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LETTERS TO THE EDITOR

One-Pot Electrochemical Synthesis of Acid Anhydrides from Alcohols

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Abstract—One-pot indirect electrochemical oxidation of alcohols in the methylene chloride–aqueous solution of sodium hydrocarbonate two-phase system in the presence of potassium iodide, 4-acetylamino-2,2,6,6-tetramethylpiperidin-1-oxyl, and 2,6-lutidine results in the formation of the corresponding acid anhydrides with yield up to 80%. The reaction occurs at room temperature and is complete after passing 6 F/mol of electricity.

Keywords: alcohol, electrochemical oxidation, carboxylic acid anhydride, nitroxyl radical, pyridine base

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We have earlier demonstrated that the oxidation of alcohols 1 with the 4-acetylamino-2,2,6,6-tetramethylpiperidin-1-oxyl (2)-iodine-pyridine catalytic system results in the formation of the corresponding symmetrical esters 3 in good yield [1]. In this study, we found that anhydride of the corresponding acid 5 is formed in up to 80% yield (along with the aldehyde 4 and ester 3) under the same conditions except for generation of iodine via electrochemical oxidation of iodide ions (Scheme 1).

Acid anhydrides form an important class of organic compounds, conventional synthesis of which includes several stages and requires the use of toxic reactants such as sulfuryl or thionyl chloride, phosgene, etc. Therefore, development of more convenient and green methods of anhydrides synthesis is a critical issue. To the best of our knowledge, the method suggested in this study is the first example of alcohols oxidation into anhydrides using nitroxyl radicals, even though examples of direct oxidation of alcohols and aldehydes into esters, amides, and nitriles have been reported [2–5].

The composition of the reaction products depended in the amount of electricity passed through the system and the nature of the used pyridine base (pyridine, 2,6lutidine, 2-methyl-5-ethylpyridine, 2,4,6-trimethylpyridine, or 4-acetylpyridine). 2,6-Lutidine was found the best catalyst in the reaction of indirect electrochemical oxidation of alcohols into the corresponding acid anhydrides. The changes in the composition of the reaction mixture in comparison with the oxidation with molecular iodine could be explained by the reactions in the electrolyte resulting in the formation of the acid. It







is known that the oxidation of alcohols with oxoammonium salts is accompanies by the formation of the corresponding acids upon even slight variation of the reaction conditions [6].

The suggested mechanism of the anhydride formation is shown in Scheme 2. In the course of the reaction, the oxoammonium salt **6** is reduced into the hydroxylamine **7**, oxidation of which yields the starting radical **2**, and the catalytic cycle is closed. The reaction occurred stepwise. At the first stage of alcohol **1** oxidation (after passing 2.2 F/mol of electricity), aldehyde **4** was formed in 95% yield. At the second stage, after passing 6 F/mol of electricity, aldehyde **4** was oxidized into the acid anhydride **5** with 100% yield (with respect to the reacted aldehyde, the conversion of the latter being 70 to 85%). If the corresponding aldehyde was used instead of the alcohol, the anhydride yield was 75% (100% with respect to the reacted aldehyde). After passing more than 6 F/mol of electricity, the reaction was slowed down, and side products were formed.

The suggested method of one-pot indirect electrochemical oxidation of alcohols was tested with a series of aliphatic, aromatic, and heteroaromatic alcohols (see the table).

Indirect electrochemical oxidation of alcohols with the 4-acetylamino-2,2,6,6-teteramethylpiperidin-1-oxyl-potassium iodide catalytic system in the presence of 2,6-lutidine^a

Alcohol	Composition of the reaction mixture after passing 6 F/mol of electricity, % ^b			
	aldehyde	ester	anhydride	acid
<i>n</i> -Hexanol	25.5	5.9	66.1	2.5
<i>n</i> -Heptanol	30.9	4.0	62.0	3.1
<i>n</i> -Octanol	13.3	4.1	80.6	2.0
<i>n</i> -Nonanol	28.6	6.0	62.7	2.7
2-Phenylethanol	78.5	7.2	9.5	4.8
Methoxybenzyl alcohol	98.0 ^c	0	0	0
2-Thiophenemethanol	97.0 ^c	0	0	0
5-Hydroxymethylfurfurol	75.0 ^d	0	0	0

^a The reaction conditions are given in the general procedure of alcohols oxidation. ^b Gas chromato–mass spectrometry data. ^c After passing 4 F/mol of electricity, 25% are the condensation products [7].

General procedure of alcohols oxidation. Electrolysis was performed in a membrane-free 150 mL electrolyzer equipped with a water jacket, thermometer, and mechanical stirrer. Anode (20 cm^2) and cathode (10 cm^2) were made of platinum plates.

Alcohol (0.04 mol), 4-acetylamino-2,2,6,6-tetramethylpiperidin-1-oxyl (0.004 mol, 0.85 g), and 0.004 mol of the corresponding pyridine base dissolved in 40 mL of methylene chloride were put in the electrolyzer. 0.06 mol (5.0 g) of NaHCO₃ and 0.01 mol (1.7 g) of KI dissolved in 80 mL of distilled water (pH of the aqueous phase 8.6) were then added. The synthesis was performed at current density 0.05 A/cm² (current 1 A) and was complete after passing 6 F/mol of electricity. After the reaction was complete, the electrolyte was treated with concentrated solution of sodium thiosulfate to remove excess of iodine. The aqueous and organic layers were separated. The aqueous layer was acidified with dilute hydrochloric acid to pH 5 and extracted with methylene chloride $(2 \times 20 \text{ mL})$; the organic phases were combined and analyzed by means of gas chromato-mass spectrometry as described elsewhere [1].

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REFERENCES

- Kashparova, V.P., Kashparov, I.S., Zhukova, I.Yu., Astakhov, A.V., Ilchibaeva, I.B., and Kagan, E.Sh., *Russ. J. Gen. Chem.*, 2016, vol. 86, no. 11, p. 2423. doi 10.1134/S1070363216110049
- Kelly, C.B., Lambert, K.M., Mercadante, M.A., Ovian, J.M., Bailey, W.F., and Leadbeater, N.E., *Angew. Chem. Int. Ed.*, 2015, vol. 54, p. 4241. doi 10.1002/anie.201412256
- Gaspa, S., Porcheddu, A., and De Luca, L., *Tetrahedron Lett.*, 2016, vol. 57, p. 3433. doi 10.1016/ j.tetlet.2016.06.115
- Reddy, K.R., Venkateshwar, M., Maheswari, C.U., and Prashanthi, S., *Synth. Commun.*, 2010, vol. 40, p. 186. doi 10.1080/00397910902838920
- 5. Das, R. and Chakraborty, D., *Catal. Commun.*, 2012, vol. 26, p. 48. doi 10.1016/j.catcom.2012.04.027
- Qiu, J.C., Pradhan, P.P., Blanck, N.B., Bobbitt, J.M., and Bailey, W.F., Org. Lett., 2012, vol. 14, p. 4034. doi 10.1021/ol301884a
- Kashparova, V.P., Klushin, V.A., Leontyeva, D.V., Smirnova, N.V., Chernyshev, V.M., and Ananikov, V.P., *Chem. Asian J.*, 2016, vol. 11, p. 2578. doi 10.1002/ asia.201600801