of the substrate can be compared with the rate of hydrogen atom abstraction from the same compounds in homogeneous reaction. It has been suggested that the methoxylation process involves reaction of an electrolytically generated radical with the substrate. This occurs by anodic discharge of methoxide ions to give methoxyl free radicals.

Analysis of the products

As per mechanism following products were obtained. The physical and analytical data of all the compounds were collected and presented. The spectral (IR, ¹H NMR, ¹³C NMR and MS) and analytical data are in good agreement with their structures.



Scheme 2

Conclusion

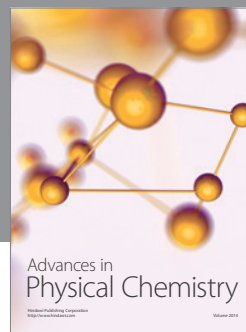
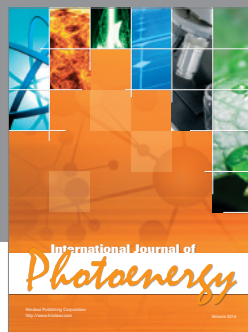
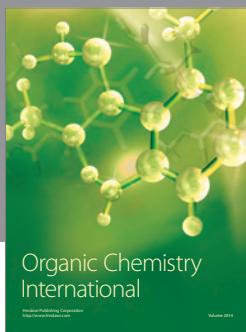
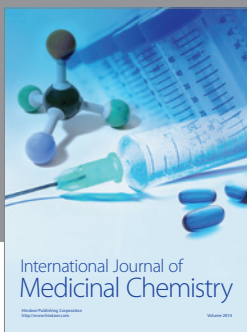
The special feature of our electrochemical substitution is that the reaction takes place at room temperature and the reaction does not require hazardous chemicals and reagents. The reaction is simple and environmentally benign; it is a part of green chemistry.

Acknowledgment

The author thanks to UGC, New Delhi for the financial assistance and Sophisticated Analytical Instrumentation Facility (SAIF), a division of CDRI, Lucknow for providing spectral and analytical data.

References

1. Clauson-Kass N, Limborg F and Glens K, *Acta Chem Scand*, 1952, **06**, 531.
2. Mann C K and Barnes K K, *Electrochemical Reactions In Non aqueous Systems*, Marcel Dekker, Inc. New York, 1970.
3. Fry A J, *Synthetic Organic Electrochemistry*, 2nd Ed., Wiley-Interscience Publication, New York, 1989.
4. Shono T, *Electroorganic Synthesis*, Academic Press Ltd., London, 1991.
5. Sharma L K, Kumar S, Yadav P and Singh R K P, *Indian J Chem*, 2008, **47B**, 1277.
6. Kumar S and Singh R K P, *J Indian Chem Soc*, 2005, **82**, 934.
7. Singh S, Kumar S, Sharma L K and Singh R K P, *J Indian Chem Soc*, 2009, **86**, 734-738.
8. Kumar S, *J Korean Chem Soc*, 2009, **53**, 159.
9. Sharma L K, Kumar S, Singh S and Singh R K P, *Russian J Electrochem*, 2010, **46**, 37.
10. Kumar S, Yadav P and Singh R K P, *Transactions of the SAEST*, 2006, **41**, 48.
11. Bockmain G and Fritz H P, *Electrochim Acta*, 1976, **21**, 1099.
12. Parker V D, Dirlan J P and Ebersson L, *Acta Chem Scand*, 1971, **B25**, 341.
13. Shono T, *Electroorganic Synthesis*, Academic Press Ltd., London, 1991, 38.
14. Weinberg N L and Belleau B, *Tetrahedron*, 1973, **29**, 279.
15. Evans D A, Tanis S P and Hart D J, *J Am Chem Soc*, 1981, **103**, 5813.
16. Inoue T, Koyama K, Matsuoka T, Matsuoka K and Tsutsumi S, *Tetrahedron Lett*, 1963, 1409.
17. Inoue T, Koyama K, Matsuoka T, Matsuoka K and Tsutsumi S, *Kogyo Kagaku Zasshi*, 1963, **66**, 1659.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

