

A mild and efficient method for the oxidation of benzylic alcohols by two-phase electrolysis

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Received 5 January 2007; revised 14 March 2007; accepted 22 March 2007

Available online 25 March 2007

Abstract—Electrochemical oxidation of benzylic and substituted benzylic alcohols by two-phase electrolysis yields the corresponding aldehydes as products. The reaction was carried out in a single compartment cell with platinum electrodes at room temperature in chloroform using an aqueous sodium bromide solution (25%) containing a catalytic amount of HBr. The two-phase electrolysis resulted in high yields (74–96%) of benzaldehyde from primary alcohols and secondary alcohols were oxidized to the corresponding ketone but only in low yields under these conditions.

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The oxidation of alcohols is an important transformation in laboratory and industrial synthetic chemistry, as the corresponding carbonyl compounds can be used as important and versatile intermediates for the synthesis of fine chemicals.^{1–3} Numerous oxidizing reagents such as chromium(VI) oxide, permanganates, ruthenium(VIII) oxide and dichromates have been employed to accomplish these transformations. Most of these reagents are, however, required in stoichiometric quantities which results in the production of large amounts of environmental waste.^{4–6} The oxidation of alcohols with molecular oxygen using transition metal salts of V,⁷ Co,⁸ Cu,⁹ Mo,¹⁰ Ru,¹¹ Rh,¹² Pd¹³ and polyoxometalates¹⁴ as catalysts has also been reported. Most of these systems catalyze the oxidation of primary as well as secondary alcohols to give the corresponding aldehydes and ketones. The selective oxidation of primary alcohols to aldehydes is crucial for the synthesis of fine chemicals such as fragrances or food additives.¹⁵

In recent years, electroorganic synthesis has attracted attention as an environmentally friendly process, because electrons are inherently environmentally friendly reagents compared with conventional oxidizing and reducing reagents. Earlier Tomov and Jansson¹⁶ oxi-

dized alcohols with electro-generated hypobromite as an emulsion using a quaternary ammonium salt as the phase-transfer agent. As the electrolysis was conducted in an emulsion phase, the voltage was high due to the poor electrical conductivity of the organic solvent and ultimately the process was not economic. Recently, nitroxyl radicals, that is, *N*-oxyl compound-mediated electrooxidation of alcohols, has been reported.^{17–19} In these processes, costly reagents were used as mediators along with the catalyst.

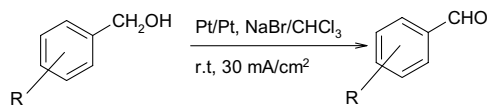
Two-phase electrolysis has a distinct advantage over conventional homogeneous electrolysis in practical electroorganic synthesis. In homogeneous systems, lower selectivity is observed due to over-oxidation of the substrate on the surface of the electrode leading to a mixture of products. In two-phase electrolysis systems, the reactive species formed by electrolytic oxidation of a halide ion in the aqueous phase, can be taken continuously into the organic phase, and then reacted with the substrate selectively to give the products. After completion of the electrolysis, separation and evaporation of the organic layer affords the product.

Presently, only a few reports on two-phase electrolysis are available for electroorganic syntheses of fine chemicals. Recently, we reported that a two-phase electrolytic system can be used readily to convert alkyl aromatic compounds to monobromo derivatives in quantitative yields.²⁰ We have further studied its application for the

Keywords: Benzyl alcohol; Oxidation; Two-phase electrolysis.

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oxidation of alcohols and herein report a mild and efficient method for the selective oxidation of alcohols to the corresponding aldehydes using electrochemically generated hypobromous acid.



Scheme 1. Electrochemical oxidation of benzylic alcohols by two-phase electrolysis.

Hypobromous acid is an inexpensive reagent and can be generated in situ by electrochemical oxidation of bromide ions in the presence of HBr. The two-phase electrolysis system consists of a 25% NaBr solution containing a catalytic amount of HBr (5%) as the aqueous phase and chloroform containing the alcohol as the organic phase. Using this system, benzylic and substituted benzylic alcohols were oxidized to the corresponding aldehydes at room temperature in a single compartment cell in high yields (Scheme 1).²¹ The yields of the products are listed in Table 1. Under these conditions, the formation of the benzaldehyde hydrate and its interaction with electro-generated hypobromite is slow

Table 1. Electrochemical oxidation of alcohols using a two-phase electrolysis system

Entry	Reactant	Product	Yield ^a (%)	Charge passed (F/mol)	Current efficiency (%)
1			96	5.5	37
2			94	5.0	36
3			90	5.5	33
4			95	6.0	36
5			85	4.0	44
6			74 ^b	2.0	74
7			96	3.0	71
8			80	4.0	40
9			0	6	—
10	CH ₂ (CH ₂) ₆ CH ₂ OH	CH ₃ (CH ₂) ₆ CHO	22 ^c	6	8
11	CH ₂ (CH ₂) ₄ CH ₂ OH	CH ₂ (CH ₂) ₄ CHO	13 ^c	6	4
12			11	6	4
13			30	6	10
14			30	6	10

^a Isolated yield.

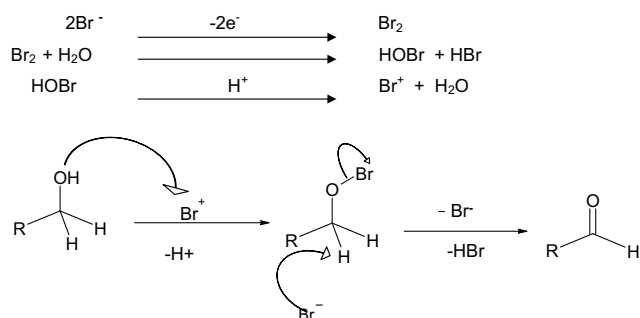
^b 7% of 3-bromo-*p*-anisaldehyde was obtained along with 15% of starting material.

^c Analyzed by GC, isolated as bisulfate adduct.

enough on the electrolysis time scale to minimize oxidation to the corresponding acid. We observed smooth oxidation of benzylic alcohols substituted with electron-donating groups such as $-\text{CH}_3$, $-\text{OCH}_3$, $-t$ -butyl (entries 5–7) with 2–4 F/mol of current, while alcohols substituted with electron-withdrawing groups (entries 2–4) required 4–6 F/mol. The highly deactivating NO_2 -substituted benzyl alcohol did not react at all. Primary aliphatic alcohols were allowed to react under these conditions but only low yields of the corresponding aldehydes were obtained (entries 9 and 10). The secondary alcohol, 1-phenylethanol, was less reactive affording the corresponding ketone in only 11% yield. This study reveals that this method can be applied to the selective oxidation of benzylic alcohols in the presence of secondary hydroxyl groups.

A possible mechanism for the oxidation, based on a literature report, is outlined in Scheme 2.²² As the electrolysis proceeds, the bromide ion is oxidized at the anode to bromine which, on hydrolysis, results in the formation of hypobromous acid and HBr. The unstable hypobromous acid forms Br^+ due to its ionic nature which subsequently oxidizes the alcohol to the corresponding aldehyde, (Scheme 2).

Considering the oxidation of benzyl alcohol to benzaldehyde as a model reaction, various electrode materials were studied to determine the effectiveness of the electrode for the oxidation of bromide ions (Table 2). Even though the other electrodes did not perform as well as Pt, commercially available graphite works quite well affording an yield of 89% benzaldehyde along with 8% of recovered benzyl alcohol.



Scheme 2.

Table 2. Efficiency of the electrode for the oxidation

Entry	Electrode		Benzaldehyde yield (%)
	Anode	Cathode	
1	Platinum	Platinum	96
2	Graphite	Platinum	92
3	Dimensionally stable anode (DSA)	Platinum	90
4	Graphite	Stainless steel	85
5	Graphite	Graphite	89

Current density = 30 mA/cm², charge passed = 5.5 F/mol, temperature = rt, agitation rate = 40–80 rpm.

In conclusion, this electrochemical method for the oxidation of benzylic alcohols to the corresponding benzaldehydes in excellent yields using in situ prepared hypobromous acid via a two-phase electrolysis constitutes a novel and an efficient alternative procedure to traditional oxidation. Easy separation of the product, a simple work-up, room temperature reaction conditions, and the reuse of the electrolyte are advantages of this two-phase electrolysis procedure.

Acknowledgements

The authors thank Professor A. K. Shukla, Director, Central Electrochemical Research Institute, Karaikudi 630 006, India and Shri. V. M. Shanmugam for Providing NMR analysis and facilities.

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- Representative procedure for the electrochemical oxidation of benzylic alcohol*: A solution of 4-methylbenzyl alcohol (Table 1, entry 5) (1.22 g, 10 mmol) in 25 ml of chloroform was taken in a beaker-type undivided cell. To the above

solution, a 25% aqueous sodium bromide solution (50 ml) containing 5 ml of HBr (46% solution, 30 mmol) was added. Two platinum electrodes each of 10 cm² area were placed in the upper layer of the aqueous phase. The organic phase alone was stirred with a magnetic stirrer at a rate of 40 rpm in such a way that the organic layer did not touch the electrodes. The electrolysis was conducted galvanostatically at a current density of 30 mA/cm² until the quantity of charge indicated in Table 1 was passed. The extent electrolysis was monitored by HPLC using a Shimpack ODS-18 column (120 × 4.5 mm) as the stationary phase. The eluent consisted of methanol/water (70:30) at a flow rate of 1 ml/min. The samples were analyzed

using a UV detector at a wavelength of 254 nm. After completion of electrolysis, the lower organic phase was separated, washed with sodium thiosulfate solution followed by water (2 × 25 ml), dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The HPLC spectrum of the crude mixture showed the presence of 88% of 4-methylbenzaldehyde along with 10% of the starting material and some minor impurities. The crude product was passed through a column of silica gel (60–120 mesh) and eluted with a mixture of ethyl acetate/*n*-hexane (1:9) to afford the pure product (1.0 g; 85%).

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