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JOINT OBTAINING OF 2,5-DIETHYL-3,4-DIHYDRO-2H-PYRAN-2-METHANOL AND SODIUM SALT OF 2,5-DIETHYL-3,4-DIHYDRO-2H-PYRAN-2-CARBOXYLIC ACID *VIA* CANNIZZARO REACTION

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Abstract. Kinetic regularities of joint obtaining of 2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt of 2,5-diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid have been investigated. Optimal synthesis conditions have been established and physico-chemical characteristics of the main products have been determined.

Key words: *a*-alkylacrolein dimers, derivatives of *a*-alkylacrolein dimers, Cannizzaro reaction.

1. Introduction

Derivatives of *a*-alkylacrolein dimmers are widely used for synthesis of dyes, plasticizers, esters, surface-active substances, and drugs. Esters of 2,5-dimethyl-3,4-dihydro-2H-pyran-2-methanol and such dihydric acids as sebacic, azelaic or adipinic acids, are used as solvents and plasticizers [1-3]. 3,4-Dihydro-2H-pyran-2-methanol and 2,5-dimethyl-3,4-dihydro-2H-pyran-2-methanol are initial reagents for the herbicides synthesis [4-5].

There are several methods of heterocyclic pyranic acids and alcohols obtaining from corresponding aldehydes. The aldehyde group oxidizes to carboxyl one under the action of organic or inorganic oxidizer. Unfortunately, the oxidation of dihydropyran-2-carbaldehydes by air oxygen or ozone, hydrogen peroxide or organic peracids is accompanied by their undesirable decomposition and formation of different by-products, rendering impossible the obtaining of desired acids. Thus T. Schenach [6] shows that it is impossible to obtain 2,5-dimethyl-3,4-dihydro-2H-pyran-2-carboxylic acid *via* oxidation of 2,5-dimethyl-3,4-dihydro-2H-pyran-2-carbaldehyde by molecular oxygen. The main identified products are acetonylacetone (~30 %), acetic acid (25 %), and formic acid (15 %).

As regards the pyranic alcohols, 2,5-dimethyl-3,4-dihydro-2H-pyran-2-methanol is obtained by catalytic hydrogenation of 2,5-dimethyl-3,4-dihydro-2-formyl-2H-pyran with the yield of 62 % [3]. The yield of 3,4-dihydro-2H-pyran-2-methanol obtained by reduction of 3,4-dihydro-2-formyl-2H-pyran with lithiumaluminumhydride is 61 % [7] and 20 % – when it is obtained by Tishchenko reaction [8].

Sodium salt of 3,4-dihydro-2H-pyran-2-carboxylic acid is obtained by saponification of 2-(3,4-dihydro-1,2-pyranyl)-methyl-3,4-dihydro-2H-pyran-2-carboxilate at the heating with small excess of NaOH 20 %-aqueous solution [9]. The yield is 70 %. Sodium salt of 2,5-dimethyl-3,4-dihydro-2H-pyran-2-carboxylic acid is obtained in a similar way by saponification of 2-carboxy-2,5-dimethyl-3,4-dihydro-2H-pyran [10]. The yield is 40 %.

However the best results (yield by all products is nearly 80 %) are obtained at joint synthesis of 2,5-dimethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt of 2,5-dimethyl-3,4-dihydro-2H-pyran-2-carboxylic acid from metacrolein dimer *via* Cannizzaro reaction [11]. Data concerning sodium salts of pyranic acids of the following terms of acrolein homologous series are absent. Therefore the aim of the present work is the investigation of kinetic regularities of joint obtaining of 2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt of 2,5-diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid *via* Cannizzaro reaction with the following choice of optimal synthesis conditions.
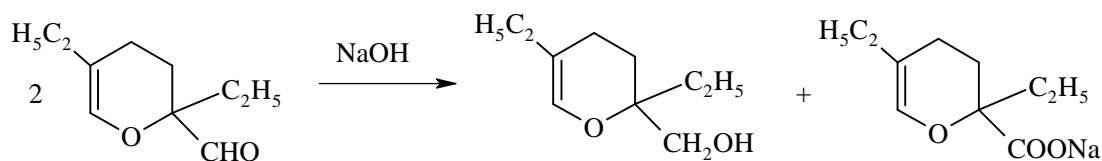
2. Experimental

2.1. Reagents

a-Ethylacrolein was synthesized *via* Mannich reaction according to the procedure described in [12]. The yield 96 %, bp 365.3 K, d_4^{20} 0.8490, n_D^{20} 1.4231, MR$_{founded}$ 25.18, MR$_{calc.}$ 24.79.

2,5-Diethyl-3,4-dihydro-2H-pyran-2-carbaldehyde was synthesized from *a*-ethylacrolein *via* Diels-Alder reaction according to the procedure described in [13]. The yield 87.1 %, bp 366-367 K/12 mm Hg, 0.9794, 1.4614, MR$_{founded}$ 47.26, MR$_{calc.}$ 47.75.

2.2. Analysis Methodic

Kinetic investigations were carried out in a glass three-neck thermostated reactor with the volume of 30 cm³, equipped with magnetic stirrer, thermometer and backflow condenser. The reaction mixture was homogeneous and reagent ratio was $2v(C_{10}H_{16}O_2): v(NaOH)$.

The reactor was loaded with 1.0018 g (0.025 mol) of NaOH and 9.02 g (11.4 ml) of ethanol was added. Then 9.9 ml (0.05 mol) of *a*-ethylacrolein dimer was added rapidly to the formed 10 %-alcoholic solution. This moment was considered as the reaction start. The samples were taken by a volumetric pipette through a backflow condenser.

The content of unreacted sodium hydroxide was determined using potentiometric titration [14].

The sample (~0.4 ml) was placed into a previously weighed beaker flask. Then the flask was closed and weighed. 10 ml of ethanol was added and the sample was titrated with 0.1 M solution of HCl in ethanol with the step of 0.1 ml.

The weight percentage concentration of sodium hydroxide was determined by the following equation:

$$\omega(NaOH) = \frac{V(HCl) \cdot C(HCl) \cdot M(NaOH) \cdot 100}{m \cdot 1000}, \%$$

where *V(HCl)* is the volume of hydrochloric acid necessary for the sample titration, ml; *C(HCl)* is molar concentration of hydrochloric acid, mol/l; *M(NaOH)* is molar mass of sodium hydroxide, g/mol; *m* is sample mass, g.

Initial and continuous molar concentrations of sodium hydroxide in the reaction mixture for the definite time *t* were calculated using the following formula:

$$C(NaOH) = \frac{\omega(NaOH) \cdot m_o \cdot 1000}{M(NaOH) \cdot V_o \cdot 100}, mol/l$$

where *w(NaOH)* is initial and continuous weight concentrations of sodium hydroxide in the reaction mixture, %; m_o is the reaction mixture total mass, g; V_o is the reaction mixture total volume, ml.

The relative error for several parallel samples was less than 3 %.

3. Results and Discussion

Obtained kinetic data (Fig. 1) show that interaction between sodium hydroxide and 2,5-dimethyl-3,4-dihydro-2H-pyran-2-carbaldehyde *via* Cannizzaro reaction is satisfactorily described by kinetic equation of the second order reaction. This corresponds with the scientific literature data, especially in the case of aromatic aldehydes [15].

Reaction rate constants (*k*, l·mol⁻¹·s⁻¹) are determined by integral method using least-squares method (LSM) and dependence 1/C(t)-1/C(0) = k·t. These rate constants and process activation parameters calculated using Arrenius equation are presented in Table 1.

From Fig. 1 one can see that the reaction proceeds with sufficiently high rate and 80 % hydroxide conversion is achieved in 1 h at 323 K.

The dependence of rate constant upon temperature is represented in Fig. 2. The activation energy is determined by slope of straight line. The activation energy value is characteristic of the second order bimolecular reactions.

Arrenius equation for the reaction rate constant is described by the following dependence:

$$k(T) = 2,9 \cdot 10^{10} \cdot \exp\left(-\frac{82}{RT}\right), 1/(mol \cdot s)$$

The activation energy value of 82 kJ/mol is typical of the reaction with half-life from several minutes to several hours at room temperature (50–80 kJ/mol) and indicates that under experimental conditions the process proceeds inside kinetic area and is not controlled by the diffusion.

The effect of temperature and sodium hydroxide concentration on the main products yield has been studied in order to establish the optimal conditions of joint obtaining of 2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt of 2,5-diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid. The results are presented in Tables 2 and 3.

One can see from the tables that maximum yield of the main products (96 %) is achieved at 323 K and 40% concentration of NaOH solution.

Desired products are synthesized and identified on the basis of the obtained data under optimal conditions.

The glass reactor was loaded with 168 g (1 mol) of dimer and 35 ml ($v_{(NaOH)}$ = 0.5 mol) of NaOH 40% aqueous solution was added dropwise for 60 min at 323 K. After interaction 200 ml of water was added to the dense homogeneous reaction mixture and transferred to the separating funnel. 2,5-Diethyl-3,4-dihydro-2H-pyran-2-methanol was extracted with diethyl ester by portions of 100 ml. Ester was distilled and 61.3 g (0.478 mol) of alcohol was obtained. After water distillation under vacuum and drying 99.7 g (0.480 mol) of sodium salt 2,5-diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid was obtained.

Material balance of joint obtaining of 2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt of 2,5-
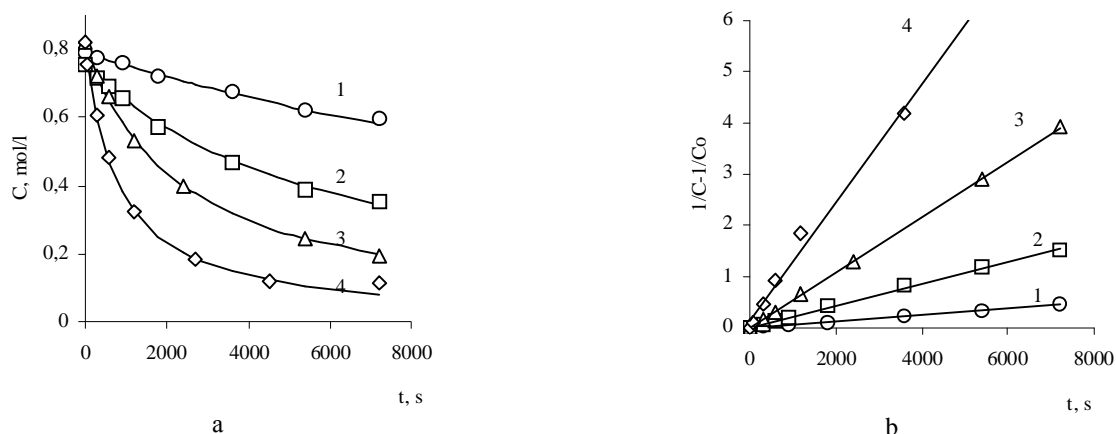
Fig. 1. Kinetic curves (a) and their anamorphoses (b) of the irreversible second order reaction for the interaction between *a*-ethylacrolein dimer and 10%- alcoholic solution of sodium hydroxide at 293 K (1), 303 K (2), 313 K (3) and 323 K (4)

Table 1

**Kinetic and activation parameters of the interaction between 10%-alcoholic solution
of sodium hydroxide and 2,5-diethyl-3,4-dihydro-2H-pyran-2-carbaldehyde *via* Cannizzaro reaction**

T, K	$(k \pm \Delta k) \cdot 10^4$, l/(mol·s)	A, l/(mol·s)	E_{act}, kJ/mol	$\Delta H^{\#}$, kJ/mol	$\Delta S^{\#}$, J/(mol·K)	$\Delta G^{\#}$, kJ/mol
293	0.64 ± 0.01					95.2
303	2.19 ± 0.07	$2.9 \cdot 10^{10}$	82.1 ± 12	79.6 ± 12	-53.2	95.7
313	5.34 ± 0.23					96.3
323	15.4 ± 0.40					96.8

Table 2

**Dependence of 2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt
of 2,5-diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid yields upon NaOH concentration at 323 K**

| wNaOH, %	m(sodium salt), g	sodium salt yield, %	m(alcohol), g	alcohol yield, %
5	21.6	21.0	17.7	20.8
10	52.8	51.3	43.1	50.7
20	70.6	68.5	57.1	67.2
30	81.6	79.2	66.4	78.1
40	99.7	96.8	81.3	95.6

Table 3

Dependence of 2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt of 2,5-diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid yields upon temperature (NaOH concentration is 40 %)

T, K	m(sodium salt), g	sodium salt yield, %	m(alcohol), g	alcohol yield, %
293	44.5	43.2	35.8	42.1
303	65.6	63.7	53.5	62.9
313	85.7	83.2	69.8	82.1
323	99.7	96.8	81.3	95.6

Table 4

**Material balance of joint obtaining of 2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt
of 2,5-diethyl-3,4-dihydro-2H-pyran-2-carbonic acid at 323 K and NaOH concentration 40 %**

Taken			Obtained		
Substance	m, g	m, %	Substance	m, g	m, %
2,5-diethyl-3,4-dihydro-2H-pyran-2-carbaldehyde	186	77.1	sodium salt 2,5-diethyl-3,4-dihydro-2H-pyran-2-carbonic acid	99.7	45.7
NaOH	20.0	9.2	2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol	81.3	37.3
H_2O	30.0	13.7	H_2O	20.0	9.2
			loss	17.0	7.8
Total	218	100	Total	218	100
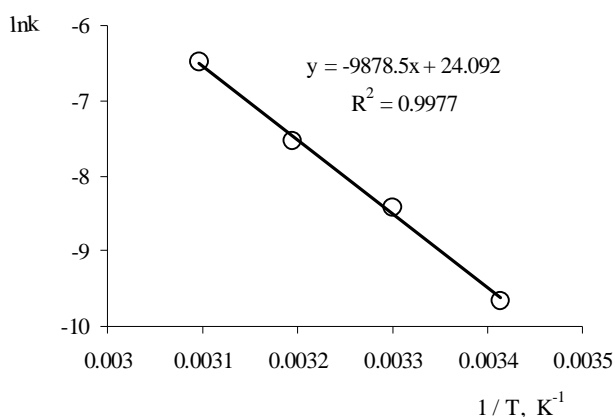
Fig. 2. Arrenius straight line of interaction between 2,5-diethyl-3,4-dihydro-2H-pyran-2-carbaldehyde with 10%-alcoholic solution of sodium hydroxide *via* Cannizzaro reaction

diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid under optimal conditions is represented in Table 4.

Sodium salt 2,5-diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid decomposes at 463 K. Yield 96.8 %. Founded, %: C 58.12; H 7.18. $C_{10}H_{15}NaO_3$. Calculated, %: C 58.24; H 7.33. NMR spectrum (in D_2O) ^1H, δ, ppm: 0.907 (3H, τ, J = 7.2, CH_3); 0.98 (3H, τ, J = 7.2, CH_3); 1.67-2.17 (8H, mm, $2CH_{2(cycle)}$, $2CH_3$–CH_2–); 6.25 (1H, c, =CH–O–).

2,5-Diethyl-3,4-dihydro-2H-pyran-2-methanol. Yield 95.6 %, bp 356-358 K/1 mm Hg, 0.9946, 1.4768. Founded, %: C 71.09; H 10.10. $C_{10}H_{18}O_2$. Calculated, %: C 70.55; H 10.66. IR spectrum (thin layer), ν, cm^{-1}: 3064, 2960–2840 (C–H); 3610 (O–H), 1672 (C=C), 1200–1000 (C–O). NMR spectrum ^1H, δ, ppm: 0.857 (3H, τ, J = 7.2, CH_3); 0.969 (3H, τ, J = 7.2, CH_3); 1.5-1.90 (8H, mm, $2CH_{2(cycle)}$, $2CH_3$–CH_2–); 6.122 (1H, c, =CH–O–); 4.140 (1H, c, OH); 3.527 (2H, c, GH_2–OH).

4. Conclusions

As a result of kinetic investigations of joint obtaining of 2,5-diethyl-3,4-dihydro-2H-pyran-2-methanol and sodium salt of 2,5-diethyl-3,4-dihydro-2H-pyran-2-carboxylic acid *via* Cannizzaro reaction it has been shown that interaction between *a*-ethylacrolein dimer and sodium hydroxide is satisfactorily described by kinetic equation for the irreversible second order reaction. It has been established that under optimal conditions at 323 K and 40 % NaOH

concentration the achieved main products yield is 96 % at practically total conversion of initial reagents.

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СУМІСНЕ ОДЕРЖАННЯ 2,5-ДІЕТИЛ-3,4-ДИГІДРО-2Н-ПІРАН-2-МЕТАНОЛУ ТА НАТРІЄВОЇ СОЛІ 2,5-ДІЕТИЛ-3,4-ДИГІДРО-2Н-ПІРАН-2-КАРБОНОВОЇ КИСЛОТИ ЗА РЕАКЦІЄЮ КАННІЦЦАРО

Анотація. *Досліджено кінетичні закономірності процесу сумісного одержання 2,5-діетил-3,4-дигідро-2Н-піран-2-метанолу та Na-солі 2,5-діетил-3,4-дигідро-2Н-піран-2-карбонової кислоти. На основі отриманих результатів встановлено оптимальні умови синтезу цільових продуктів та встановлені їх фізико-хімічні характеристики.*

Ключові слова: *димери α-алкілакролеїнів, похідні димерів α-алкілакролеїнів, реакція Канніццаро.*