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# Synthesis Of Divinyl Ester Of Adipic Acid

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**Abstract.** *In this work mono- and divinyl esters of adipic acid with using of homogenocatalytical vinylation by acetylene of adipic acid in solution of dimethylformamide (DMF) in the presence of zinc acetate as catalyst (10% by mass of adipic acid) and AlCl<sub>3</sub>•6H<sub>2</sub>O (10% by mass zinc acetate ) in the temperature range of 80-130 °C have been synthesised. The synthesis of divinyl ester of adipic acid has also been studied using vinyl acetate. The influence of the nature of the catalyst and temperature on the yield of the product was studied. The structure of the synthesized mono- and divinyl esters of adipic acid were confirmed by FT-IR, <sup>1</sup>H-NMR, LC/MS and <sup>13</sup>C-NMR spectral analysis and some their physical constants were determined.*

**Key words:** *adipic acid, acetylene, vinylation, 2-chloro-4,6-dimethoxy- 1,3,5-triazine, vinyl acetate, potassium vinylate, mono and divinyl esters of adipic acid.*

## 1. INTRODUCTION

At present time different organic compounds are synthesized from products of oil and gas processing in the world. [1]. Acetylene is obtained by pyrolysis of methane and on its base substances are synthesized which are used in medicine, chemical industry, technology and many other areas.

On the base of carboxylic acids compounds with different properties are synthesized. Vinyl esters of carboxylic acids are a widespread compounds and they are used in various industries [2], as dyes for light industry materials, leather processing, paper and wood materials, as well as spray preparations for cosmetology, also as a monomer in the preparation of polymers or copolymers, they are thermostable and harmless to the body. Proceeding from this, medical equipment and devices are prepared from nylon. They transmit ultra and radio waves (RF), heat-resistant up to 250 °C and are inhibitors of the pigment melanin.

In the world every year by the oxidation of benzene obtained from 6 billion barrels of oil adipic acid is synthesized and its 60% is consumed for production of nylon fiber [3]. Adipic acid is widely used in mainly for production of polyurethanes, resins, adhesives, as well as in a food and pharmaceutical industries [4]. In particular vinyl ester of hyaluronic acid is widely used for the treatment and healing of wounds, by effective influence on the cellular matrixes. Divinyl ester of this acid also increases the activity of vinyl ester of hyaluronic acid. Therefore investigation of synthesis of mono and divinyl esters of adipic acid is important both in theoretical and practical points of view [5].

## EXPERIMENTAL SECTION

**General.** The major chemicals were purchased from Qingdao Sigma Chemical Co., Ltd. All commercially available reagents were used without further purification. Solvents were dried by standard methods before using. All reactions were carried out in oven-dried glassware under N<sub>2</sub>, with magnetic stirring, and they were monitored by TLC (Merck Al-backed plates pre-coated with silica (0.25 mm, 60 F<sub>254</sub>). Purification was performed by column chromatography (CC) with silica gel (SiO<sub>2</sub>; 60 – 120 mesh), elution with hexanes/AcOEt. IR spectres were recorded as KBr pellets or film on Infrared Fourier spectrometer IR Tracer-100. NMR spectres were recorded on a Unity 400 plus instrument (Varian) with an operating frequency of 400 MHz for <sup>1</sup>H in CD<sub>3</sub>OD. HMDS (0 ppm) was used as an internal standard in the <sup>1</sup>H NMR spectra. In the <sup>13</sup>C NMR spectres, the chemical shift of the solvent was used as an internal standard (CD<sub>3</sub>OD, 39.52 ppm relative to TMS). Multiplicities are marked as s=singlet, d=doublet, t=triplet, q=quartet, quint.=quintet, m=multiplet. Melting points were measured on an Electrothermal 9100 apparatus. MS: Agilent 6420 Triple Quad LC/MS.

**The process of vinylation of adipic acid by acetylene.** In four-neck flask by volume of 200 ml, equipped with a fridge, thermometer, tube for introduction of acetylene and mixer, 100 ml of the solvent dimethylformamide (DMFA); 0.1 mole of adipic acid; zinc acetate as catalyst (10% by mass of adipic acid) and AlCl<sub>3</sub>•6H<sub>2</sub>O (10% by mass zinc acetate ) have been played. The reaction mixture was heated in a thermostat to temperature 120 °C. Acetylene was introduced through a tube at constant stirring. The acetylene feed rate was controlled via a foam flowmeter. Eight hours later the reaction was stopped and after cooling the reaction mixture was extracted with a tertiary methyl butyl ether. The extract was removed in vacuum. The residue was dried in a vacuum desiccator to a constant mass, than has been purified in column chromatography using the system hexane:ethyl acetate (5:1). Mono- and divinyl esters of adipic acid were extracted from the product.

**General procedure for the synthesis of divinyl esters of adipic acid.** 0.01 Mole adipic acid and 0.02 mole (1.76 g) 2-chloro-4,6-dimethoxy-1,3,5-triazine were dissolved in 20 ml tetrahydrofuran. The solution was cooled to 0-5 °C. After that 2.2 ml (0.02 mol) of N-methylmorpholine was added at constant stirring. The second flask suspension of 0.02 mole (1.12 g) of tertiary potassium butylate in 20 ml of tetrahydrofuran was prepared and cooled to -30-(-40) °C. In this suspension solution of 1.84 ml (0.02 mol) of vinyl acetate in 4 ml of THF was added drop by drop for 10-20 min. It was observed that at addition of vinyl acetate the temperature has lowered to -30 °C, 30 min. stirred. After that the content of the first dish was gradually added to the second dish for 30 min. After that the reaction was continued for another 2 h. at a temperature of -30 - (-40) °C. Then 30 ml of 5% NH<sub>4</sub>Cl solution was added. At the same time the temperature was not raised from -10 °C. The possessed was extracted with a tertiary methyl butyl ether (15 ml), the solvent was distilled, the residue was washed sequentially with cooled 0.5 M NaHCO<sub>3</sub> solution, water, 1 M NaHSO<sub>4</sub> solution, water, a saturated potassium chloride solution. The extract was dried 5 g Na<sub>2</sub>SO<sub>4</sub> and filtered, the solvent was distilled in vacuum. The residue was dried in a vacuum desiccator to a constant mass, than has been purified in column chromatography using the system hexane:ethyl acetate

(5:1). FT-IR, Mass,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectras of the synthesized compound were recorded.

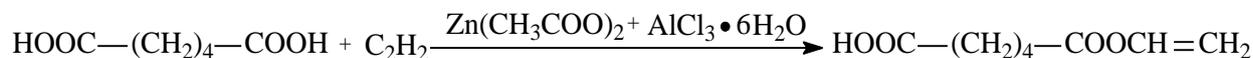
### *Selected spectroscopic data*

**Monovinyl adipate.** Yield: 57%. M.p. 105 °C. B.p. 307 °C. FT-IR (film): 3439, 2931, 1722, 1662, 1496, 1396, 1254, 1094, 1062.  $^1\text{H-NMR}$ : (400 MHz,  $\text{CD}_3\text{OD}$ ): 7.44 (1H, dd,  $J=14.8$ , 7.8 Hz), 5.12 (1H, dd,  $J=14.8$ , 2.3 Hz), 5.0 (1H, dd,  $J=7.8$ , 2.3 Hz), 2.31-2.37 (4H, 2.34 (t,  $J=7.4$  Hz), 2.33 (t,  $J=7.4$  Hz)), 1.52-1.6 (4H, tt,  $J=7.5$ , 7.4 Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 177.0, 170.8, 141.4, 98.2, 34.9, 33.8, 25.0, 24.5. MS: Agilent 6420 Triple Quad LC/MS:  $m/z$  173.186,  $\text{C}_8\text{H}_{13}\text{O}_4^+$ ; calc. 174.432

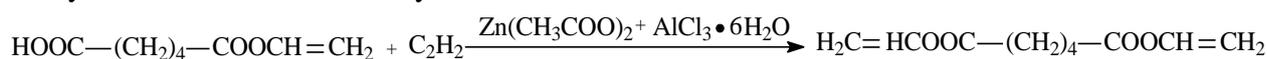
**Divinyl adipate.** Yield: 86%. M.p. 10 °C. B.p. 262 °C. FT-IR (film): 2945, 1749, 1645, 1462, 1365, 1132, 947.  $^1\text{H-NMR}$ : (400 MHz,  $\text{CD}_3\text{OD}$ ): 7.20 (2H, q,  $J=14.01$ , 6.28 Hz), 4.8 (2H, dd,  $J=6.33$ , 1.53 Hz), 4.5 (2H, dd,  $J=6.33$ , 1.52 Hz), 2.38 (4H, t,  $J=7.12$  Hz), 1.56 (4H, m,  $J=7.0$ , 7.1 Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ): 171.724, 142.328, 97.891, 34.073, 24.881. MS: Agilent 6420 Triple Quad LC/MS:  $m/z$  199.224,  $\text{C}_{10}\text{H}_{15}\text{O}_4^+$ ; calc. 199.300.

## 2. RESULTS AND DISCUSSION

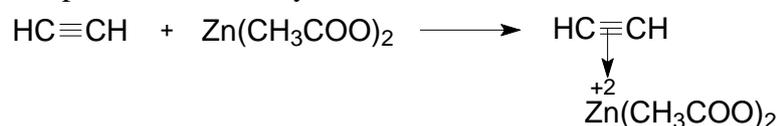
In this investigation mono- and divinyl ethers of adipic acid with using of homogeneous-catalytical vinylation of adipic acid in solution of dimethylformamide (DMF) in the presence of zinc acetate as catalyst (10% by mass of acid) and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (10% by mass zinc salt) in the temperature range of 80-130 °C have been obtained. The reaction has proceeded as follows:



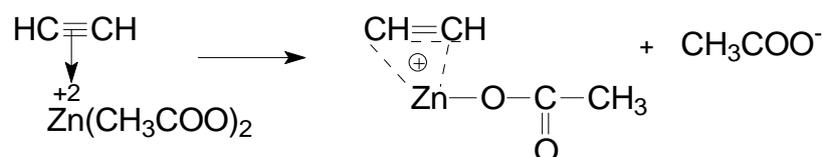
The forming monovinyl ester of adipic acid has reacted with acetylene in the presence of a catalyst with formation of divinyl ester:



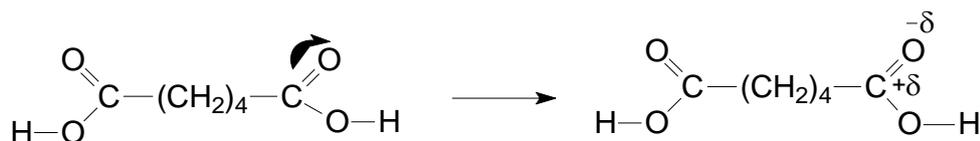
The reaction mechanism is as follows. The process was carried out with formation of  $\pi$ -complex between acetylene and zinc acetate:



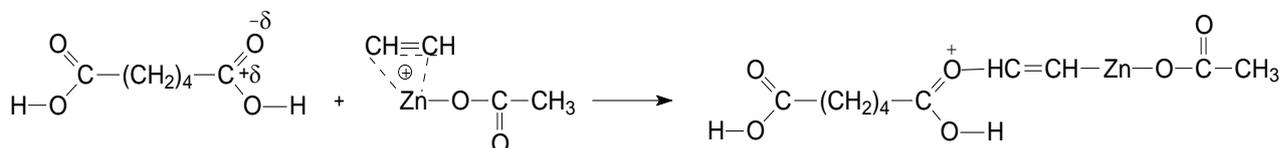
the in the result of rupture in it of one  $\pi$ -bond, the  $\delta$ -complex and anion of acetic acid were formed:



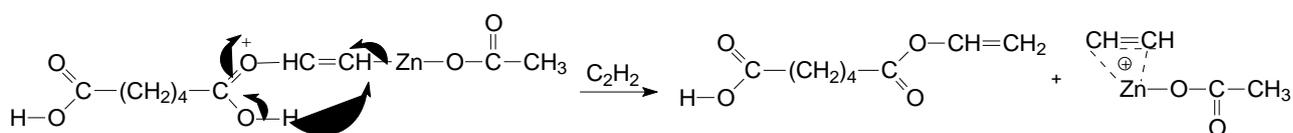
Owing to the high electron density of carbonyl oxygen of adipic acid it becomes partially negative charged:



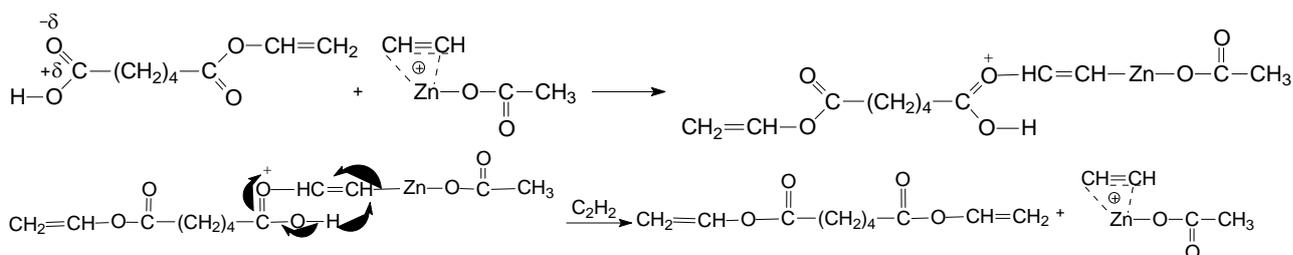
At reaction of acetozinc vinyl cation with adipic acid anion interacts intermediate carbocation was formed:



which has regrouped with the decomposition and formation of monovinyl ester of adipic acid:



In the same time through a second carboxyl group divinyl ester of adipic acid has formed.



Analysis of the obtained results has shown that temperature significantly has influenced on vinylation of adipic acid in the range of 80-130 ° C. In all cases adipic acid in combination with it's monovinyl ester has formed also divinyl ester. Yields of esters have depended on the temperature and duration of the reaction (Table 1).

Table 1. The effect of temperature and duration of the process on the yields of vinyl esters of adipic acid (zinc acetate as catalyst (10% by mass of adipic acid) and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (10% by mass zinc acetate ))

Temperature, °C	Duration of reaction, h	The yield of monovinyl ester, %	The yield of divinyl ester, %
80	2	26	1.8
	4	33	6
	6	41	10
	8	46	13
90	2	30	5
	4	36	9
	6	42	13
	8	45	17

100	2	35	8
	4	42	11
	6	50	16
	8	51	18
110	2	36	10
	4	46	13
	6	53	17
	8	55	20
120	2	39	14
	4	48	16
	6	54	19
	8	57	22
130	2	30	10
	4	27	9
	6	25	7
	8	23	5

At increasing of temperature from 80 to 120 °C the yields of monovinyl and divinyl esters of adipic acid have increased from 26 to 57% and from 1,8 to 22% correspondently. A further increasing of temperature has coursed decreasing of their yields, what can be explained by formation of such by-products as oligomers or polymers; formation of small quantities of vinyl acetate and acetaldehyde was also observed. That is 120 °C is optimal temperature for synthesis vinyl esters of adipic acid. Yields of monovinyl and divinyl esters of adipic acid were 57 and 22% correspondently (table 1).

By-products include a small amounts of vinyl acetate and acetaldehyde. Their formation was explained by the fact that a intermediate complex interacting with the acetate anion has given vinyl acetate. At experimental conditions: 8 hours, temperature 120 °C the yields of adipic acid monovinyl ester was 57 % and divinyl ester was 22%.

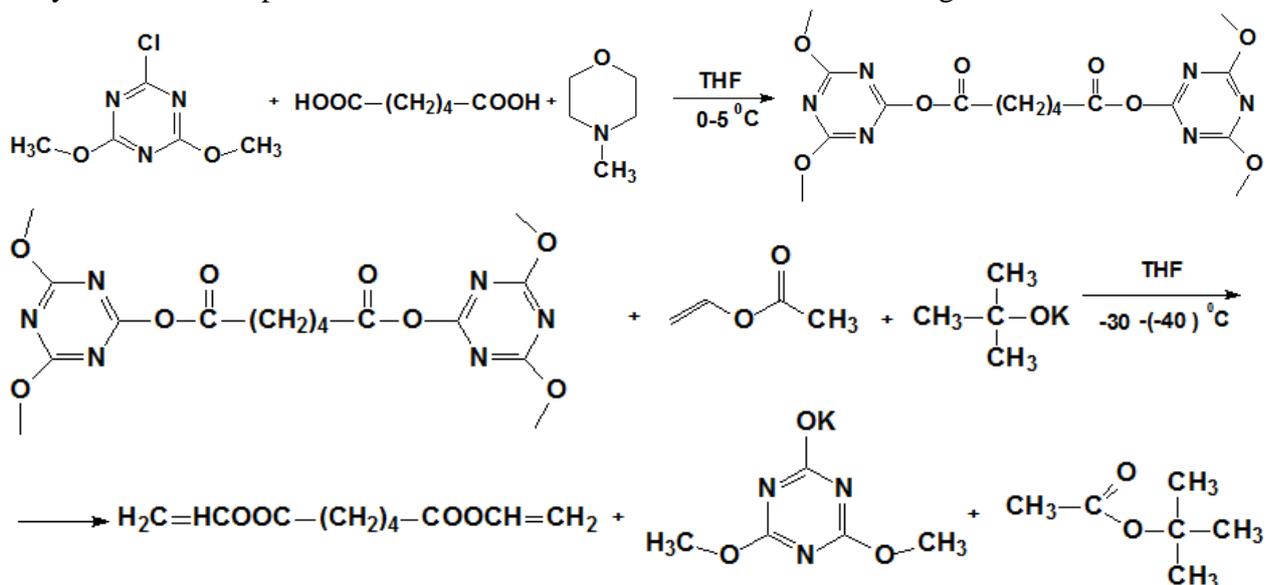
Vinyl esters of carboxylic acids have an important role in organic synthesis. Particularly, vinyl esters of carboxylic acids are used in cycloadditions, cyclopropanations, hydroformylations, metathesis reactions and Claisen rearrangements, as well as Heck reactions. Vinyl esters and ethers are also used as substrates for asymmetric hydrolysis and alcoholysis reactions [6-12]. There are some reports on organic synthesis such as the preparation of vinyl esters of carboxylic acids. In the presence of catalysts such as mercury acetate, palladium, ruthenium, rhenium and other reactions of aliphatic and aromatic acids with acetylene were carried out with formation of corresponding vinyl esters with the highest yields. Some studies in the synthesis of vinyl esters of carboxylic acids as catalysts is also used cancerogene of complexes metals and vinyl silanes [13-16].

Vinyl esters have possessed by many opportunities, but the difficulties in their synthesis have limited their scope. The method of vinylation of carboxylic acids with acetylene is convenient and cost-effective. However, the harsh reaction conditions coupled with safety concerns associated with the explosive nature of acetylene have limited commercial manufacture of vinyl esters by this method. Alternatively, vinyl transfer from vinyl acetate to aliphatic,

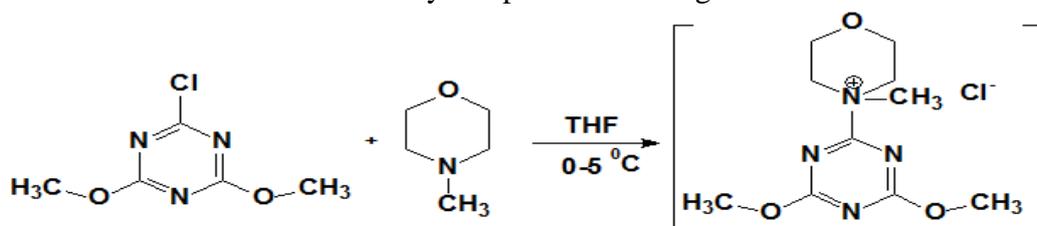
aromatic, and heteroaromatic alcohols and acids is safe and efficient method of synthesis of corresponding vinyl esters [17].

Nowadays 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) is used for activation of carboxylic acids in the synthesis of esters, amides, anhydrides and peptides. CDMT has reacted with carboxylic acids in the presence of N-methylmorpholine in a mild conditions with formation of 2-acyloxy-4,6-dimethoxy-1,3,5-triazine [18,19].

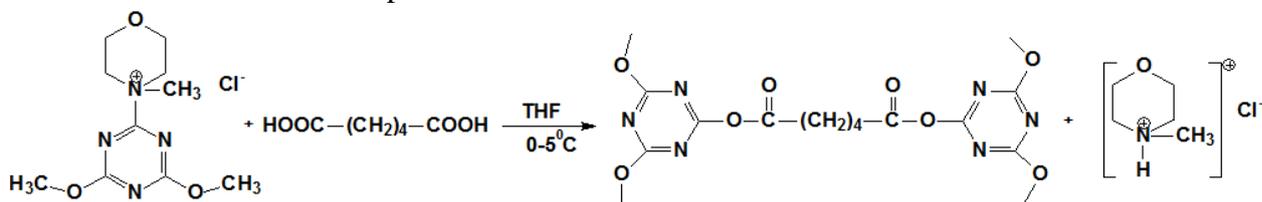
In this work the divinyl ester of adipic acid was synthesized by reaction of adipic acid with vinyl acetate in the presence of CDMT. The reaction scheme is following:



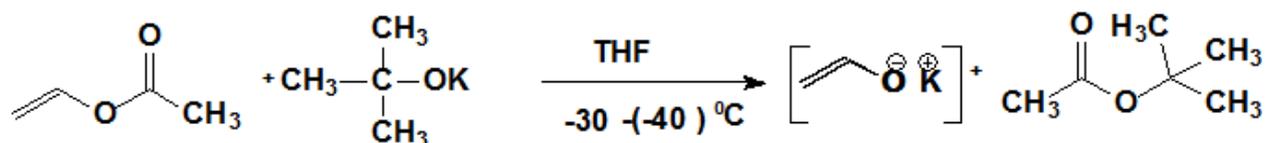
The active triazine ester of adipic acid was obtained by reaction of adipic acid with CDMT in the presence of N-methylmorpholine. The reaction mechanism was following: initially CDMT has reacted with N-methylmorpholine forming an intermediate active complex:



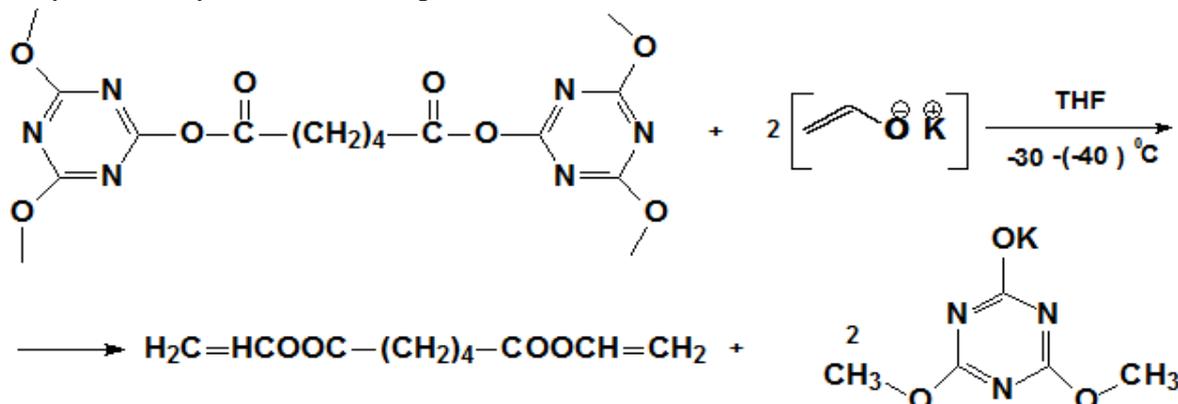
which has interacted with adipic acid with formation of its triazine ester:



In the next step the triazine ester of adipic acid has reacted with vinyl acetate in the presence of tertiary potassium butylate with formation of vinyl esters of adipic acid. Initially, tertiary potassium butylate has reacted with vinyl acetate by nucleophilic attack with formation of tertiary butyl ether and potassium vinylate:



In a result of the reaction of a triazine ester of adipic acid with two molecules potassium vinylate, divinyl ester of the adipic acid was formed:



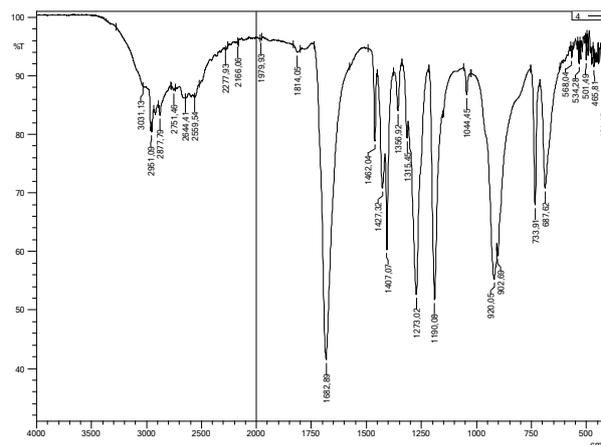
By the interaction of a triazine ester of adipic acid and vinyl acetate with the participation of tertiary potassium butylate divinyl ester of adipic acid was synthesized. It should be noted that adipic acid triazine ester was formed in the presence CDMT. The effect of molar ratio of initial reagents on the product yield was investigated (Table 2).

Table 2. The effect of the molar ratio of the initial compounds on the yield of adipic divinyl ester, (THF solvent, temperature -30 - (-40) °C)

№	The molar ratio of the initial compounds		The yield of divinyl ester of adipic acid, %
	adipic acid	vinyl acetate	
1	1	2.0	73
2	1	2.2	79
3	1	2.4	86
4	1	2.6	82

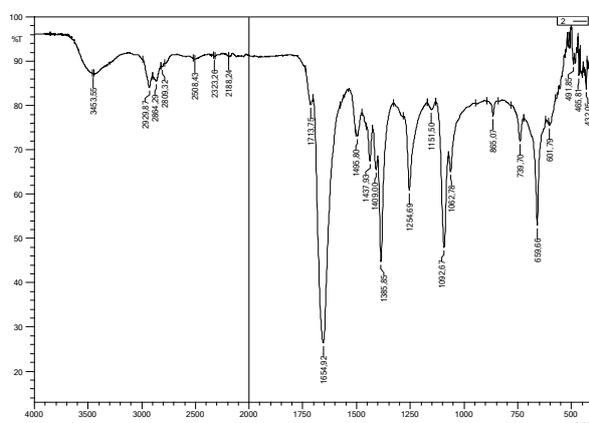
A discussion of the results have shown that the molar ratio of adipic acid: vinyl acetate significantly has affected an the yield of the resulting product. Changing molar ratio from 1: 2 to 1: 2.6 has led to increasing yield of adipic acid divinyl ester from 73 to 86%. It was also revealed that the composition of the products small amount of monovinyl and triazine esters of adipic acid was observed. The structures of the synthesized mono- and divinyl esters of adipic acid were confirmed by FT-IR, <sup>1</sup>H-NMR, LC/MS and <sup>13</sup>C-NMR spectral analysis.

In the IR spectrum of adipic acid (Fig.1.) peak of absorption of stretching vibrations at  $3031\text{ cm}^{-1}$  belonging to the hydroxyl group of the carboxyl peaks, at  $2961\text{ cm}^{-1}$   $\text{CH}_2$  group, at  $2936\text{ cm}^{-1}$  hydroxyl  $-\text{CH}_2\text{-OH}$  group, at  $1682\text{ cm}^{-1}$   $\text{C=O}$  group, at  $1430\text{ cm}^{-1}$   $-\text{CH}_2-$  group, at  $1090\text{ cm}^{-1}$   $\text{C-OH}$  group were observed.



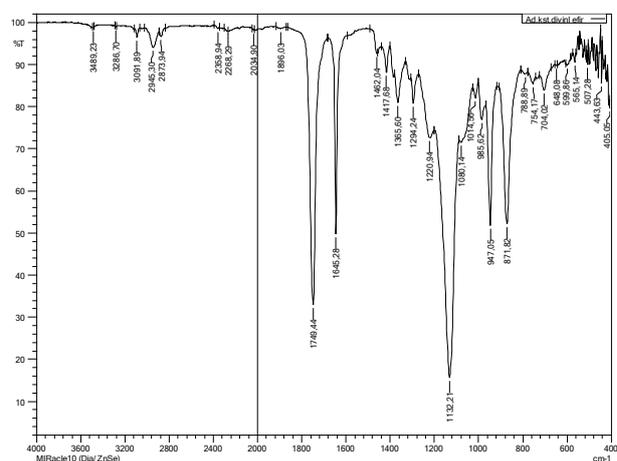
**Figure 1. FT-IR spectrum of adipic acid**

In FT-IR spectrum monovinyl ester of adipic acid (Fig.2.) the absorption of  $\text{C=O}$  group was observed at  $1722\text{ cm}^{-1}$ . Absorption peak at  $1094\text{ cm}^{-1}$  related to the stretching vibration of the ether ( $-\text{C-O-C}-$ ) group, at  $1254\text{ cm}^{-1}$  hydroxyl of the  $\text{C-OH}$  group, at  $885\text{ cm}^{-1}$  deformation vibrations  $=\text{CH}_2$  groups, at  $2930\text{-}1409\text{ cm}^{-1}$   $=\text{CH}-$  groups, and at  $3439\text{ cm}^{-1}$  hydroxyl group,  $1652\text{ cm}^{-1}$  stretching vibrations of the vinyl ( $-\text{CH}=\text{CH}_2$ ) group have been observed.

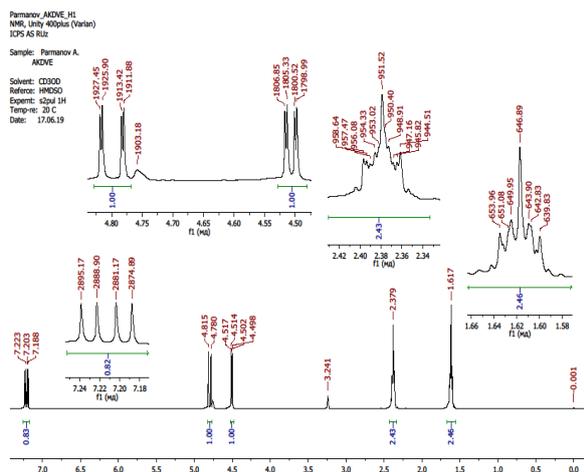


**Figure 2. FT-IR spectrum of monovinyl ester of adipic acid**

In the IR spectrum of divinyl ester of adipic acid (Fig.3.) absorption peaks related to the hydroxyl group are not observed. Peaks at  $2945\text{-}2873\text{ cm}^{-1}$   $-\text{CH}_2-$  groups, at  $1365\text{ cm}^{-1}$ , the grading vibrations of  $-\text{CH}_2-$  groups, at  $1749\text{ cm}^{-1}$  are carbonyl groups, and  $1132\text{-}1294\text{ cm}^{-1}$  are an ester ( $-\text{C(O)-O-C}-$ ) groups. Valence vibrations  $=\text{CH}-$  groups at  $3091\text{ cm}^{-1}$ , and deformation vibrations at  $1417\text{ cm}^{-1}$  were observed. A double bond ( $-\text{CH}=\text{CH}_2$ ) was observed at  $1645\text{ cm}^{-1}$ .

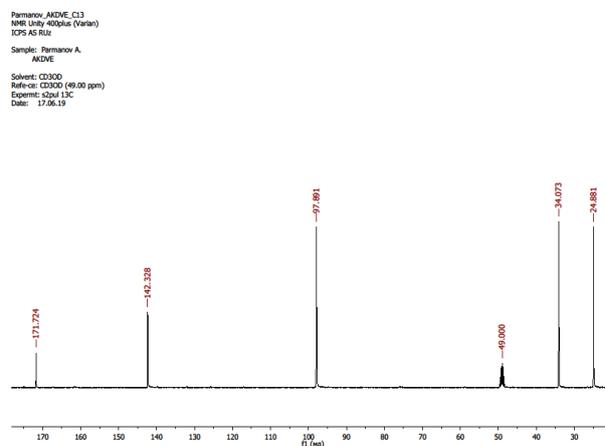


**Figure 3. FT-IR spectrum of divinyl ester of adipic acid**



**Figure 4.**  $^1\text{H}$ \_NMR spectrum of divinyl ester of adipic acid

In the  $^{13}\text{C}$ \_NMR spectrum of divinyl ester (Fig.5.), carbon atoms of the vinyl ( $\text{CH}_2=\text{CH}$ -) group are observed at 98.2 and 141.4 ppm. The carbon of the carboxyl group is at 171.724, and the carbon atom of the methylene group ( $\text{CH}_2$ ) is observed at 34.07 ppm. -24.881 ppm.



**Figure 5.**  $^{13}\text{C}$ \_NMR spectrum of divinyl ester of adipic acid

The structure of divinyl ester of adipic acid was proved by the chromatomass spectrum, while its ion peak is 199.3000 (Fig. 6).

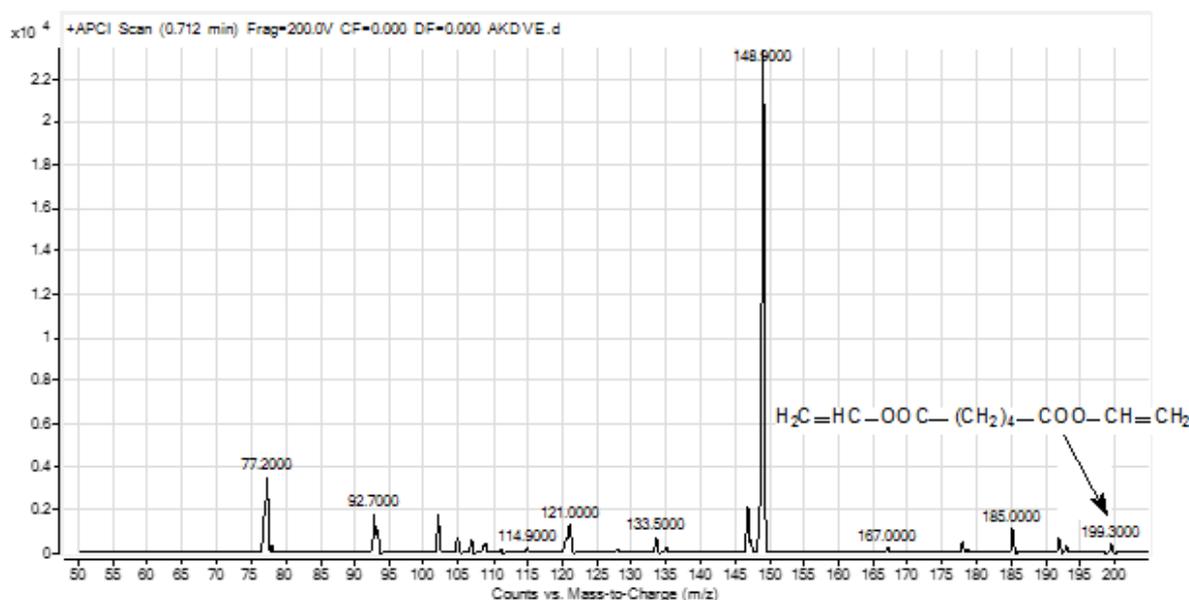


Figure 6. Mass spectrum of divinyl ester of adipic acid

Some physical constants of mono and divinyl esters of adipic acid were determined.

Table 3. Some physical constants of mono and divinyl esters of adipic acid

Nº	Vinyl esters of adipic acid	T <sub>mp.</sub> , °C	T <sub>bp.</sub> , °C	d <sub>4</sub> <sup>20</sup> , g/cm <sup>3</sup>	n <sub>D</sub> <sup>20</sup>
1.	Monovinyl adipate	105	307	1,544	1,5462
2.	Divinyl adipate	10	262	1,039	1,2572

### 3. CONCLUSION

The adipic acid vinylation reaction was carried out in the presence of zinc acetate and AlCl<sub>3</sub>•6H<sub>2</sub>O as catalysts. Its optimal conditions for the synthesis of mono- and divinyl esters of adipic acid were determined: catalyst Zn(CH<sub>3</sub>COO)<sub>2</sub>+AlCl<sub>3</sub>•6H<sub>2</sub>O 10% by mass of adipic acid, reaction time 8 hours. The yields of mono- and divinyl ester, were 57 and 22% respectively.

By reaction of 2-chloro-4,6-dimethoxy-1,3,5-triazine in the presence of N-methylmorpholine, adipic acid triazine ester was synthesized. By the interaction of the obtained triazine ester with vinyl acetate in the presence of tertiary potassium butylate, adipic acid divinyl ester was synthesized. In this case the effect of the molar ratio of acid to vinyl acetate on the yield of divinyl ester was established. Its maximum (86%) was observed at molar ratio 1: 2.4.

The structures of the synthesized mono- and divinyl esters of adipic acid were confirmed by FT-IR, <sup>1</sup>H-NMR, LC/MS and <sup>13</sup>C-NMR spectral analysis and some their physical constants were determined.

### *Acknowledgement*

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### *Conflict Of Interests*

The authors declare the absence of conflict of interests.

## **4. REFERENCES**

- [1] A.B.Parmanov, S.E.Nurmanov, Beata Kolesinsko, Tomash Maniecki, O.E.Ziyadullayev. Homogeneous vinylation of 2-hydroxy-2-phenylethanal acid // Azerbaijan chemical journal. –Azerbaijan, -2019, № 4. P. 32-34. (Springer).
- [2] A.Ziyadullaev, S.Nurmonov, A.Parmonov. Study of the catalytic reaction of acetylene with cyanuric acid//Journal of science. Lyon, France №8, 2020. P. 11-14.
- [3] 3. Nicholas S, Kruyerand P, Peralta Y. Metabolic engineering strategies to bio-adipic acid production. Current Opinion in Biotechnology. 45, 136–143 (2017).
- [4] Van Duren et al. Biotechnology and Bioengineering, 108. 1298-1306 (2011).
- [5] Xiao-Hua Qin, Peter Gruber, Marica Markovic, Plochberger, Enrico Klotzsch, Jürgen Stampfl, Aleksandr Ovsianikov, Robert Liska. Enzymatic synthesis of hyaluronic acid vinyl esters for two-photon microfabrication of biocompatible and biodegradable hydrogel constructs. J. Royal Society of Chemistry (2014).
- [6] Ruihang Jiang et al. Tetrahedron Letters 59, 3279–3282 (2018).
- [7] Esquivias J. et al. J. Am. Chem. Soc. 129, 1480 (2007).
- [8] Kim J. J., Alper H. Chem. Commun. 3059 (2005).
- [9] Terada Y., Arisawa M., Nishida A. Angew. Chem., Int. Ed. 43, 4063 (2004).
- [10] Wei X., Lorenz J.C., Kapadia S., Saha A., Haddad N., Busacca C.A., Senanayake C.H., J. Org. Chem. 72, 4250 (2007).
- [11] Liu S., Berry N., Thomson N., Pettman A., Hyder Z., Mo J., Xiao J., J. Org. Chem. 71, 7467 (2006).
- [12] Martinez-Montero S., Fernandez S., Sanghvi Y.S., Gotor V., Ferrero M., Org. Biomol. Chem. 9, 5960 (2011); Trost B.M., Malhotra S., Mino M., Rajapaksa N.S. Chem. Eur. J. 14, 7648 (2008).
- [13] Chae S. Yi, Ruili Gao. Scope and Mechanistic Investigations on the Solvent-Controlled Regio- and Stereoselective Formation of Enol Esters from the Ruthenium-Catalyzed Coupling Reaction of Terminal Alkynes and Carboxylic Acids. Organometallics. 28, 6585–6592 (2009).
- [14] Jun Gao, Dongrui Guan, Dongmei Xu, Liwen Zhao, Lianzheng Zhang, Min Li. Bull. Chem. Soc. Ethiop. 32(2), 351-359 (2018).
- [15] Hideto Nakagawa, Yoshio Okimoto, Satoshi Sakaguchi and Yasutaka Ishii. Synthesis of enol and vinyl esters catalyzed by an iridium complex. Tetrahedron Letters 44, 103–106 (2003).

- [16] Ruimao Hua, Xin Tian  $\text{Re}(\text{CO})_5\text{Br}$ -Catalyzed Addition of Carboxylic Acids to Terminal Alkynes: A High Anti-Markovnikov and Recoverable Homogeneous Catalyst. *J. Org. Chem.* 69, 5782-5784 (2004).
- [17] Parmanov A.B., Nurmonov S.E., Beata Kolesinsko, Khandamov B.N. Synthesis of vinyl esters of carboxylic acids with the participation of 2-chloro-4,6-dimethoxy-1,3,5-triazine. Youth is the driving force behind the development of science. In. Conf. Chimkent, Kazakhstan, 183-185 (2019).
- [18] Kaminski, Z.J. A new reaction of 2-chloro-4,6-dimethoxy-(diaryloxy)-1,3,5-triazines with carboxylic acids leading to hitherto unknown 2-acyloxy-4,6-dimethoxy-(diaryloxy)-1,3,5-triazines. *J. Prakt. Chem.* 332, 579–581 (1990).
- [19] Zbigniew J. Kaminski, Beata Kolesinska, Marcinkowska Małgorzata. Mild and efficient synthesis of carboxylic acid anhydrides from carboxylic acids and triazine coupling reagents. *Synthetic communications*. Vol. 34, Issue 18, 3349–3358 (2004).