

## Chemistry

THREE STEP SYNTHESIS OF ESTERS OF 1,4-BUTANEDIOL  
AND HIGHER FATTY ACIDS FROM 1,4-DICHLORO-2-BUTENE AS  
SIDE-PRODUCT OF CHLOROPRENE MANUFACTURING PROCESS

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The method for producing esters of 1,4-butanediol from 1,4-dichloro-2-butene as by-product of chloroprene production is developed. The synthesis comprises of the steps of dichlorobutene hydrolysis, hydrogenation of the resulting butenediol and esterification of the resulting butanediol, with higher carboxylic acids, i.e. stearic, oleic and palmitic. The esterification reaction is carried out in the presence of acid catalyst without solvent or in solvent toluene. The corresponding esters are defined by their physical and chemical constants.

**Keywords:** glycols and polyhydric alcohols, erythritol, mannitol, sorbitol.

**Introduction.** Esters of glycols and polyhydric alcohols are important products of chemical synthesis and are produced by chemical industry in large amounts. Ethylene glycol, propylene glycol, the isomeric butylene glycols, glycerol, pentaerythritol, polyethylene glycols of various molecular weights, hydrogenation products of sugars (erythritol, mannitol, sorbitol) and other compounds have been used as alcohol components. To acquire esters, typically, saturated or unsaturated higher fatty acids are used having a minimum number of carbon atoms 10 that are stearic, oleic, ricinoleic, and etc. The esters of glycols and polyhydric alcohols are normally used as lubricating oils, plasticizers, oil-additives, heat-resistant motor oils in car and even in aircraft engines [1, 2].

In contrast with natural fats and oils (which are esters of higher fatty acids and glycerin) the synthetic esters have higher thermal stability and wider spectrum of physical chemical properties, technical and operational indicators.

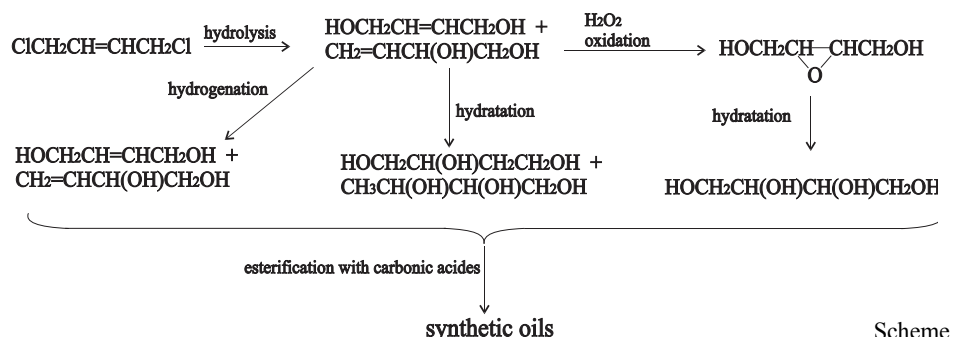
At a chemical plant “Nairit” CJSC, during the chloroprene production from butadiene, a by-product 1,4-dichloro-2-butene (1,4-DCB) is formed, which as a part of the chloro organic wastes is utilized through incineration. Based on the formed product we propose arranging the synthesis of wide range of synthetic oils as described in the Scheme.

Variety of physical and chemical properties of new synthetic oils can be obtained through the use of fatty acids with different hydrocarbon radicals, C<sub>18</sub> to C<sub>10</sub>. At this stage we have studied the synthesis of some esters of 1,4-butanediol with stearic, palmitic and oleic acids.

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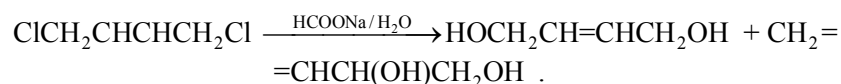
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### Results and Discussion.

#### *Production of 2-Butenediol-1,4 (2-DB-1,4) and 3-Butenediol-1,2 (3-DB-1,2).*

The first synthesis of 2-DB-1,4 through 1,4-DCB hydrolysis is described in [3]. The reaction of dichlorobutenes hydrolysis in chloroprene production is described in [4]. Industrial works on production of 2-DB-1,4 and tetrahydrofuran through 1,4-DCB hydrolysis with aqueous solutions of alkali salts of carboxylic acids are also known [5, 6].



The reaction of 2-DB-1,4 hydrolysis was performed with acetate, format and sodium oxalates in accordance with the method proposed in [5, 6] (Tab. 1).

Table 1

*1,4-DCB hydrolysis in aqueous solutions of salts at temperature 100–110 °C*

Quantity of 1,4-DCB, mol	Salt of carbonic acid	Quantity of salt, mol	Quantity of sodium carbonate, mol	Quantity of water, mL	Reaction duration, h	Yield of glycols, mol %	
						3-DB-1,2	2-DB-1,4
0.2	sodium oxalate	0.2	0.2	300	2	27.4	46.6
0.2	– – –	0.1	0.4	300	2	31.5	37.6
0.2	– – –	0.05	0.2	400	2	30.8	39.2
0.2	– – –	0.025	0.2	500	2	27.9	29.1
0.2	sodium acetate	0.2	–	300	2	12.9	22.0
0.2	– – –	0.4	–	400	4	10.8	36.2
0.4	sodium formiate	0.8	0.4	500	24	21.0	49.0
0.4	– – –	0.8	0.4	220	24	22.8	56.9

It is noticeable that during the hydrolysis reaction of dichlorobutene, formiate, acetate, and sodium oxalate are roughly the same activity. During the reaction, isomeric 2-DB-1,4 and 3-DB-1,2 are produced with a ratio from 2 : 1 to 1 : 1. In fact, for increasing the yield of butenediols, it is very important to assure slightly alkaline reaction conditions, which is achieved by adding an excess of sodium carbonate, as in case of reducing the pH of the solution the reaction stops due to the release of HCl.

The total yield of glycols approximates to 70%. Since in all experiments the initial dichlorobutene has reacted entirely, thus, it may be also assumed the possibility of soluble polyesters and resinous substances formation. From the aqueous solution 2-DB-1,4 is isolated by vacuum distillation.

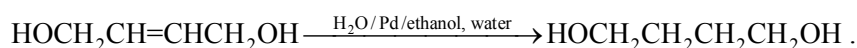
*1,4-Butanediol Production.* The hydrogenation of 2-DB-1,4 is performed under static conditions at atmospheric pressure, at temperature 20–80°C in the presence of palladium hydroxide catalysts (5%) precipitated on the calcium carbonate (Tab. 2).

Table 2

*Hydrogenation of 1,2-DB-1,4 at temperature 25°C*

Composition of the reaction mixture				Consumption H <sub>2</sub>		
2-DB-1,4, <i>mol</i>	Catalyst's quantity, <i>mol</i>	Solvent	Solvent's quantity, <i>mL</i>	Theoretical, <i>mL</i>	Experimental	
					<i>mL</i>	<i>mol %</i>
0.05	0.5	ethanol	50	124.4	118.5	95.2
–  –	0.2	–  –	25	–  –	119.0	95.6
–  –	0.1	–  –	25	–  –	123.0	97.7
–  –	0.1	water	25	–  –	108.0	86.5
–  –	0.2	–  –	25	–  –	103.0	82.0

In this series of experiments influence of temperature, solvents, and amounts of catalyst on the yield of glycol have been studied. The reaction rate is measured based on the hydrogen uptake rate in a volumetric kit.



As can be seen from the Table, the volume of absorbed hydrogen is close to the calculated one. Once the quantity of catalysts is decreased, the volume of absorbed hydrogen accordingly increases, while the hydrogenation rate decreases. It is important to mention, that the reaction flows with a higher conversion in the ethanol as compared with water (H<sub>2</sub> consumption 97.7%, as compared with 86.5%).

The preparative production of 1,4-butanediol is carried out in the flow reactor at atmospheric pressure and in alcohol or water.

*Esterification of 1,4-Butanediol with Stearic, Oleic and Palmitic Acids.* At this stage of the study the esterification 1,4-butanediol in a classical method [7] was performed; in a combined reactive – distillation kit, using acid catalysts. The process is done without a solvent at temperature 120–180°C or in boiling toluene (at 108 °C) with a simultaneous azeotropic distillation of toluene–water mixture. After toluene cooling, water condensate is separated, water volume is measured, and the toluene is recycled back to the reactor. The reaction is conducted as long as water is released from the azeotropic mixture, then heating is continued under a nitrogen stream for 2 h (Tab. 3).

Table 3

*Esterification of 1,4-butandiole with RCOOH*

(molar ratio alcohol to acid 1:1.1, R<sup>1</sup> = C<sub>17</sub>H<sub>35</sub>, R<sup>2</sup> = C<sub>15</sub>H<sub>27</sub> and R<sup>3</sup> = C<sub>17</sub>H<sub>33</sub>)

Acid	Toluene, weight % to RCOOH	Catalyst	Quantity of catalyst, weight % to RCOOH	<i>t</i> , °C	Reaction duration, <i>h</i>	Yield, <i>mol %</i> to RCOOH
1	2	3	4	5	6	7
R <sup>1</sup> COOH	–	HCl	120	115	10	54
R <sup>1</sup> COOH	–	H <sub>2</sub> SO <sub>4</sub> <sup>a)</sup>	20	160	6	10
R <sup>1</sup> COOH	–	HBr	20	160	6	20

1	2	3	4	5	6	7
R <sup>1</sup> COOH	200	HClO <sub>4</sub> <sup>b)</sup>	10	110	6	10
R <sup>1</sup> COOH	400	HClO <sub>4</sub>	5	110	10	65
R <sup>1</sup> COOH	300	CuSO <sub>4</sub> <sup>a)</sup>	20	110	8	15
R <sup>2</sup> COOH	–	HCl	100	125	10	32
R <sup>2</sup> COOH	–	HBr	100	125	10	30
R <sup>2</sup> COOH	200	HClO <sub>4</sub> <sup>b)</sup>	10	110	4	15
R <sup>3</sup> COOH	–	HCl	100	160	6	45
R <sup>3</sup> COOH	–	HBr	20	160	6	18
R <sup>3</sup> COOH	200	HCl	150	110	8	60
R <sup>1</sup> COOH + R <sup>2</sup> COOH (1:1)	200	HClO <sub>4</sub>	5	110	12	70
R <sup>1</sup> COOH + R <sup>2</sup> COOH (1:1)	200	HCl	150	110	12	65
R <sup>1</sup> COOH + R <sup>2</sup> COOH (1:1)	250	H <sub>2</sub> SO <sub>4</sub>	10	120	12	45
R <sup>2</sup> COOH + R <sup>3</sup> COOH (1:1)	200	HCl	150	110	12	75

a) Resignification and deactivation of catalyst; b) burst after toluene evaporation.

**Experimental Part.** The data presented in Tab. 3 display the encountered difficulties, while performing the reaction through the classical methods [7, 8]. In many experiments, the abundant resignification has been observed, also there were difficulties associated with separation of reaction products and starting materials. Apparently, mineral acids as catalysts are not efficient enough to produce high boiling oils.

*2-Butendiole-1,4 Production.* In the 1.0 L volume flask with a reflux condenser a mixture of 25 g (0.2 mol) 1,4-DCB, 21.2 g (0.2 mol) sodium carbonate, 26.8 g (0.2 mol) sodium formiate or 26.8 g (0.2 mol) sodium oxalate in 500 mL water is mixed up for 3 h during boiling. In the ice-cooled receiver acetaldehyde and 1,2-epoxy-3-butene are condensed. The aqueous phase is saturated with sodium chloride and extracted with ether. Ether is evaporated, the residue is weighed and analyzed on gas liquid chromatography. A mixture of 3-BD-1,2 and 2-BD-1,4 is produced. Butendioles are separated through vacuum distillation; 3-BD-1,2 with b.p. 105–110°C/15 mm Hg,  $n_D^{20}$  1.4752; 2-BD-1,4 with b.p. 135°C/15 mm Hg,  $n_D^{20}$  1.4640.

*1,4-Butanediol Production.* In a thermostatic flask with a volume of 150 mL with a magnetic stirrer and a reflux condenser 3 g of 1,4-DB-2 in 30 mL of solvent is placed, air is squeezed out of the flask with hydrogen, 1 g of catalyst is added and hydrogenation is performed. Hydrogen uptake was recorded on a volumetric kit.

To produce sufficient amount of 1,4-butanediol (with a purpose to perform its esterification) hydrogenation of 2-BD-1,4 is done in a laboratory flow kit in the presence of 95° ethanol and at 25°C temperature. The reaction mixture composition is: 250 mL alcohol, 2-BD-1,4 250 mL, 2 g catalyst, hydrogen transmission speed of 60 mL/min. The reaction finishes in 2 h. 1,4-butanediol is isolated from the aqueous solution by vacuum distillation.

*1,4-Butanediol Esterification with Fatty Acids.* In the thermostatic flask with a volume of 300 mL with a magnetic stirrer and descending condenser 3 g (0.033 mol) butanediol, 20 g (0.07 mol) stearic acid (R<sup>1</sup>COOH), 44 mL toluene are placed and heated to boiling while the stirrer is on. Air is squeezed out of the reactor with nitrogen. After removing the moisture, catalyst is added to the reactor: HCl and

HBr are bubbled in gaseous form, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> are poured in a liquid form, and CuSO<sub>4</sub> is added in the form of calcined dry powder. Distilled water or toluene azeotrope with water is collected in the Dean-Stark trap flask. Toluene is decanted, dried up over CaCl<sub>2</sub> and recycled to the reactor. After stopping the reaction, the reaction mixture is washed with a solution of potassium carbonate in order to remove the non-reacted acid and catalyst. The remainder is extracted with diisopropyl ether, the ether is dried over CaCl<sub>2</sub> and evaporated. The residue is weighted and analyzed. Similarly the alkylation reactions of oleic (R<sup>2</sup>COOH) and palmitic (R<sup>3</sup>COOH) acids have been performed.

*Stearic Ester of Butanediol.* Freezing point 54÷56°C. FTIR, cm<sup>-1</sup>, 2880, 2995 (CH<sub>2</sub>) (CH<sub>2</sub>); 1440, 1418 (C–C); 973, 915 (CH<sub>2</sub>); 1783 (C=O); 1230, 1080 (C–O). <sup>1</sup>H NMR, δ, ppm: 0.95 t (6H, CH<sub>3</sub>); 1.25 m (68H, CH<sub>2</sub>); 2.15 m (4H, COCH<sub>2</sub>); 3.4 m (4H, OCH<sub>2</sub>).

*Oleic Ester of Butanediol.* Freezing point –26÷–24°C. FTIR, cm<sup>-1</sup>, 2880, 2995 (CH<sub>2</sub>); 1440, 1418, (C–C), 973, 915 (CH<sub>2</sub>); 1670 (CH=); 1783 (C=O), 1230, 1080 (C–O). <sup>1</sup>H NMR, δ, ppm: 0.95 t (6H, CH<sub>3</sub>); 1.3 m (56H, CH<sub>2</sub>); 1.45 t (4H, COCH<sub>2</sub>); 2.34 d.d. (4H, =CH); 3.4 m (4H, OCH<sub>2</sub>).

*Palmitic Ester of Butanediol.* Freezing point 54÷56°C. FTIR, cm<sup>-1</sup>, 2880, 2995 (CH<sub>2</sub>); 1440, 1418 (CH<sub>2</sub>); 973, 915 (CH<sub>2</sub>); 1783 (C=O); 1230, 1080 (C–O). <sup>1</sup>H NMR, δ, ppm: 0.95 t (6H, CH<sub>3</sub>); 1.25 m (60H, CH<sub>2</sub>); 2.15 m (4H, COCH<sub>2</sub>); 4.1 t (4H, OCH<sub>2</sub>).

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