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BRIEF COMMUNICATIONS

Oxidation of Alcohols by Iodine in the Presence of Nitroxyl Radicals Generated Electrochemically

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Abstract—Oxidation of primary and secondary alcohols in the two-phase system of methylene chloride–aqueous solution of sodium hydrocarbonate in the presence of the mediator system of potassium iodide–nitroxyl radical was studied. It is supposed that under these conditions the iodonium ion generated on a platinum electrode is the primary oxidizing agent.

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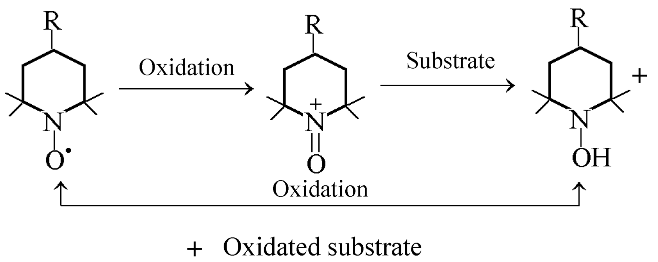
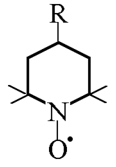
Selective oxidation of alcohols up to aldehydes is one of the oldest problems of organic synthesis. An examination of published data shows that the most promising is the method of alcohols oxidation using a catalytic system containing a nitroxyl radical of the 2,2,6,6-tetramethylpiperidine series and an inexpensive primary oxidizing agent, for example a hypochlorite or other oxidizing agents including anodic oxidation of a nitroxyl radical [1, 2]. The pathway of the oxidation of organic compounds using nitroxyl radicals as catalysts is shown in scheme 1.

Scheme 1.



However in some cases the application of such strong oxidizing agents as NaOCl is unacceptable, as it can give rise to the oxidation of other functional groups or to the halogenation of a substrate [3]. The oxidation of alcohols can be carried out in mild conditions in the presence of crystalline iodine and a nitroxyl radical. A disadvantage of this method is a considerable iodine consumption (2 mol of iodine per 1 mol of alcohol) and the formation of coproducts (potassium iodide) [3].

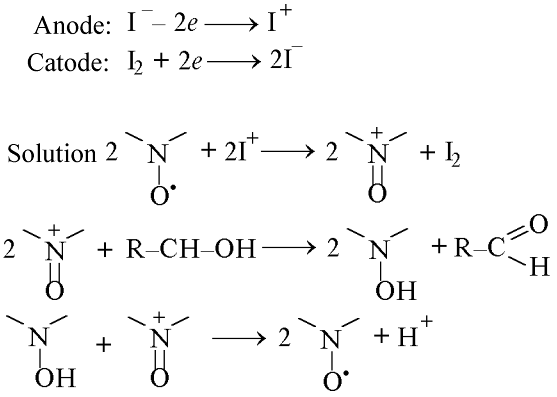
In the present work we have offered the electrochemical procedure for the oxidation of primary and secondary alcohols up to corresponding carbonyl compounds with application of the two-mediator system of nitroxyl radical (I-III) - potassium iodide:



I: R=$NHCOCH_3$
II: R=$NHCOC_6H_5$
III: R=$OCOC_6H_5$

It is known that in the case of electrochemical oxidation of alcohols in the presence of only potassium iodide primary alcohols are oxidized up to ethers of acids and secondary alcohols - up to corresponding ketones. In this case the iodonium ion is the oxidizing agent [4, 5]. It was found that the presence of a catalytic amount of a nitroxyl radical of the 2,2,6,6-tetramethylpiperidine series changes radically the reaction direction. Primary alcohols in this case are oxidized only up to corresponding aldehydes. A possible mechanism of the reaction of alcohols oxidation by the system nitroxyl radical - potassium iodide is shown in Scheme 2.

Scheme 2.



It is possible that the role of the primary oxidizing agent can be also played by other products of the electrochemical transformations of the iodide anion (I_2 and I·), which can oxidize the nitroxyl radical up to the oxoammonium cation [6].

Electrochemical oxidation of alcohols in presence of the mediator system of potassium iodide–4-acetylamino-2,2,6,6-tetramethylpiperidine-l-1-oxyl (**II**) in the two-phase system of methylene chloride–aqueous solution of 0.6 M $NaHCO_3$ (pH 8.6.)

The data on the electrochemical oxidation of alcohols with application of the mediator system of nitroxyl radical (**I**)–(**III**)– potassium iodide are presented in the table. In all cases the structure of the nitroxyl radical practically did not affect the carbonyl compound yield. Differences in the yields of products did not exceed 5%.

The oxidation reaction was carried out in a two-phase system of organic solvent–water. As organic phases we used methylene chloride, toluene, and carbon tetrachloride. No essential differences in the reaction yields depending on the organic phase were observed.

The rate of the oxidation reaction substantially depends on the pH of medium. In an alkaline medium ($NaHCO_3$ solution) the reaction passes faster than in the neutral (see the table, experiments nos. 4 and 7) that confirms the mechanism proposed earlier for the oxidation of alcohols by oxoammonium salts [7]. It is connected with the fact that in the alkaline medium alcohol enters the reaction as an alkoxide.

The oxidation of alcohols in the presence of a smaller amount of the nitroxyl radical and potassium iodide (see the table, experiments nos. 3, 6, and 8) results in a decrease in the yield of the corresponding carbonyl compound (in terms of an initial alcohol).

Concentration of reagents, M: 0.05 alhohol/0.005 (10 mol %) (**II**)/0.01 (20 mol %) KI

Run no.[b]	Alcohol	Yield[a] of aldehyde of ketone (with respect to initial alcohol), %, at Q, Φ mol^{-1}	
		2	4
1	Benzyl	62.5	95 (85)[b]
2	Phenylethyl	60.3	90 (75)[b]
3	"	43.6	72
4	"	23.0	52
5	Cyclohexanol	48.7	85 (80)[c]
6	"	30.0	65
7	"	25.0	67
8	"	27.0	57
9	1-Butanol	42.0	85
10	1-Pentanol	46.5	89
11	2-Propanol	38.7	80

[a] By GLC data

[b] Experiments nos. 3 and 6: concentrations of reagents, M, is 0.05 alhohol/0.005 (10 mol %) (**II**)/0.005 (10 mol %) KI; experiments nos. 4 and 7: pH of electrolyte is 6.86 (buffer solution 0.05 M Na_2HPO_4 and 0.05 M KH_2PO_4); experiment no. 8: concentrations of reagents, M, is 0.05 alhohol/0.0005 (1 mol %) (**II**)/0.001 (2 mol %) KI.

[c] Yield of isolated product.

EXPERIMENTAL

In the experiments we used "Aldrich" reagents; 2,2,6,6-tetramethylpiperidine nitroxyl radicals were synthesized according to the procedures [8] by the oxidation of corresponding sterically-hindered piperidines. Reaction products were analyzed by the method of gas-liquid chromatography. The data of the chromatographic analysis (gas chromatograms) were obtained on an LKhM-8 MD chromatograph (detector katharometer; gas-carrier helium; column length 1.5 m, column diameter 3 mm; carrying agent Chromaton-N-AW; immobile phase PEG-4000; throughput rate of helium 4 ml/10 s; sensitivity 1 : 3). The content of products was determined by peak areas in the approximation of equal sensitivity coefficients of the detector to analyzed substances. Accuracy of measuring areas was 5 rel %. The thin-layer chromatography was carried out on Al_2O_3 (II degree of activity after Brockman, eluent CH_2Cl_2, developer I_2 vapor).

The technique of the electrochemical oxidation of alcohols using the mediator system of nitroxyl radical (**I**)–(**III**)–potassium iodide in the two-phase system of methylene chloride–$NaHCO_3$ aqueous solution (pH 8.6) was as follows.

An alcohol, 0.05 mol, dissolved in 30 ml of methylene chloride, $NaHCO_3$, 5 g (0.06 mol), and KI, 2 g (0.01 mol), dissolved in 70 ml of distilled water were poured in a 150 ml diaphragmless electrolyzer supplied with a mechanical stirrer, a water jacket, and two platinum electrodes (anode 20 cm^2, cathode 15 cm^2). Then 0.005 mol of the nitroxyl radical was added. Electrolysis conditions: temperature 20–25°, current strength of 0.5 A (anode current density 0.025 A cm^{-2}), maximal voltage on the electrolyzer 10 V, and intensive stirring. The synthesis was finished after passing 4 Φ mol^{-1} of electricity. After electrolysis termination the organic layer was separated. The aqueous layer was extracted with methylene chloride (2 × 50 ml), organic extract were merged and dried by anhydrous sodium sulfate. According to TLC, reaction mixtures contained two substances, an initial alcohol and an oxidation product. Contents of alcohol and aldehyde (ketone) were determined by the GLC method.

To isolate an aldehyde (ketone), the solvent was removed, and the residual was distilled in vacuo: cyclohexanone at 60–62°C (10 mm Hg); phenylacetic aldehyde at 78–79°C (10 mm Hg), and benzaldehyde at 62–63°C (10 mm Hg). The yield of the corresponding carbonyl compound was 75–85% (of isolated product).

CONCLUSIONS

The electrochemical oxidation of primary and secondary alcohols using the mediator system of a nitroxyl radical of the 2,2,6,6-tetramethylpiperidine series–potassium iodide results in the formation of aldehydes and ketones, respectively, with a high yield of the compounds.

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