Original Research Article

Catalytic Reaction with Benzoic Acid Phenylacetylene in the Presence of Complex Catalysts

ABSTRACT

In this work, we studied the processes of vinyl ester formation by the addition of benzoic acid to phenylacetylene in the presence of complex catalysts of diacetate-di (2-amino-5-methylthio-1,3,4-thiadiazolo) cobalt(II) ($[Co(C_3H_5N_3S_2)_2(CH_3COO)_2]$ and tetrakis(2-amino-5-ethylthio-1,3,4-thiadiazole)-zinc(II) dinitrate ($[Zn(C_4H_7S_2)_4](NO_3)_2$): 1-phenylvinyl benzoate and *anti*-Markovnikov coupling product - styryl benzoate The effect of the nature of solvents on the yields of products in the presence of the $[Zn(C_4H_7S_2)_4](NO_3)_2$ complex catalyst was studied. The structure of the synthesized vinyl esters was proved by IR, ^1H NMR, ^{13}C NMR spectroscopies.

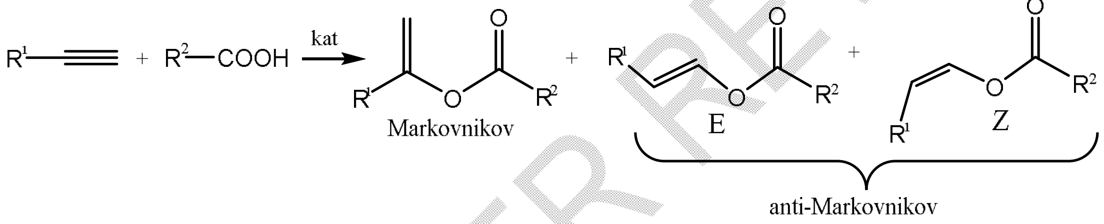
Keywords: Benzoic acid, phenylacetylene, Markovnikov couplings, *anti*-Markovnikov couplings, 1-phenylvinyl benzoate, styryl benzoate.

1. INTRODUCTION

Vinyl esters of carboxylic acids are active compounds and are used as intermediates in organic synthesis, polymerization, hydrogenation, cross-internationalization reactions. The addition of carboxylic acids to alkynes proceeds under mild reaction conditions, in the presence of metal catalysts, with the formation of vinyl esters [1-4].

Mercury salts were originally used as catalysts in this reaction, but their high toxicity limited their use. Various metal complex catalysts: Ru, Pd, Rh, Ir, Re, Au, and Ag affect the course of these reactions in different ways and have different selectivity. However, these metals are expensive and their complexes are relatively unstable [5–7]. The synthesis of vinyl esters using inexpensive and widely available metal catalysts is one of the urgent problems. In the last decade, organic reactions in the presence of zinc and cobalt catalysts have become widespread. The use of inexpensive metal compounds instead of expensive metal compounds makes it possible to achieve not only economy, but also high activity and different selectivity. Hydrogenation by activation of alkynes in the presence of a cobalt catalyst, such reactions as hydroboration and hydroacylation, are well studied, the process proceeds with the formation of an intermediate product Co(I)-H. Recently, salts and complexes of cobalt with tridentate ligands have shown high activity in various catalytic organic reactions. Complexes with tridentate ligands NNN, NNP, and PNP containing nitrogen and phosphorus have been synthesized [8-11].

When carboxylic acids react with known terminal alkynes, Markovnikov and Anti-Markovnikov (Z/E) coupling products are formed: three isomeric mixtures of 1-alkenyl esters in various ratios.



This reaction was first carried out in 1980 in the presence of a ruthenium complex catalyst. Later, studies were carried out with catalysts such as rhodium, rhenium, iridium, gold and bimetals. The ruthenium catalyst has been extensively studied due to its high efficiency and ease of synthesis. Some ruthenium complex catalysts allow regio- and stereoselective control of the reaction. The coordination of an alkyne by a metal ion affects the regioselectivity of the reaction [12].

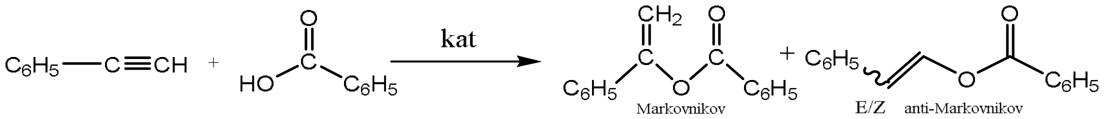
2. MATERIAL AND METHODS

IR spectra of synthesized substances on a Bruker Fure Invenio S-2021 spectrometer in the range 4000 – 400 cm–1. recorded. The 1H NMR spectra of CDCl3 were recorded on a Unity+400 instrument (Varian) with an operating frequency of 400 MHz. GMDS was used as an internal standard in the 1H NMR spectra. The chemical shift of the solvent in the 13C- spectra was used as an internal standard. The results of mass spectrometry of substances "Agilent Technologies 7890B Network GC system" are obtained on gas chromatography-mass spectrometers.

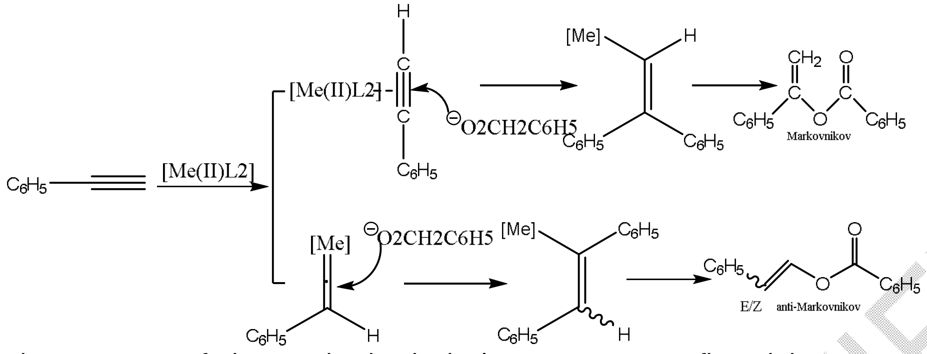
Reaction of benzoic acid with phenylacetylene in the presence of catalytic systems. Synthesis of 1-phenylvinylbenzoate. A mechanical stirrer, a reflux condenser, and an addition funnel were installed in a 100 ml three-necked flask. 1.22 g (1 mmol) of benzoic acid (C_6H_5COOH), 1.02 g (1.1 ml, 1 mmol) of phenylacetylene (C_6H_5CCH), catalyst (0.01 mmol) were added to the flask and dissolved in 20 ml of toluene. The reaction mixture was heated in a thermostat at 110 °C with stirring for 24 hours. The reaction mixture was extracted with diethyl ether (3 x 15 ml) and washed successively with 0.5 M $NaHCO_3$ solution, distilled water, 1 M aqueous $NaHSO_4$ solution, distilled water, saturated potassium chloride solution and distilled water. The extract was dried over 5 g of Na_2SO_4 or K_2CO_3 for 12 h and filtered. The solvent was removed in vacuo. The residue was dried in a vacuum desiccator to constant weight.

3. RESULTS AND DISCUSSION

$[Co(C_3H_5N_3S_2)_2(CH_3COO)_2]$ and $[Zn(C_4H_7S_2)_4](NO_3)_2$ complex processes of vinyl ester formation upon addition of benzoic acid to phenylacetylene were carried out in the presence of catalysts. The reaction scheme is as follows.



Based on the literature sources, the following mechanism for the coupling of carboxylic acids with phenylacetylene in the presence of a catalyst was proposed:



The structure of the synthesized vinyl esters was confirmed by IR, 1H-, 13C NMR and chromato-mass spectral analysis (Fig. 1-4).

1-Phenylvinylbenzoate. Yield 67%. Yellow liquid. 1H NMR: d 5.34 (1H, d, J=2.4 Hz), 5.74 (1H, d, J=2.4 Hz), 7.31-7.53 (5H, 7.37 (tt, 7.2, 1.3 Hz), 7.41 (dddd, J = 7.7, 7.2, 1.8, 0.5 Hz), 7.46 (dddd, J = 8.5, 7.5, 1.3, 0.4 Hz)), 7.60 (1H, tt, J = 7.5, 1.5 Hz), 8.04 (2H, dddd, J = 8.5, 1 .9, 1.5, 0.4 Hz), 8.36 (2H, dtd, J = 7.7, 1.2, 0.5 Hz). 13C NMR: d 91.0 (1C, s), 125.2 (1C, s), 125.7 (2C, s), 127.8-127.8 (2C, 127.8 (s), 127, 8 (s)), 128.3-128.5 (4C, 128.4 (s)). s), 128.4 (s)), 129.5 (1C, s), 129.7 (2C, s), 149.5 (1C, s), 164.0 (1C, s).

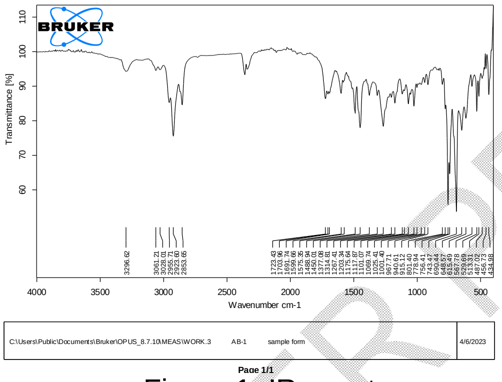


Figure 1. IR spectrum of 1-phenylvinyl benzoate

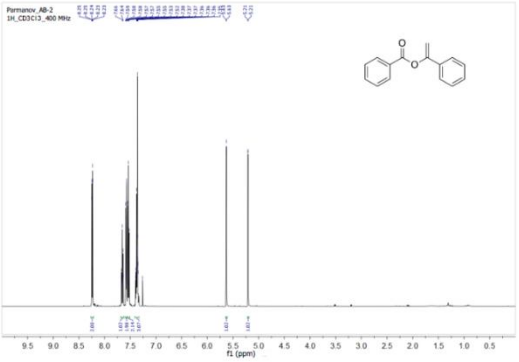


Figure 2. 1H NMR spectrum of 1-phenylvinyl benzoate

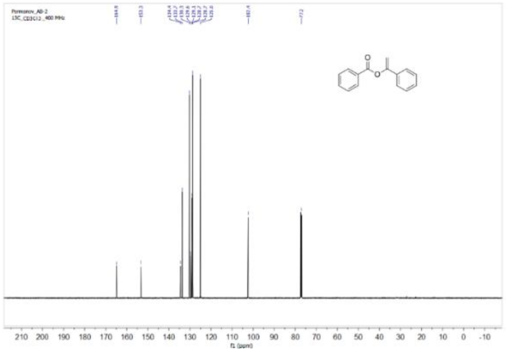


Figure 3. 1-phenylvinyl benzoate 13C NMR spectrum

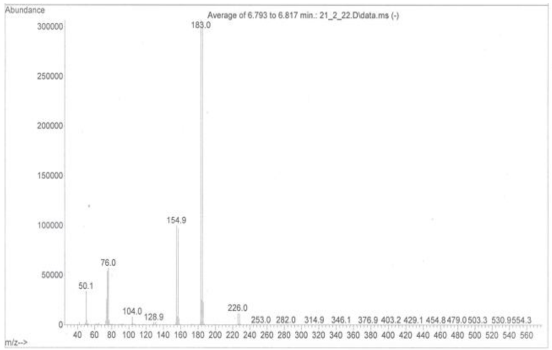


Figure 4. Chromato-mass spectrum of 1-phenylvinylbenzoate

Specific absorption regions are observed in the IR spectra of compounds containing a vinyl ester group. The IR spectrum of 1-phenylvinyl benzoate (Fig. 1) does not show an intense absorption band characteristic of three bonds. A symmetric stretching vibration of the methylene group (=CH$_2$) in the vinyl group was observed in the region of 2853 cm^{-1}, and a weak sharp bending vibration was observed at 1450 cm^{-1}. Intense absorption lines of the carbonyl group (C=O) were observed in the region of 1723 cm^{-1}. Stretching vibrations characteristic of the ether bond (C-O-C) were observed in the absorption region of 1267 cm^{-1}. The interring vibrations of the aromatic ring manifested themselves in the region of 1488 cm^{-1}, the bending vibrations characteristic of the C–H bond of the ring manifested themselves in the region of 801 cm^{-1}, and the stretching vibrations were characteristic of the =C–H bond. appeared in the region of 3000 cm^{-1}. The pointed stretching peaks ($-C=CH_2$) characteristic of the vinyl group were observed in the region of 1680 cm^{-1}.

^{1}H NMR spectrum of 1-phenylvinyl benzoate (Fig. 2) 5.21-5.63 ppm spheres show doublet signals of two proton atoms in the vinyl group. The multiplet signal of two protons at position 2,6 of the aromatic ring in the phenylacetylene residue is 8.25 ppm. in the field, and the doublet-doublet signals of aromatic atoms of protons in the residues of phenylacetylene and benzoic acid are 7.35-7.65 ppm. seen in the fields.

In the ^{13}C spectrum of 1-phenylvinylbenzoate (Fig. 3), the signal of the carbon atom occupied by the carboxyl group of the aromatic ring in the benzoic acid residue is 164.9 ppm. in a sphere, and the signal of carbon atoms of the aromatic ring is 125-134 ppm. seen in the fields. The carbon atoms in the vinyl group are 153.4 ppm. (C=) and 102.4 ppm. (CH_2=) was observed in the fields.

In the chromato-mass spectrum of the synthesized 1-phenylvinyl benzoate (Fig. 4), the formation of ions was determined, corresponding to their molecular weight, and the mass of fragment ions formed as a result of their fragmentation. The 1-phenylvinylbenzoate peak of the molecular ion He was 226.0. The chromato-mass spectrum of fragment ions formed from a molecular ion is presented in turn. Also the mass in the spectrum 76, m/z=50.

The reaction was carried out in a toluene solution at a temperature of 110 ^{o}C for 24 hours. The starting benzoic acid and phenylacetylene were obtained in a 1:1 molar ratio, and the catalyst was prepared at 1 mol % relative to the starting benzoic acid. The results obtained are presented in the table (Table 1).

Table 1

The reaction of benzoic acid with phenylacetylene, catalyst-1 mol%, temperature-110 ^{0}C, solvent toluene

№	Catalysts	Total yield, %	Yield of 1-phenylvinyl benzoate, %	Yield of styryl benzoate (E/Z), %
1	$[Zn(C_4H_7S_2)_4](NO_3)_2$	67	80	20
2	$[Co(C_3H_5N_3S_2)_2(CH_3COO)_2]$	55	90	10

It can be seen from the results obtained that the catalysts lead to the formation of the Markovnikov coupling product 1-phenylvinyl benzoate in large quantities. The activity and selectivity of catalysts are affected by the basicity of the ligand. The highest activity was achieved on the zinc complex catalyst; the total yield of the product in the reaction of benzoic acid with phenylacetylene was 67%. The product of the Markovnikov combination: 1-phenylvinyl benzoate (80%) formed more, and the product of the anti-Markovnikov combination - styryl benzoate - 20%. In the reaction with a cobalt complex catalyst, the total yield of the product was 55%, 1-phenylvinyl benzoate (90%), styryl benzoate 10%.

We studied the effect of various solvents on the product yield in the presence of the $[Zn(C_4H_7S_2)_4](NO_3)_2$ complex catalyst. In the process, non-polar solvents such as carbon tetrachloride, toluene and cyclohexane showed high activity. The reaction was carried out in solutions of carbon tetrachloride, cyclohexane, toluene, THF and dioxane at a temperature of 60 ^{0}C. Under these conditions, no product was formed in a solution of THF and dioxane (Table 2).

Table 2

Influence of the solvent on the addition of benzoic acid to phenylacetylene, catalyst $[Zn(C_4H_7S_2)_4](NO_3)_2$

№	Solvent	Total yield, %	Temperature, ^{0}C	1 mol % $[Zn(C_4H_7S_2)_4](NO_3)_2$	
				Yield of 1-phenylvinylbenzoate, %	Yield of styryl benzoate (E/Z), %
1	CCl_4	64	75	75	25

2	Cyclohexane	60	80	83	17
3	Toluene	67	110	80	20
4	THF	40	67	65	35
5	Dioxane	43	101	77	23
1	CCl_4	53	60	70	30
2	Cyclohexane	50		81	19
3	Toluene	55		77	23
4	THF	-		-	-
5	Dioxane	-		-	-

When the process was carried out at the boiling point of each solvent, the overall yield of the product was in the range of 40-67%, and the yield of 1-phenylvinyl benzoate was in the range of 65-83% of the overall yield. The maximum yield in a toluene solution (110 0C) was 67%. It was shown that the reaction proceeds according to the Markovnikov coupling reaction in a cyclohexane solution with a total yield of 60%, and the yield of 1-phenylvinyl benzoate is 83% relative to the total product (table). Dioxane (43%) and tetrahydrofuran (40%) from solvents with relatively high polarity showed a relatively low overall product yield. Dioxane and tetrahydrofuran solvents failed to isolate the product at the boiling point of the solvent.

4. CONCLUSION

The catalytic reaction of the coupling of phenylacetylene with benzoic acid in the presence of $[Co(C_3H_5N_3S_2)_2(CH_3COO)_2]$ and the $[Zn(C_4H_7S_2)_4](NO_3)_2$ complex was carried out in the presence of catalysts. In this case, the product of the Markovnikov coupling, 1-phenylvinyl benzoate, is formed in a larger amount. The total yield of the product in the reaction of benzoic acid with phenylacetylene in the presence of the most active complex zinc catalyst was 67%. We studied the effect of various solvents on the product yield in the presence of the $[Zn(C_4H_7S_2)_4](NO_3)_2$ complex catalyst. The reaction was carried out in a solvent medium of carbon tetrachloride, cyclohexane, toluene, THF, and dioxane. When carrying out the reaction at the boiling point of the solvent, the total yield of the product was 40-67%. The yield of 1-phenylvinyl benzoate was determined to be in the range of 65-83% compared to the overall yield. The maximum yield in a toluene solution (110 ^{0}C) was 67%.

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