ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 8, pp. 1428−1430. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.V. Pyatnitsyna, M.M. El'chaninov, A.P. Savost'yanov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 8, pp. 1328−1331.

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Procedures for Recovery of Crystalline 2-Butyne-1,4-diol from Industrial Aqueous Solutions and for Its Purification

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Received December 22, 2008

Abstract—Four procedures for recovery of crystalline 2-butyne-1,4-diol from aqueous solutions and for its purification were examined. Samples of crystalline 2-butyne-1,4-diol containing 98.5 to 99.9 wt % target product were obtained.

DOI: 10.1134/S1070427209080205

1,4-Butynediol (BYD) is a valuable compound for electroplating and for synthesis of widely used polymeric materials, medicines, and household chemical products. The commercial procedure for BYD production (Reppe method) is based on condensation of acetylene with formaldehyde on a copper–bismuth catalyst [1]. Commercial BYD is produced as solution containing no more than 60% main substance. It also contains impurities of intermediates and by-products of the alkynol synthesis and tars (the figure a, Table 1).

Because of stringent requirements imposed upon the quality of BYD-based monomers, it seemed topical to check various procedures for BYD recovery and purification with the aim of their subsequent use in commercial or laboratory processes.

EXPERIMENTAL

Let us consider four procedures for preparing purified BYD from aqueous solutions containing condensation products of acetylene and formaldehyde (Table 2).

(1) Extraction with organic solvents. To recover BYD, we used organic solvents immiscible with water. With respect to the extraction efficiency, they can be ranked in the following order: ethyl acetate > chloroform > benzene > carbon tetrachloride. The extraction allows the formaldehyde content in the product to be decreased by an order of magnitude (the figure b), but the amounts of methanol and propargyl alcohol remain virtually unchanged. The other drawbacks of this method are considerable (50–70 ml g^{-1} BYD) consumption of the organic solvent for the product recovery and low yield of BYD due to its high solubility in water.

(2) Vacuum distillation. The process is performed in two steps. In the first step, water and low-boiling impurities are removed in a vacuum, and the second step involves vacuum distillation of BYD. Analysis of the product obtained shows that distillation allows removal of major amounts of formaldehyde, methanol, and propargyl alcohol (the figure c, Table 1). Apparently, formaldehyde and propargyl alcohol may be formed in certain amounts at the end of distillation, owing to partial decomposition of the bottom residue. The advantages of this process are low (d 3 wt %) total loss of BYD with the water fraction and due to tarring, and also the possibility of preparing the product without using organic solvents.

When performing the process, it should be taken into account that BYD can decompose with explosion in the presence of alkaline impurities and heavy metal salts [2, 3]. Therefore, exhaustive distillation of the product should be avoided.

(3) Distillation–recrystallization. To prepare samples of increased quality, vacuum-distilled BYD was recrystallized from ethyl acetate–ether. Instead of ether, other compounds poorly dissolving BYD can be used, in particular, benzene, chloroform, methylene chloride, and other chlorinated hydrocarbons. Recrystallization allows the product quality to be improved (the figure d, Table 2). In particular, the content of formaldehyde and propargyl alcohol is decreased, and methanol is fully removed.

(4) Purification with activated carbon and crystallization. To eliminate vacuum distillation and the corresponding explosion hazard, a procedure was developed for BYP purification by boiling the commercial product with activated carbon. The solution purified to remove tars was vacuum-evaporated and crystallized under the conditions similar to those of procedure 3. Chromatographic analysis of the product obtained revealed increased (compared to distillation) content of propargyl alcohol which cannot be efficiently removed by this procedure. At the same time, simple implementation, safety, and high yield of BYD make this procedure quite acceptable for preparative purposes.

The starting chemicals were 2-butyne-1,4-diol solution [TU (Technical Specification) 64-5-52–79], distilled water [GOST (State Standard) 6709–72], ethyl acetate, and benzene.

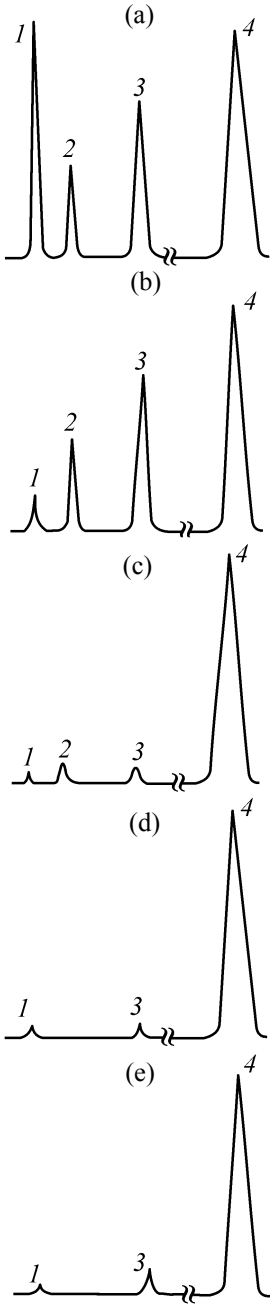
Chromatographic analysis was performed with a Tsvet-104 device (column length 2.0 m, inside diameter 3 mm, carrier gas nitrogen, column temperature 60–200°C, support Chromaton Super 0.16–0.20 mm, stationary phase polyethylene glycol 15000).

(1) Extraction with ethyl acetate. In a 1-l separating funnel, 500 ml of BYD was extracted with 3–4 250-ml portions of ethyl acetate. The extracts were combined, and the solvent was distilled off first at atmospheric pressure and then in a vacuum (10–20 mm Hg).

(2) Vacuum distillation was performed on a laboratory installation consisting of a still heated with Wood's alloy, a dephlegmator, a capillary, a condenser, and a receiving flask. The water fraction was distilled off at a pressure of 20 mm Hg and bath temperature not exceeding 120°C. The remaining crude BYD was distilled at a pressure of 13 mm Hg and bath temperature not exceeding 180°C. To prevent BYD crystallization, the temperature of water fed to the condenser jacket was no less than 70°C.

(3) To 100 g of BYD prepared by vacuum distillation, we added 400 ml of ethyl acetate and refluxed the mixture until the BYD dissolved. The flask was cooled to 40°C, and 400 ml of ether was added with stirring. In so doing, BYD precipitated as snow-white crystals. For complete precipitation, the flask was cooled for 2–3 h at 0°C with intermittent stirring of the contents, so as to prevent agglutination of the crystals. The BYD precipitate was filtered off on a Bьchner funnel and washed with 100 ml of ether. The product was dried in a vacuum oven at room temperature.

(4) In a 1-l Erlenmeyer flask, 800 ml of a 50% aqueous solution of BYD was boiled with 20 g of OUB activated carbon for 5–10 min, after which the carbon was filtered off on a Bьchner funnel. If necessary, the procedure was repeated 2–3 times to obtain a light yellow filtrate. The clarified solution was placed in a 1-l round-bottomed flask,



Chromatograms of BYD of various extents of purity: (a) aqueous solution of products of BYD synthesis; BYD: (b) prepared by extraction, (c) prepared by vacuum distillation, (d) prepared by vacuum distillation followed by crystallization, and (e) purified by boiling with activated carbon followed by crystallization. Peaks: (*1*) formaldehyde, (*2*) methanol, (*3*) propargyl alcohol, and (*4*) BYD.

Table 1. Vacuum distillation of aqueous solution of 1,4-butynediol

Solution	Conditions			Amount		Weight fraction of components, %					
	τ, min	*P*, mm Hg	*T*, °C	g	%	BYD	propynol	Methanol	formaldehyde	water	tars
Initial mixture	–	–	–	55.15	100	57.38	0.29	0.04	1.49	39.65	1.15
Water fraction	40	20	115	22.87	41.40	0.17	0.70	0.05	3.59	95.49	–
BYD fraction	25	13	145	30.78	55.81	99.74	0.06	0.03	0.06	0.11	–
Bottoms	–	–	–	1.54	2.79	–	–	–	–	–	–

Table 2. Preparation of purified 1,4-butynediol

Procedure for recovery and purification	Process conditions			BYD quality parameters						
	T, °C	*P*, mm Hg	Yield, %	appearance	T_m, °C	weight fraction of components, %				
						main substance	propynol	methanol	form-aldehyde	water
Extraction	20–25	Atmospheric	5–10	Yellow crystals	54-56	98.486	0.622	0.096	0.296	0.50
Vacuum distillation	140–150	10-20	97–98	Pale yellow fusion cake	56-57	99.756	0.056	0.028	0.06	0.10
Distillation–crystallization	140–150	10–20	85–90	Colorless plates	57–58	99.872	0.038	–	0.04	0.05
Clarification with carbon and crystallizeation	100	20	90–92	Yellowish or colorless crystalline powder	56.5–57.5	99.717	0.143	–	0.06	0.08

and water was distilled off at a pressure of 20 mm Hg with heating on a water bath. The residue while hot was poured into a 3-l flask containing 1 l of ethyl acetate. To remove the remaining water, 100–150 ml of the solvent was distilled off. Then the solution was cooled to 20–25°C, and 1 l of benzene was added with vigorous stirring. In so doing, BYD started to crystallize. The flask was cooled at 0°C for 2–3 h, with intermittent stirring of the contents. The BYD precipitate was filtered off, washed with benzene (250–300 ml), and dried in a vacuum oven at room temperature.

CONCLUSION

The most efficient and safe procedure for recovery and purification of 2-butyne-1,4-diol from aqueous solutions is treatment with activated carbon, followed by crystallization, because of simple implementation and high yield of the target product.

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