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Research Article

ELECTROCHEMICAL DEOXIMATION OF SUBSTITUTED BENZALDOXIMES USING POTASSIUM PERCHLORATE MEDIATOR

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ABSTRACT

Deoximation of substituted benzaldoximes in biphasic medium yields the corresponding carbonyl compound. The reaction has been carried out in a beaker with platinum electrodes at room temperature using an aqueous potassium perchlorate solution containing a catalytic amount of sulphuric acid. The electrolysis results in good yields.

Keywords: Deoximation, potassium perchlorate, substituted benzaldoximes, carbonyl compounds.

INTRODUCTION

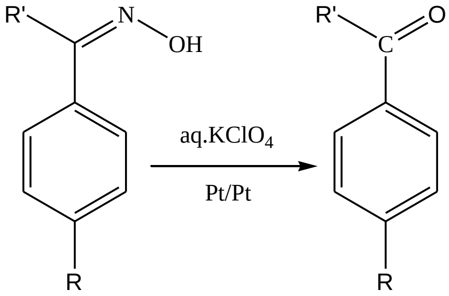
The environmental impact of electrochemistry needs to be assessed by looking at the global cell reaction. Oxidative electrochemical technologies offer an alternative solution to many environmental problems in the industry, because electrons provide a versatile, efficient, cost-effective, easily automatable, safe and clean reagent.[1,2]

Oximes are very useful in organic chemistry as protecting groups and synthetic intermediate for producing amines[3] and nitriles.[4] These highly crystalline compounds can be prepared from carbonyl and non-carbonyl compounds.[5,6] They are used for purification and characterization of aldehydes and ketones. The regeneration of carbonyl compound from oxime provides an alternative method for the preparation of these compounds. They act as good intermediate for many reactions such as the preparation of amides by Beckmann rearrangement.[7] Oximes play an important role in various fields such as crystal engineering, pharmaceuticals, polymer sciences etc. Naturally occurring oximes are rare; a discovery of such type is lycoposerramine-B. Katakawa *et al*.[8] have reported the presence of an oxime alkaloid in Lycopodium, which produces structurally complex alkaloids and potent acetylcholine esterase inhibitors.[9]

The deoximation of aromatic oximes to corresponding aldehydes have been investigated with catalyst 2,6-Dicarboxypyridinium chlorochromate,[10] Poly [N-(4-pyridiniumdichromate)-*p*-styrenesulphonamide],[11] titanium silicate,[12] bismuth trichloride,[13] $K_3[Fe(CN)_6].3H_2O$,[14] Perumal *et al*.[15] have reported a method for the cleavage of oximes[16] to carbonyl compounds using readily available urea nitrate in acetonitrile-water (95:5) medium, under microwave irradiation, in 80-95% yield. Quaternary salts of pyridoxal oxime[17] have been synthesized by the quaternization of pyridoxal oxime with substituted phenacyl bromides using microwave heating. Microwave-assisted rapid synthesis was done both in solvent (acetone) and under solvent-free conditions. Aromatic and aliphatic oximes have been deoximated in chloroform-water to the corresponding aldehydes with dilute hydrogen peroxide and triscetylpyridinium tetrakis(oxodiperoxotungsto) phosphate[18] as catalyst.

A wide array of readily prepared pivalates of ketoximes converted to the corresponding ketones in good yields by treatment with iron powder in THF containing catalytic amounts of both trimethylsilyl chloride and glacial acetic acid[19] at room temperature. Zheng *et al.* have reported oxidation of oximes to the corresponding ketones and aldehydes with manganese dioxide catalyzed by kieselguhr[20] under solvent-free conditions. A reusable catalytic system for a facile deprotection of oximes to corresponding carbonyl compounds, using TBHP as the oxidant over $CeO_2–ZrO_2$ catalyst, under solvent-free reaction conditions.[21]

Recently, we reported that the conversion of aromatic oximes to corresponding aldehydes[22] in good yield through a biphasic electrolysis using potassium perchlorate mediator. On extension of the work, Herein, we report on electrochemical deoximation of substituted benzaldoximes to corresponding carbonyl compounds using potassium perchlorate as a mediator with Pt/Pt electrode combination as shown in scheme 1.



R=H, CH_3, phenyl, iso-propyl, NO_2
R'= H, CH_3, phenyl
Scheme 1: Deoximation of substituted oximes using perchlorate in biphasic medium

MATERIALS AND METHODS

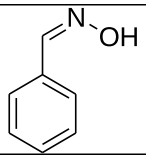
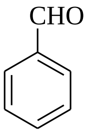
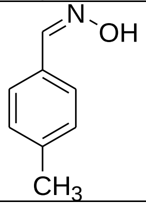
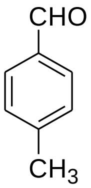
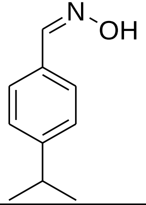
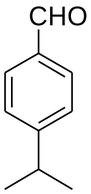
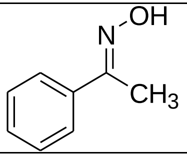
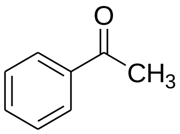
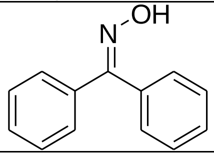
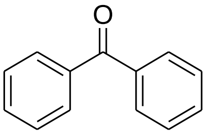
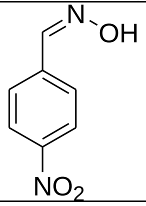
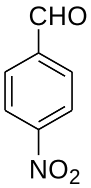
The chemicals used in the present study were purchased from Alfa aesar. High purity solvents were used. For all the experiments double distilled water was employed. For the direct current source for electrolysis an Aplab power source was used. The electrolytes were prepared by using deionised water. Two platinum sheets each of 15 cm^2 area were used as the electrodes. Shimadzu HPLC with LC-8A column (250 mm×4.6 mm) as the stationary phase. The eluent consisted of acetonitrile/water (60:40) at flow rate of 1mL/min. Samples were analysed by UV detector at a wavelength of 254 nm.

A solution of substrate (substituted benzaldoximes) (1.0 g, 10 mmol) in chloroform (25 mL) was taken in a beaker. To the solution 90 mL of potassium perchlorate (3.0 g, 21.6 mmol) containing 10.2 mmol (1 g) sulphuric acid was added. The aqueous upper layer contained the potassium perchlorate as a mediator and sulphuric acid to maintain acidic medium and for conductivity purpose. The substrate was present in the lower organic phase. Then two platinum electrodes (each of 15 cm^2 area) were introduced into the aqueous phase till they just touched the organic phase. The electrode distance was maintained at 2 cm. The magnetic stirring was kept at the rate of 60 rpm. The electrolysis was conducted galvonostatically at a current density of 50 mA cm^{-2} while maintaining the temperature at 30-40°C. After passing 2-6 F charge per mole of substrate, the stirring was stopped. The lower organic phase containing the product was separated by separating funnel. The aqueous phase was washed twice with chloroform (2×25 mL) and dried over anhydrous sodium sulphate and the solvent was removed by distillation. The reaction was monitored by a HPLC and Thin layer chromatography (TLC). By designing and optimizing the electrolysis conditions, high yields of desired products were achieved. All yields refer to isolated product.

RESULTS AND DISCUSSION

The electrochemical deoximation of substituted benzaldoximes to corresponding carbonyl compounds were carried out using potassium perchlorate as a mediator at room temperature. The charge was passed between 2-6 F/mol to identify the maximum yield of the products. Table 1 contains the results obtained for the deoximation of substituted benzaldoximes.

Table 1: Electrochemical deoximation of substituted benzaldoximes

S.No.	Substrate	Charge passed (F/mol)	Product	Yield (%)	Current efficiency (%)
1		6		80	26
2		6		78	26
3		6		53	17
4		6		77	25
5		6		63	21
6		6		49	16

The following are the findings of the study

- ✓ Static nature of *p*-tolualdehyde oxime resulted 78% yield of the product. On the other hand the less static nature of cuminaldehyde oxime resulted in the formation of only 53% of cuminaldehyde (entry 2 and 3).
- ✓ The acetophenone and benzophenone oximes (entry 4 and 5) gave the corresponding ketones 77% and 63% respectively. The low yield with respect to benzophenone oxime is due to the steric nature of the phenyl group. Comparing the yields of ketones, acetophenone shows more yields (77%) than benzophenone (63%).
- ✓ *p*-nitrobenzaldehyde gave very low yields 49% (entry 6) when compared to benzaldehyde oxime. It may be due to the highly deactivating nature of nitro-group at para- positions.

CONCLUSION

In conclusion, the main advantages embrace the increase in selectivity deoximation of substituted benzaldoximes to the corresponding carbonyl compound products, a decrease in energy consumption due to acceleration of electrode reactions and the most important, a decrease in negative environmental effect due to a substantial decrease in amounts of side products. These advantages create the prerequisites for the application of organic electrosynthesis on industrial scale. On the whole, the proposed electrochemical process and reaction setup are simple and contribute to an extent as a greener synthesis.

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