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SYNTHESIS OF VINYL ESTERS OF SOME AROMATIC CARBOXYLIC ACIDS FROM VINYL ACETATE

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In this work by the reaction of derivatives of benzoic acid containing substituents in the aromatic ring with vinyl acetate in the presence2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) vinyl esters of aromatic carboxylic acids have been synthesized. The influence of the nature of the initial compounds, temperature, zinc trifluoromethyl-sulfonate ($Zn(OTf)_2$), dilithium 3,3′-diphenylbinaphtholate (3,3′-Ph_2BINOL-2Li), tertiary potassium butylate ($KO^{tr}Bu$), butyllithium (BuLi) on the yield of synthesized compounds was investigated. The structure of the synthesized vinyl esters was proved by IR, ^1H NMR, ^{13}C NMR spectroscopies.

Keywords: *Aromatic carboxylic acids, 2-chloro-4,6-dimethoxy-1,3,5-triazine, active triazine esters of carboxylic acids, vinylacetate, vinyl esters of aromatic carboxylic acids.*

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Introduction

Various organic compounds are synthesized from products of the secondary processing of oil and gas [1]. In particular, acetylene-based substances obtained as a result of methane pyrolysis are widely used in medicine, industry, mechanical engineering, and many other ranges. [2]. Vinyl acetate currently used commercially falls into this category [3].

Vinyl esters of carboxylic acids are widely used in practice, especially, vinyl benzoates as biomaterials, paints, adhesives, medical devices, paper coatings, paints, and building materials, in organic synthesis and pharmaceutical chemistry [4]. There are several reports on the synthesis of vinyl esters of aliphatic, aromatic, and heteroaromatic acids. In the presence of catalysts such as mercury acetate, palladium, ruthenium, rhenium, and other reactions of aliphatic and aromatic acids with acetylene with the formation of corresponding vinyl esters with high yields were carried out, and also metals complexes and vinyl silanes also were used as catalysts [5–8].

Vinyl esters have possessed by many opportunities, but the difficulties of their synthesis limit their scope. The method of vinylation of carboxylic acids with acetylene is convenient and cost-effective, but complex conditions of its carrying out in association with the explosive nature of acetylene limit the commercial manufacture of vinyl esters by this method[9].

Although the synthesis of vinyl esters has been known since 1912, many methods are unique but yields of products under laboratory conditions are very low. The vinyl exchange at using vinyl acetate in the presence of catalytic amounts of mercury salts was first carried out in 1941 by Herman and Hexnel and in 1943 by Toussiant and McDowell [10]. Currently, one of the widely used methods for the formation of vinyl esters is the exchange reaction between carboxylic acid and vinyl acetate. The incorporation of the vinyl group of vinyl acetate into aliphatic, aromatic, and heteroaromatic acid is a safe and efficient method of synthesis of vinyl esters [11].

Scientific research have been carried out by the world's leading scientists by methods of synthesizing vinyl esters of various carboxylic acids. As a result of systematic analysis of the effects of reagent, substrate, solvent, catalyst amount and nature, temperature, and duration of reaction, the most alternative conditions for the process were determined and correspondently, the increasing product yield was achieved [12–18]. In particular, the scientific team of Ruihang Jiang has carried out the synthesis of vinyl esters of aromatic carboxylic acids with different substituents in the molecule by exchanging reactions with vinyl acetate. As a result of the nucleophilic addition of vinyl acetate to the complex formed by aromatic carboxylic acid with $RhCl_3 \cdot 3H_2O$, has carried at with formation of vinyl esters with high yields [4].

Nowadays, 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) is used for the activation of carboxylic acids in the synthesis of esters, amides, anhydrides, and peptides. 2-Chloro-4,6-dimethoxy-1,3,5-triazine has reacted with a carboxylic acid in the presence of N-methylmorpholine (NMM) in a smooth condition with the formation of 2-aryloxy-4,6-dimethoxy-1,3,5-triazine [19, 20].

Currently, several new organic compounds – alcohols, ethers, acids, elemental organic compounds – have been synthesized by scientists of the world by using zinc triflate, butyllithium, potassium tert-butylate and lithium binaphtholate reagents, and some of them are produced in the industry in large scale [21, 22].

Except for vinyl acetate and vinyl benzoate, most vinyl esters are not produced industrial scale. Therefore, synthesizing carboxylic acid vinyl esters based on vinyl acetate under normal atmospheric pressure without the participation of toxic and expensive metal catalysts is considered an urgent task.

Experimental part

Materials and methods

The major chemicals such as 2-chloro-4,6-dimethoxy-1,3,5-triazine, vinyl acetate, tetrahydrofuran, tertiary potassium butylate, and N-methylmorpholine were purchased from Qingdao Sigma Chemical Co., Ltd. (Qingdao, China).The solvents before using were dried by standard method[23] and distilled from Na. All reactions were carried out in oven-dried glassware under N_2 at stirring and the reaction progress and the identity of the synthesized compounds were controlled by TLC on Silufol UV-254 (Czech Republic) and Merck silica gel 60F254 (Germany) plates in hexanes/AcOEt 5:1 (a), 10:1 (b) systems, visualization in UV light and iodine vapor. FT-IR Spectrums were recorded as the film with Infrared Fourier spectrometer FTIRNicolet-iS50 (Raman module, Waltham, MA, USA), and An Invenio-R FT-IRSpectrometer (Bruker, USA) was used to record the FT-IRspectra (scanning from 400 to 4000 cm -1);^{1}H NMR spectrums were recorded on Varian Unity+400 instrument (400 MHz) at 20–25 ^oC $CDCl_3$, CD_3OD, Pyridine-d_5, DMSO-d_6 internal standard HMDS (δ. 0.05 ppm). Multiplicities are marked as s=singlet, d=doublet, t=triplet, q=quartet, quint.=quintet, m=multiplet.

General procedure for the synthesis of vinyl esters of aromatic carboxylic acids

One-necked 50 mL round-bottom flask was charged with 0.01 mole carboxylic acid and 0.01 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^{0}C. After that 1.1 ml (0.01 mol) of N-methylmorpholine was added at constant stirring. In the second flask suspension of an equivalent mole of reagent (0.005 mole-$Zn(OTf)_2$, 0.005 mole-3,3′-Ph_2BINOL-2Li, 0.01 mole-$KO^{tr}Bu$, 0.01 mole-BuLi) in 10 ml of tetrahydrofuran was prepared and cooled to -30^{0}C, then the solution of 0.92 ml (0.01 mol) of vinyl acetate in 2 ml of THF was added drop by drops for 10–20 min. It was observed that in addition to vinyl acetate the temperature was lowered to -30^{0}C after 30 min. stirring. After that, the content of the first flask was added gradually to the second for 30 min. After that, the reaction was continued for another 2 h. at -30^{0}C. Then 20 ml of 5% NH_4Cl solution was added. At the same time, the temperature was not raised above -10^0C. The contents were extracted with diethyl ether (3x20 ml), the solvent was distilled, and the residue was washed sequentially with cooled 0.5 M $NaHCO_3$, water, 1 M $NaHSO_4$, water, and saturated potassium chloride solution. The extract was dried and filtered, the solvent was distilled in a vacuum. The residue was dried in a vacuum exicator to constant mass. FT-IR, ^{1}HNMR, and ^{13}CNMR spectrums of the synthesized compounds were recorded.

Vinyl benzoate (I). ^{1}H NMR (400 MHz, CD_3OD): δ 7.97 (d, *J*=9.2, 2H), 7.41-7.55 (m, 4H), 5.03 (dd, *J*=14.5, 6.4, 1H), 4,67 (dd, *J*=6.0, 1.8, 1H). ^{13}C NMR (100.6 MHz, CD_3OD): δ 164.7, 142.5, 134.8, 130.8, 129.9, 129.6, 98.6.FTIR (film): 3092, 2995, 2590, 2495, 1828, 1728, 1645, 1492, 1452, 1246, 1176.

Vinyl phenylacetate (II). ^{1}HNMR (400 MHz, DMSO-d_6): δ 7.64 (tr, 1H), 7.57 (d, *J*=7.3, 2H), 7,32 (m, 1H), 7.10-7.17 (m, 2H), 4.81 (dd, *J*=14.0, 6.2, 1H), 4.50 (dd, *J*=6.7, 1.7, 1H), 3.76 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 155.9, 148.3, 132.4, 127.9, 126.2, 124.3, 40.3, 39.5.

Vinyl 4-methylbenzoate (III). ^{1}H NMR (400 MHz, CD_3OD): δ 7.99 (d, *J*=8.4, 2H), 7.55 (dd, *J*=14.6, 6.4, 1H), 7.41 (m, 2H), 4.88 (dd, *J*=12.7, 1.6, 1H), 4.51 (dd, *J*=6.4, 1.5, 1H), 1.43 (s, 3H). ^{13}C NMR (400 MHz, CD_3OD): δ 172.6, 144.5, 141.0, 139.2, 131.3, 129.2, 128.3, 95.1, 31.1.

Vinyl 4-Methoxybenzoate (IV). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76-3.64 (dd, 1H, trans of CH_2), 4.02 (s, 3H, CH_3), 4.45-4.37 (dd, 1H, sis of CH_2), 6.87-6.44 (m, 2H, 2CH of Ph), 7.51-7.47 (tr, 1H, CH of Vin), 8.04-7.87 (m, 2H, 2CH of Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): 142.8,134.6, 132.8, 114.2, 113.8, 97.6, 80.4.IR (film): 2974 sm^{-1} (-CH_3), 2840 sm^{-1} (>CH), 1724-1705 sm^{-1} (=C-H), 1645-1604 sm^{-1} (-C=C-), 1459-1421 sm^{-1} (=C-H), 1088-1025 sm^{-1} (-C-O-O-), 869-844 sm^{-1} (=CH_2), 688-611 sm^{-1} (Ar, CH).

Vinyl 3,4-Dimethoxybenzoate (V). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J=6.8, 1H), 7.62 (dd, J=13.2, 6.4, 1H), 7.25 (s, 1H), 6.98 (d, J=8.4, 1H), 5.10 (dd, J=13.6, 1.7, 1H), 4.49 (dd, J=6.2, 1.8, 1H), 4.17 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 149.2, 147.5, 142.4, 132.7, 123.4, 114.9, 112.2, 97.4, 55.9.

Vinyl 2-bromobenzoate (VI). ^{1}H NMR (400 MHz, CD_3OD): δ 3.71 (tr, 1H, CH of Vin), 4.00 (dd, 1H, trans of CH_2), 4.08 (dd, 1H, sis of CH_2), 7.53-7.34 (m, 3H, 3CH of Ph), 7.79-7.67 (m, 1H, CH of Ph). ^{13}C NMR (400 MHz, CD_3OD): δ 99.0, 121.93, 128.43, 129.71, 132.06, 133.49, 134.28, 135.23, 169.58, 171.82, 175.59. IR (film): 3114.8-2940 sm^{-1} ((Ar)=C-H), 1732.8 sm^{-1} (>C=O), 1653.4 sm^{-1} (-C=C-), 1488 sm^{-1} (Ar, =C-H), 1380-1245 sm^{-1} (-C-O-C-, asymm.), 1071.1-1026.2 sm^{-1} (-C-O-C-, symm.), 716.6-646.2 sm^{-1} (C-Br).

Vinyl 4-bromobenzoate (VII). ^{1}H NMR (400 MHz, CD_3OD): δ 3.72 (tr, 1H, CH of Vin), 4.00 (dd, 1H, trans of CH_2), 4.05 (dd, 1H, sis of CH_2), 7.63-7.61 (m, 1H, CH of Ph), 7.79-7.77 (dd, 1H, CH of Ph), 7.94-7.92 (m, 2H, 2CH of Ph). ^{13}C NMR (100.6 MHz, CD_3OD): δ 49.0, 93.36, 127.34, 130.51, 132.45, 132.71, 133.04, 171.12, 171.85. IR (film): 3367-3085 sm^{-1} (Ar, =C-H), 2979 sm^{-1} (=C-H), 1732.5 sm^{-1} (>C=O), 1647.6-1587 sm^{-1} (-C=C-), 1481-1368 sm^{-1} (Ar, =C-), 1271-1072.9 sm^{-1} (-C-O-C-), 868-672 (C-Br).

Vinyl 4-Fluorobenzoate (VIII). ^{1}H NMR (400 MHz, Pyridine-d_5): δ

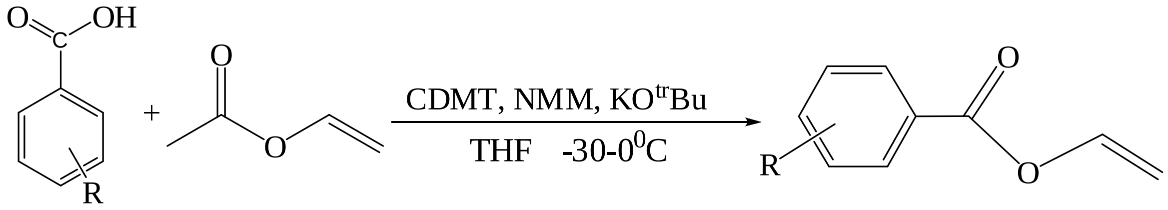
5.06-5.00 (dd, 1H, trans of CH_2), 5.15-5.13 (dd, 1H, sis of CH_2), 7.12 (m, 2H, 2CH of Ph), 7.21 (dd, 1H, CH of Ph), 7.38 (tr, 1H, CH of Vin), 8.67 (dd, 1H, CH of Ph). ^{13}C_NMR (400 MHz, Pyridine-d_5): δ 155.8,151.4, 133.7, 129.9, 123.6, 112.2, 97.7.

Vinyl 4-nitrobenzoate (IX). ^{1}H NMR (400 MHz, CD_3OD): δ 3.81 (dd, 1H, trans of CH_2), 3.98 (dd, 1H, sis of CH_2), 8.13-8.10 (m, 2H, 2CH of Ph), 8.24-8.22 (m, 1H, CH of Vin), 8.32 (m, 2H, CH of Ph). ^{13}C NMR (400 MHz, CD_3OD): δ 170.6, 131.2, 130.0, 124.6, 124.0, 93.6. IR (film): 3109.8 sm^{-1} (Ar, =C-H), 2964.5(=C-H), 1727.7 sm^{-1} (>C=O), 1658.5 sm^{-1} (-C=C-, assym), 1567.6-1533.7 sm^{-1} (-C-NO_2), 1413 sm^{-1} (=C-H), 135-1298.3 sm^{-1} (-C-N-), 825.5-721.8 sm^{-1} (-C-NO_2, valence, intensive).

Vinyl 4-*tert*-butylbenzoate (X). ^{1}H NMR (400 MHz, CD_3OD): δ 7.94 (d, J=6.9, 2H), 7.77 (m, 1H), 7.72 (d, J=7.2, 2H), 5.04 (dd, J=14.2, 6.1, 1H), 4.67 (dd, J=6.7, 1.8, 1H), 1.43 (s, 9H). ^{13}C NMR (400 MHz, CD_3OD): δ 172.4, 133.1, 129.6, 127.6, 125.5, 95.7, 36.7, 31.1.

Results and Discussion

In this work vinyl esters of aromatic carboxylic acids based on vinyl acetate were synthesized according to Scheme 1:

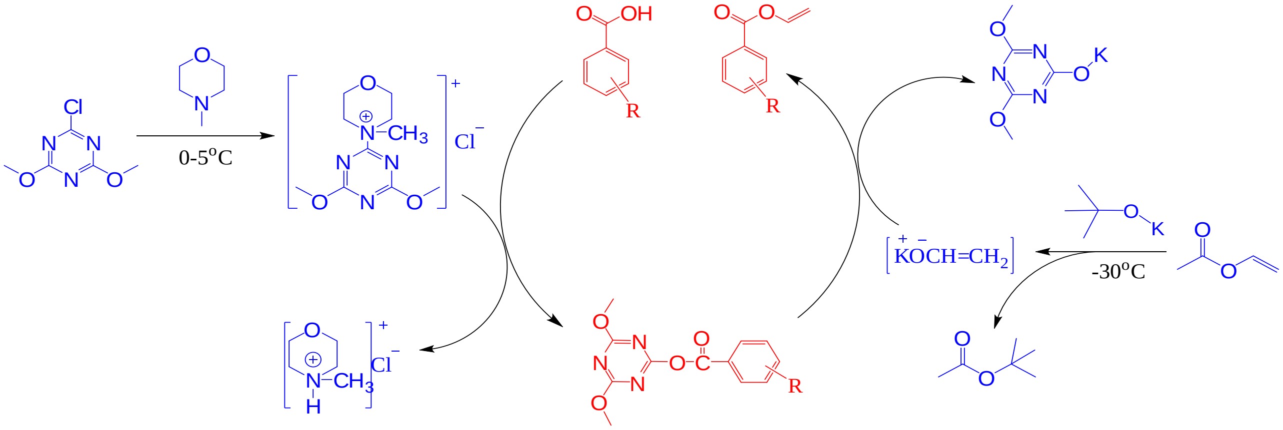


Scheme 1. Synthesis of vinyl esters of aromatic carboxylic acids

where: I=C_6H_5COOH; II=$C_6H_5CH_2COOH$; III= 4-CH_3-C_6H_4COOH; IV=4-CH_3O-C_6H_4COOH; V=3,4-$(CH_3O)_2$-C_6H_3COOH; VI=2-Br-C_6H_4COOH; VII=4-Br-C_6H_4COOH, VIII=4-F-C_6H_4COOH, IX=4-O_2N-C_6H_4COOH; X=4-$(CH_3)_3C$-C_6H_4COOH.

In this work, nucleophilic coupling reactions of some aromatic carboxylic acids with different substituents with vinyl acetate were investigated in the presence of 2-chloro-4,6-dimethoxy-1,3,5-triazine, the appropriate vinyl esters were synthesized and the influence of temperature, nature of the starting materials, $Zn(OTf)_2$, 3,3′-Ph_2BINOL-2Li, $KO^{tr}Bu$, BuLi on the yield of the products was determined. This process was carried out in two steps: initially, the active triazine ester of the acid was obtained by a reaction of 2-chloro-4,6-dimethoxy-1,3,5-triazine with carboxylic acids, then vinyl oxy ion formed by the reaction of vinylacetate with nucleophilic reagent, corresponding vinyl ester was obtained as a result of nucleophilic substitution of active triazine ester of acid.

In the general case, the process scheme can be presented as follows: initially, N-methylmorpholine reacts with 2-chloro-4,6-dimethoxy-1,3,5-triazine forming an intermediate active complex, which then has reacted with aromatic carboxylic acids with the formation of 2-aryloxy-4,6-dimethoxy-1,3,5-triazine, which reacts with vinyl acetate in the presence of tertiary potassium butylate which formation of corresponding vinyl esters. Initially, tertiary potassium butylate reacts with vinyl acetate under the action of a nucleophilic attack forming tertiary butyl ether and potassium vinyl (Scheme 2).



Scheme 2. The suggested mechanism of synthesising the vinyl esters of aromatic carboxylic acids on the base vinyl acetate.

Vinyl esters of benzoic acid and its derivatives with various substituents in its ring have been synthesized. The effect of temperature on the yield of vinyl ester was studied in an interval of 0-(-30)^{0}C. In selected systems, carboxylic acid: vinylacetate: 2-chloro-4,6-dimethoxy-1,3,5-triazine: reagents- Zn(OTf)$_2$, 3,3′-Ph$_2$BINOL-2Li, KO^{tr}Bu, BuLi were obtained in the equimolar ratio in THF solution. Experimental conditions of synthesis of vinyl esters in the presence of catalytic reagents: 3,3′-Ph$_2$BINOL-2Li/THF< BuLi/THF< KO^{t}Bu/THF < Zn(OTf)$_2$/THF were determined (Table 1).

Vinyl esters were synthesized with maximum yield (I−69; II−72; III−75; IV−82; V−74, VI−44; VII-60; VIII-66; IX-59; X-78%) in the presence of Zn(OTf)$_2$/THF at -30^{0}C. The effect of the molar ratio of initial reagents on the yield of aromatic carboxylic acid vinyl esters was analyzed systematically in the presence of Zn(OTf)$_2$ (Table 2).

At a of -30^{0}C vinyl esters were synthesized with relatively high yieldsat mol ratio of carboxylic acid:vinylacetate: CDMT: Zn(OTf)$_2$ 1.0:1.2:1.2:1.2.The yield of aromatic carboxylic acid vinyl esters increases in row: the 2-Br-C$_6$H$_4$COOH < 4-O$_2$N-C$_6$H$_4$COOH < 4-Br-C$_6$H$_4$COOH < 4-F-C$_6$H$_4$COOH < C$_6$H$_5$COOH< 3,4-CH$_3$O-C$_6$H$_3$COOH < C$_6$H$_5$CH$_2$COOH < 4-(CH$_3$)$_3$C-C$_6$H$_4$COOH < 4-CH$_3$-C$_6$H$_4$COOH< 4-CH$_3$O-C$_6$H$_4$COOH series and it’s values wereequaled to 49, 65, 67, 73, 82, 82, 85, 85, 88 and 91% respectively. Since the formation of vinyloxy ion from vinylacetate is a reversible process, increasing the temperature from -30 to 0^{0}C leads to decreasing of yield of vinyl ester. It is shown from the experimental results that the yield of vinyl esters has decreased with the increasing of acidity of selected carboxylic acids. This situation can be explained by the fact that the 2-hydroxy-4,6-dimethoxy-1,3,5-triazine ion is difficult to leave from the active triazine ester of a carboxylic acid with increasing acid strength. Ionization of the active triazine ester 2-hydroxy-4,6-dimethoxy-1,3,5-triazine with this acid couch can lead to a vibrational state.If the 4-substituted group is an electron donating, it affects the aromatic ring with an electron effect and facilitates the formation of an active triazine ester.

Table 1. Effect of reagents on carboxylic acid vinylester yield (carboxylic acid: vinylacetate: CDMT: metall reagents in 1:1:1:1 mole ratio, temperature -30^{0}C, solvent THF)

Reagents	Yield of product, %									
	I	II	III	IV	V	VI	VII	VIII	IX	X
3,3′-Ph$_2$BINOL-2Li	44	49	51	56	50	34	44	49	46	62
BuLi	51	57	60	65	58	34	46	51	46	63
KO^{tr}Bu	67	71	74	81	72	42	57	63	56	75
Zn(OTf)$_2$	69	72	75	82	74	44	60	66	59	78

Table 2. Effect of temperature, mole ratio and nature of reagents on yield of carboxylic acid vinyl esters (solvent THF)

R-COOH: CH$_3$-COO-CH=CH$_2$ mole ratio	Temperature, ^{0}C	Yield of product, %									
		I	II	III	IV	V	VI	VII	VIII	IX	X
	Zn(OTf)$_2$										
1:1.0	-30	69	72	75	82	74	44	60	66	59	78
	-20	63	70	73	79	72	42	57	63	56	74
	0	47	52	54	58	52	30	40	45	40	53
1:1.2	-30	82	85	88	91	82	49	67	73	65	85
	-20	74	83	86	87	80	46	63	66	61	75
	0	55	61	64	65	58	33	44	47	43	54
1:1.4	-30	64	66	68	70	63	38	52	56	50	65
	-20	57	64	66	67	61	36	48	50	47	57
	0	42	47	49	50	44	26	33	36	33	41

The structure of the synthesized vinyl esters was confirmed by spectroscopic methods. (^{1}H, ^{13}C NMR and IR; see also SupplementaryMaterials), as a result of the analysis of ^{1}H NMR spectrums, it was found that the vinyl group contained –CH_2 chemical shift regions in the range of 3.76–4.99 ppm, and –CH of the vinyl group was obtained 7.14–7.67 ppm. In addition, in IR was observed the vinyl group (–$CH=CH_2$) in the regions of 1246 and 1645 cm^{-1} respectively.

Conclusions

In this work, the reactions of vinyl substitution of some aromatic carboxylic acids with different substituents with vinyl acetate were carried out in the presence of 2-chloro-4,6-dimethoxy-1,3,5-triazine and vinyl esters of 4-methoxybenzoic, 4-tertiary butylbenzoic, 3,4-dimethoxybenzoic, 4-methylbenzoic, 4-fluorbenzoic, 2-brombenzoic, 4-brombenzoic, phenylacetate, 4-nitrobenzoic and benzoic acid were synthesized. In the process, an exchange reaction of the vinyl group takes place between the triazine active ester of carboxylic acid and vinyl acetate. It was determined that the yield of vinyl esters of aromatic carboxylic acids has increased in the order: of $3,3'\text{-}Ph_2BINOL\text{-}2Li/THF<BuLi/THF<KO^tBu/THF<Zn(OTf)_2/THF$. If the 4-substituted substituent contains a pair of electrons, which affects the aromatic ring and, facilitates the formation of active triazine ester accordingly the yield of the product has increased. It is shown that it is becoming difficult to remove 2-hydroxy-4,6-dimethoxy-1,3,5-triazine ion from their active triazine ester with increasing acidity of carboxylic acid, as a result, the yield of vinyl esters has decreased.

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Conflicts of Interest

Authors declare no conflict of interest.

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VİNİLASETATDAN BƏZİ AROMATİK KARBOKSİL TURŞULARININ VİNİL ESTERLƏRİNİN SİNTEZİ

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Bu işdə aromatik karboksilik turşuların 2-xloro-4,6-dimetoksi-1,3,5-triazin (CDMT) vinil efirlərinin iştirakı ilə aromatik halqada əvəzediciləri olan benzoy turşusunun törəmələrinin vinil asetatla reaksiyası ilə müəyyən edilmişdir. sintez olunur. İlkin birləşmələrin təbiətinin təsiri, temperatur, sink triflorometil-sulfonat ($Zn(OTf)_2$), dilitium 3,3′-difenilbinaftolat (3,3′-Ph_2BINOL-2Li), üçüncü dərəcəli kalium butilat ($KO^{tr}Bu$), butillitium (BuLi) sintez edilmiş birləşmələrin məhsuldarlığı tədqiq edilmişdir. Sintez edilmiş vinil efirlərinin quruluşu IR, ^1H NMR, ^{13}C NMR spektroskopiyaları ilə sübut edilmişdir.

Açar sözlər: *Aromatik karboksilik turşular, 2-xloro-4,6-dimetoksi-1,3,5-triazin, karboksilik turşuların aktiv triazin efirləri, vinilasetat, aromatik karboksilik turşuların vinil efirləri.*