

Facile synthesis of vinyl esters of aromatic carboxylic acids with participation of 2-chloro-4,6-dimethoxy-1,3,5-triazine

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Abstract. In this work, the reaction of derivatives of benzoic acid containing substituents in the aromatic ring (1a-o) with 2-chloro-4,6-dimethoxy-1,3,5-triazine (4) in the presence of N-methylmorpholine (6) has been synthesized active triazine esters of carboxylic acids (3a-o). These compounds obtained in the presence of potassium butylate (7) in reaction with vinyl acetate (2) have formed vinyl esters of corresponding aromatic carboxylic acids (5a-o). The electronic effect of the substitutor in the aromatic ring affects on carrying out of the reaction and the nature of obtained products. The structure of the synthesized vinyl esters of aromatic carboxylic acids was confirmed by FT-IR, ¹H-NMR, ¹³C-NMR, and LC/MS spectral analysis, and some of their physical constants were determined.

1 Introduction

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 [1-7]. Several reports on synthesizing vinyl esters of aliphatic, aromatic, and heteroaromatic acids exist. 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 are carried out; also the synthesis of vinyl esters of carboxylic acids was also carried in the presence of such catalysts as metals complexes and vinyl silanes [8-13].

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

Alternatively, vinyl transfer from vinyl acetate to aliphatic, aromatic, and heteroaromatic alcohols and acids has provided a safe and efficient synthesis of

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corresponding vinyl esters without catalysts by the reaction of vinyl acetate on carboxylic acids is an important task. Incorporating the vinyl group of vinyl acetate into aliphatic, aromatic, and heteroaromatic acids provides safe and efficient methods of synthesizing vinyl esters [14].

Nowadays, 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) is used to activate carboxylic acids in synthesizing 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 in mild conditions with the formation of 2-aryloxy-4,6-dimethoxy-1,3,5-triazine [15, 16].

This work effectively synthesized vinyl esters of aromatic carboxylic acids based on vinyl acetate without a catalyst (Fig.1).

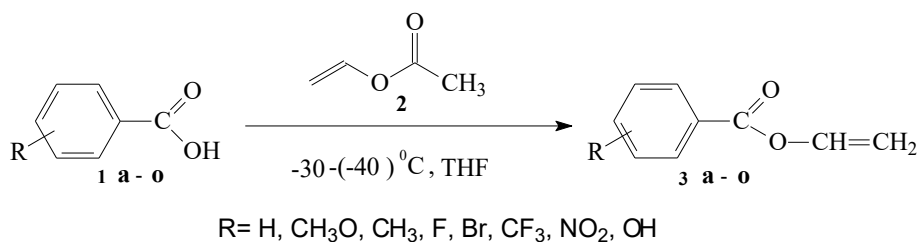


Fig. 1. Synthesis of vinyl esters of aromatic carboxylic acids

2 Methods

The major chemicals were purchased from Qingdao Sigma Chemical Co., Ltd. All commercially available reagents were used without further purification. Standard methods dried solvents before use. All reactions were carried out in oven-dried glassware under N₂, at stirring, and they were monitored by TLC (Merck Al-backed plates pre-coated with silica (0.25 mm, 60 F254). Purification was performed by column chromatography (CC) with silica gel (SiO₂; 60 – 120 mesh) purchased from SRL; elution with hexanes/AcOEt. FT-IR Spectres were recorded as a film with an Infrared Fourier spectrometer FTIR Nicolet-250. NMR specters were recorded on a Unity 400 plus instrument (Varian) with an operating frequency of 400 MHz for ¹H in CD₃OD. HMDS (0 ppm) was used as an internal standard in the ¹H_NMR spectrum. In the ¹³C_NMR spectrums, the chemical shift of the solvent was used as an internal standard (CD₃OD, 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 LC/MS: Agilent 6420 Triple Quad LC/MS.

General procedure for the synthesis of vinyl esters of aromatic carboxylic acids (5a-o) 0.001 Mole carboxylic acid (1a-o) 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 °C. After that, 1.1 ml (0.01 mol) of N-methylmorpholine was added at constant stirring. In the second flask suspension of 0.01 mole (1.12 g) of tertiary potassium butylate in 10 ml of tetrahydrofuran was prepared and cooled to -30 –(-40) °C. to which solution of 0.92 ml (0.01 mol) of vinyl acetate in 2 ml of THF was added drop by drop for 10-20 min. It was observed that with the addition of vinyl acetate, the temperature was lowered to -30 °C after 30 min stirring. 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 -30 (-40) °C. Then 20 ml of 5% NH₄Cl solution was added. At the same time, the temperature was not

raised from $-10\text{ }^{\circ}\text{C}$. The possessed was extracted with a tertiary methyl butyl ether (15 ml), the solvent was distilled, and the residue was washed sequentially with cooled 0.5 M NaHCO_3 solution, water, 1 M NaHSO_4 solution, water, a 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 than has been purified in column chromatography using the system hexane:ethyl acetate (5:1). FT-IR, Mass, $^1\text{H_NMR}$, $^{13}\text{C_NMR}$, and LC/MS spectrums of the synthesized compounds were recorded.

3 Results and discussion

In this work, the active triazine esters of aromatic carboxylic acids (3a-o) were synthesized by a reaction of benzoic acid derivatives containing various substituents in the aromatic ring (1a-o) with 2-chlorine-4,6-dimethoxy-1,3,5-triazine (4) in the presence of N-methylmorpholine (6). According to the reaction of the resulting 3a-o compounds with vinyl there, potassium (12), formed by the interaction of vinyl acetate (2) with tertiary potassium butylate (7), and the corresponding vinyl ethers (5a-o) were synthesized. The reaction was carried out as follows (Fig. 2-3):

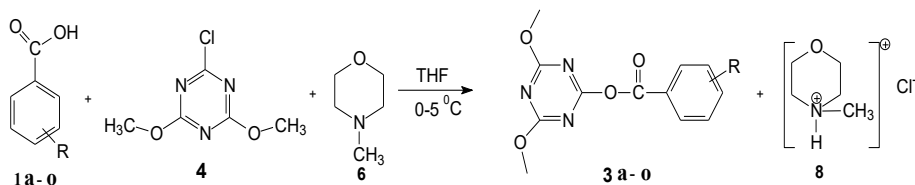


Fig. 2. Formation of triazine active esters of aromatic carboxylic acids

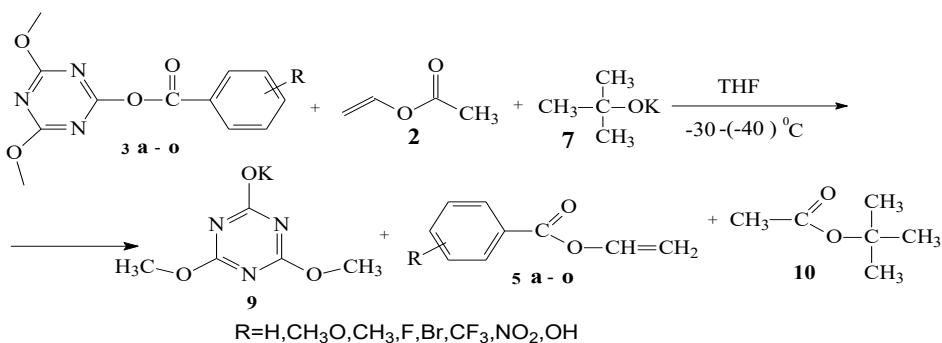
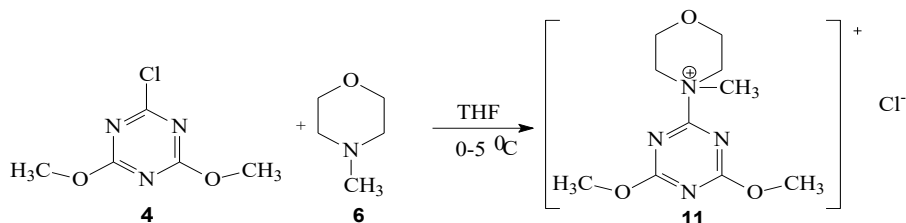
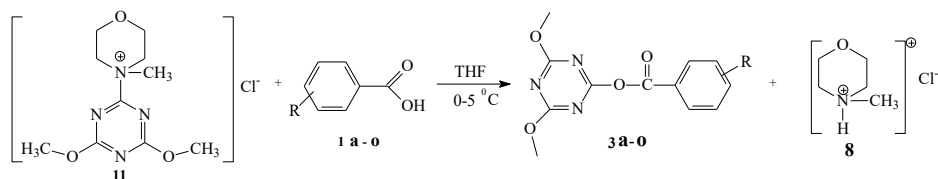


Fig. 3. Formation of vinyl esters of aromatic carboxylic acids from triazine active esters

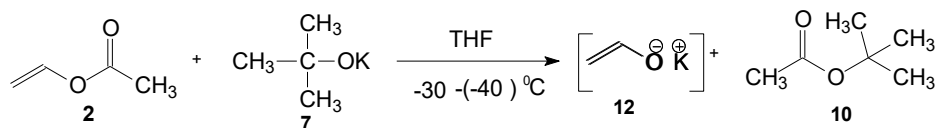
The reaction mechanism is as follows: initially, 6 reacts with 4 forming an intermediate active complex (11):



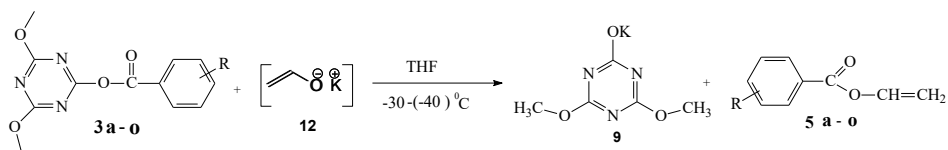
which than has reacted with 1a-o with formation of 2-aryloxy-4,6-dimethoxy-1,3,5-triazine (3a-o).



The synthesized 3a-o reacts with tertiary potassium butylate (2) with a formation corresponding 5a-o. Initially, 7 reacts with 2 under the action of a nucleophilic attack forming tertiary butyl ether (10) and acetate 12:



During of reaction of the 3a-o with 12 the 5a-o has been formed:



Vinyl esters of some carboxylic acids have been studied. Derivatives of benzoic acid and vinyl esters having various aromatic rings have been synthesized. Obtained results are presented in Table 1.

Table 1. Synthesis of vinyl esters of aromatic carboxylic acids

№		Carboxylic acids	The yield of vinyl ester, %	T _{mp} , °C
1	1 a	C ₆ H ₅ -COOCH	67	viscous liquid
2	1 b	C ₆ H ₅ -CH ₂ COOH	71	viscous liquid
3	1 c	4-CH ₃ -C ₆ H ₄ -COOH	74	viscous liquid
4	1 d	4-F-C ₆ H ₄ -COOH	63	viscous liquid
5	1 e	3-F ₃ C-C ₆ H ₄ -COOH	52	viscous liquid
6	1 f	2-Cl-C ₆ H ₄ -COOH	45	viscous liquid
7	1 g	4-Cl-C ₆ H ₄ -COOH	59	viscous liquid
8	1 h	2-Br-C ₆ H ₄ -COOH	42	viscous liquid
9	1 i	4-Br-C ₆ H ₄ -COOH	57	58–60
10	1 j	3-OH-C ₆ H ₄ -COOH	48	66
11	1 k	2-OH-C ₆ H ₄ -COOH	54	64
12	1 l	3-O ₂ N-C ₆ H ₄ -COOH	59	57–59
13	1 m	4-O ₂ N-C ₆ H ₄ -COOH	56	75–77
14	1 n	4-CH ₃ O-C ₆ H ₄ -COOH	81	59–61
15	1 o	3,4-(CH ₃ O) ₂ -C ₆ H ₃ -COOH	72	57-59

The structures of the synthesized vinyl esters of aromatic carboxylic acids were

confirmed by FT-IR, $^1\text{H-NMR}$, LC/MS, and $^{13}\text{C-NMR}$ spectral analysis; the obtained spectrum FT-IR is presented in Fig. 4:

The following signals corresponding to the vinyl group: stretching vibrations of the $=\text{CH}$ group in the region of 3091 cm^{-1} ; deformation vibrations, respectively, in the region of 1452 cm^{-1} ; bending vibrations characteristic of the $=\text{CH}_2$ group were observed in the region of 871 cm^{-1} . In the 1728 cm^{-1} region, intense absorption signals for the $\text{C}=\text{O}$ carbonyl group and average absorption signals corresponding to aromatic rings were observed in the $1600\text{--}1492\text{ cm}^{-1}$ region. Stretching vibrations for the C-O-C and $-\text{CH}=\text{CH}_2$ groups of the vinyl group were observed in the regions of 1246 and 1645 cm^{-1} , respectively.

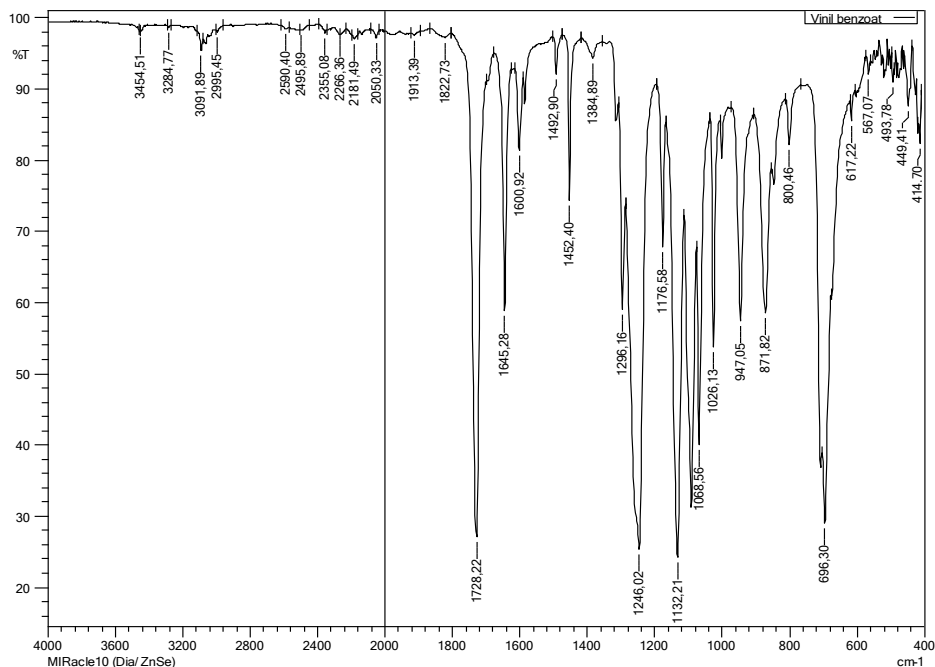
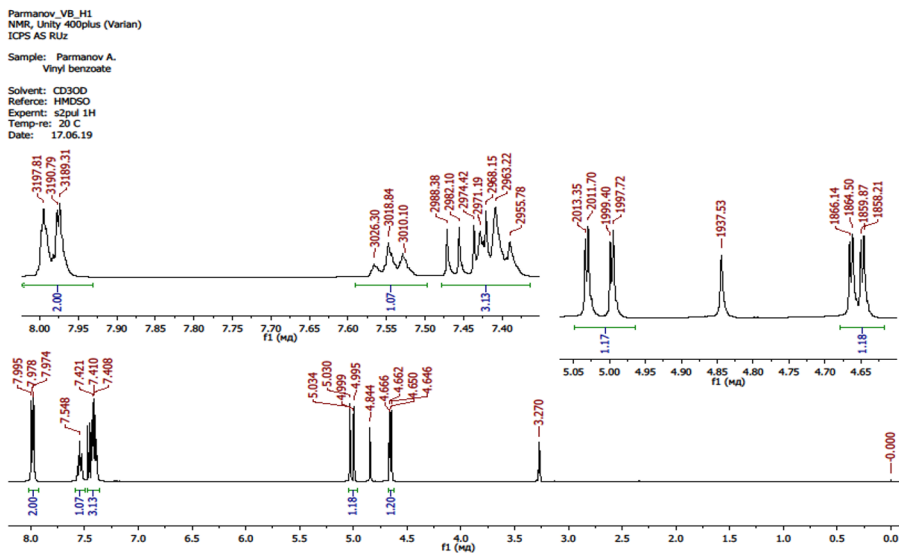


Fig. 4. FT-IR spectrum of vinyl ester of benzoic acid

The characteristic signals for aromatic protons in position-2,6 of the vinyl ester of benzoic acid in the $^1\text{H-NMR}$ spectrum (Fig. 5) appear as a doublet in the region of 7.9-8.0 ppm in the position of protons 3,4,5- aromatic ring formed signals in the form of a multiplet in the region of 7.38-7.47 ppm respectively. In the region in the form of a doublet-doublet 5.05-4.65 ppm and triplet 7.55 ppm, signals were observed for the corresponding atoms of two protons of the methylene group ($\text{CH}_2=$) and a proton of the methylenide group ($\text{CH}=\text{}$) respectively.



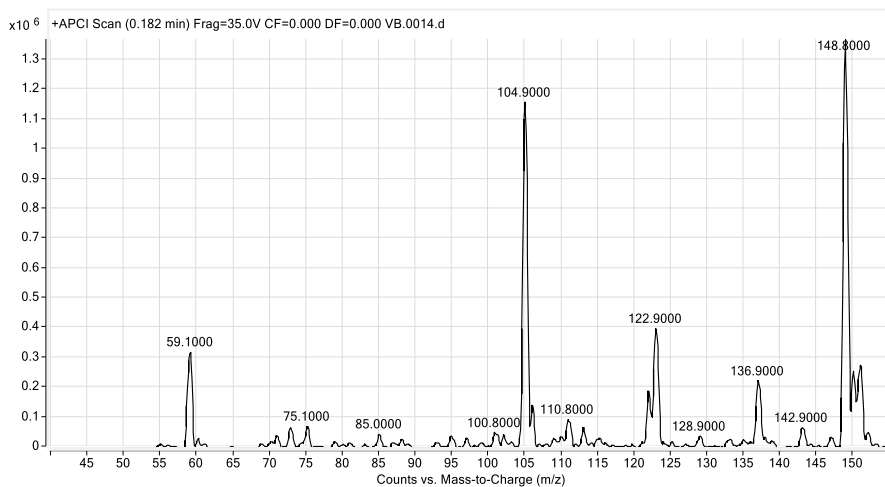


Fig. 7. Chromato-mass spectrum of vinyl ester of benzoic acid

4 Conclusions

Analysis of the results has shown that the reaction vinyl of ester the carboxylic acid with the triazine ester was carried out. The electronic effect of the substituents in the aromatic ring affects the yield of the reaction. It has been determined that with an increasing the acid strength of carboxylic acids, the yield of the corresponding vinyl esters has decreased, which can be explained as follows: if there are paired electrons in the 4th position of the aromatic ring, they have affected on mesomeric electronic effect and facilitates on the formation of an active triazine acid ester. Owing to the increasing acidity of carboxylic acid, the elimination of the 2-hydroxy-3,5-dimethoxy-1,3,5-triazine ion from the active triazine ester of the carboxylic acid becomes more difficult, and owing to which decreasing of the yield of the corresponding vinyl esters was observed. In addition, it was observed that the nitrogen atom in nitrobenzoic acid is also an electrophilic center, so the formation of by-products was also observed.

Acknowledgments

The authors are thankful for financial support of the Foundation science of Uzbekistan (Grant No. AM-Φ3-2019081449) and the Institute of Organic Chemistry, Faculty of Chemistry, and Lodz Polytechnic University.

References

1. Ruihang Jiang, Zhangpei Chen, Kun Zhan. *Tetrahedron Letters* 59 (2018) 3279–3282.
2. J. Esquivias, R. G. Arrayar s, J. C. Carretero, *J. Am. Chem. Soc.* 2007, 129, 1480.
3. H. M. L. Davies, B. Hu, *J. Org. Chem.* 1992, 57, 3186. J. J. Kim, H. Alper, *Chem. Commun.* 2005, 3059.
4. Y. Terada, M. Arisawa, A. Nishida, *Angew. Chem., Int. Ed.* 2004, 43, 4063.
5. X. Wei, J. C. Lorenz, S. Kapadia, A. Saha, N. Haddad, C. A. Busacca, C. H. Senanayake, *J. Org. Chem.* 2007, 72, 4250.

6. S. Liu, N. Berry, N. Thomson, A. Pettman, Z. Hyder, J. Mo, J. Xiao, J. Org. Chem. 2006, 71, 7467.
7. S. Martinez-Montero, S. Fernandez, Y. S. Sanghvi, V. Gotor, M. Ferrero, Org. Biomol. Chem. 2011, 9, 5960.
8. S. Yi. Chae, Gao Ruili. Organometallics 2009, 28, 6585–6592.
9. Jun Gao, Dongrui Guan, Dongmei Xu, Liwen Zhao, Lianzheng Zhang and Min Li. Bull. Chem. Soc. Ethiop. 2018, 32(2), 351-359.
10. Hideto Nakagawa, Yoshio Okimoto, Satoshi Sakaguchi and Yasutaka Ishii. Tetrahedron Letters 44 (2003) 103–106.
11. Ruimao Hua, Xin Tian. J. Org. Chem. 2004, 69, 5782-5784.
12. Sh.A. Mirsagatov, I.B. Sapaev. Photoelectric and Electrical Properties of a Reverse - Biased p-Si/n-CdS/n⁺-CdS Heterostructure//Inorganic Materials, 2014, Vol. 50, No. 5, pp. 437–442.
13. Sh.A. Mirsagatov, I.B. Sapaev. Injection Photodiode Based on a p-Si-n-CdS-n⁺-CdS// Semiconductors, 2014, Vol. 48, No. 10, pp. 1363–1369.
14. A.B. Parmanov, S.E. Nurmonov, B.N. Khandamov, Beata Kolesinsko. Synthesis of vinyl esters of carboxylic acids with the participation of 2-chloro-4, 6-dimethoxy-1, 3, 5-triazine // International conference “Youth as a driving force for the development of science”,–Chimkent, Kazakhstan-2019. P. 183-185.
15. J. Zbigniew, Kaminski, Beata Kolesinska, Marcinkowska Małgorzata. Synthetic communications. Vol. 34, No. 18, pp. 3349–3358, 2004.
16. A.B.Parmanov, S.E.Nurmonov, Sh.Djumagulov, J.Isomidonov. Synthesis of divinyl ester of adipic acid // European Journal of Molecular & Clinical Medicine. ISSN:2515-8260. Vol.07, Iss. 07, 2020. P. 909-920.