ISSN 1070-4272, Russian Journal of Applied Chemistry, 2006, Vol. 79, No. 12, pp. 2037–2038. © Pleiades Publishing, Inc., 2006. Original Russian Text © E.V. Pyatnitsyna, M.M. El'chaninov, A.P. Savost'yanov, 2006, published in Zhurnal Prikladnoi Khimii, 2006, Vol. 79, No. 12, pp. 2061–2062.

BRIEF COMMUNICATIONS

Electrolytic Reduction of 2-Butyne-1,4-diol as a Route to *trans*-2-Butene-1,4-diol

E. V. Pyatnitsyna, M. M. El'chaninov, and A. P. Savost'yanov

South-Russian State Technical University (Novocherkassk Polytechnic Institute), Novocherkassk, Rostov oblast, Russia

Received December 21, 2005; in final form, September 2006

Abstract—The effect of the cathode material on the electrochemical transformations of 2-butyne-1,4-diol at atmospheric pressure was studied by chromatographic analysis. The optimal parameters of the selective synthesis of *trans*-2-butene-1,4-diol were determined.

DOI: 10.1134/S1070427206120287

Among the starting compounds for preparing polyurethanes [1], detergents, alkyd resins [2], Endosulfan insecticide, plasticizers, and drugs [3], compounds containing the required functional groups are of particular importance. Among such compounds is 2-butene-1,4-diol (BED) whose synthesis by catalytic hydrogenation of 2-butyne-1,4-diol (BYD) yields a ~90 : 10 mixture of *cis* and *trans* isomers.

With the aim to examine the effect of the *trans* isomer on the properties of SKU-90 urethane rubber, we developed in this study a procedure for regioselective synthesis of *trans*-BED.

EXPERIMENTAL

Previously *trans*-BED has been prepared from divinyl via dihalo derivatives [4, 5] and diacetoxy-2butene [6, 7]. The drawbacks of these methods are multistep procedure, presence of isomers, and lacrimogenic properties of the intermediate dihalobutenes. Another pathway involves chemical reduction of BYD in a nitrogen atmosphere with chromium(II) sulfate [8]. However, such steps of this procedure as intermediate reduction of chromium(III) sulfate with zinc dust in a nitrogen atmosphere, followed by filtration (also in an inert atmosphere), prevent commercial implementation of the process.

To simplify the synthesis of the target product, we attempted electrochemical reduction of BYD in the

presence of $CrSO_4$ on stationary solid cathodes. In this case, the reduction of $Cr_2(SO_4)_3$ to $CrSO_4$ with hydrogen liberated at the cathode occurs in aqueous solution at atmospheric pressure:

$$2Cr^{3+} + H_2^0 \longrightarrow 2Cr^{2+} + 2H^+,$$
$$HOH_2C-C=C-CH_2OH \xrightarrow{2H^+, 2e} HOH_2C \xrightarrow{H} HOH_2C \xrightarrow{H} HOH_2C$$

To evaluate the qualitative and quantitative characteristics of the BYD transformation, we examined the effect of the cathode material on the electrolytic reduction. The electrolysis conditions were as follows: catholyte temperature $20-60^{\circ}$ C, pH 2–3, cathodic current density 0.02 A cm⁻², BYD concentration 1.16 M, and cromium(III) sulfate concentration 0.2 M. The amount of electricity passed was 300% of that required theoretically for complete conversion of BYD into *trans*-BED.

The electrolytic reduction of BYD occurs on all the electrodes examined, but only on lead cathodes the BED yield based on BYD is reasonably high (see table), 60–70%, with 98–99% selectivity with respect to the desired product and 97–98% isomeric purity. Electrolysis on porous stainless steel provides high selectivity with respect to the desired product, but its yield based on BYD is lower. With copper, nickel,

Cathode material	BYD conversion	BED yield based on BYD	Selectivity with respect to trans-BED
	%		
Smooth Cr18Ni10Ti steel	66.8	12.2	13.5
Copper	90.0	32.5	33.7
Porous Cr18Ni10Ti steel	62.5	42.5	100.0
Nickel	31.5	17.3	18.1
Lead	99.2	66.1	98.8
Zinc	72.6	15.5	23.7
Iron	64.0	17.3	18.0

Effect of cathode material on electrolytic reduction of BED

zinc, and iron cathodes, both the product yield and the selectivity of the cathodic reduction were low (see table).

For the electrochemical synthesis we used a cell in the form of a cylindrical glass vessel (serving as a cathode chamber) with a temperature-control jacket. The vessel lid had opening for the anode chamber, thermometer, current lead to the cathode, and stirrer. The cathode and anode compartments were separated by a porous tubular diaphragm with a blind bottom. The anode was platinum, the anolyte was 15% sulfuric acid, and the catholyte was purified BYD in 0.2 M chromium(III) sulfate.

To purify BYD, a commercial solution of BYD was boiled with activated charcoal to remove tars. The resulting solution was evaporated in a vacuum, and BYD was crystallized from a mixture of ethyl acetate with methylene chloride.

The initial and final reaction products were analyzed with a Tsvet-104 chromatograph under the following conditions: column length 2.0 m, inside diameter 3 mm; carrier gas nitrogen; column temperature $60-200^{\circ}$ C; support Chromaton Super 0.16-0.20 mm; stationary phase polyethylene glycol 15000. For better separation of *cis*- and *trans*-BED, the samples were acetylated by the procedure described in [9].

The reaction product was isolated as follows. After the disappearance of the initial BYD from the chromatogram, the contents of the cathode chamber were neutralized with a concentrated ammonia solution to pH 8–9, after which the precipitate of chromium(III) hydroxide was filtered off on a Büchner funnel. Water was distilled off from the filtrate in a water-jet-pump vacuum under heating on a water bath. The residue was distilled in a vacuum (10 mm Hg), and the fraction boiling at 125–127°C was collected. The yield of *trans*-BED was about 66%. The isomeric purity of the product exceeded 98%.

CONCLUSIONS

(1) Electrolytic reduction of butyne-1,4-diol on a lead cathode is a stable process at $20-60^{\circ}$ C and cathodic current density of 10-90 A dm⁻².

(2) The lowest amount of the passed electricity ensuring complete reduction of butyne-1,4-diol is 2.5 A h per gram of the starting compound; the current efficiency by 2-butene-1,4-diol is 53%.

(3) Freshly prepared $Cr_2(SO_4)_3$ solution can be used repeatedly without a decrease in the yield of *trans*-2-butene-1,4-diol.

REFERENCES

- Sokol'skii, D.V., Pak, A.M., and Ten, E.I., in *Doklady IV Vsesoyuznoi konferentsii po khimii atsetilena* (Proc. IV All-Union Conf. on Acetylene Chemistry), Alma-Ata: Inst. Khim. Nauk Akad. Nauk Kaz. SSR, 1972, vol. 3, pp. 254–259.
- 2. FRG Patent 2412341.
- 3. Mel'nikov, N.N., *Khimiya i tekhnologiya pestitsidov* (Chemistry and Technology of Pesticides), Moscow: Khimiya, 1974.
- Stepanov, N.A., Ovchinnikova, T.F., Kryukov, S.I., et al., in Osnovnoi organicheskii sintez i neftekhimiya: Mezhvuzovskii sbornik nauchnykh trudov (Basic Organic Synthesis and Petroleum Chemistry: Intercollegiate Coll. of Scientific Works), Yaroslavl: Yaroslav. Politekh. Inst., 1975, issue 4, pp. 39–43.
- 5. JPN Patent 51-18927.
- 6. JPN Patent 12333.
- 7. JPN Patent 56-18584.
- 8. Castro, C.E., J. Am. Chem. Soc., 1961, vol. 83, pp. 3262–3267.
- 9. Dorofeenko, T.N., Zhdanov, Yu.A., Dumenko, V.I., et al., *Khlornaya kislota i ee soedineniya v organicheskom sinteze* (Perchloric Acid and Its Compounds in Organic Synthesis), Rostov-on-Don: Rostov. Gos. Univ., 1965.