

## Synthesis of Aromatic Acetylenic Alcohols and their Vinyl Esters

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### Abstract

*Synthesized aromatic acetylenic alcohols reacting phenylacetylene and crotonaldehyde, as well as some ketones (acetone, methylethylketone, methylisopropylketone, pinokalineandacetophenone) based organomagnesium compounds. Catalytic vinylation reaction with aromatic acetylenic alcohols homogeneous methods. Scientifically proven influence of various factors-the molar ratio of the starting materials, temperature and the nature of the solvent on the yield. The optimal conditions for the synthesis of a high yield in the process.*

**Keywords:** phenylacetylene, organomagnesium compounds, ketones, aromatic acetylenic alcohols, vinyl esters.

### Introduction

Acetylene hydrocarbons and various derivatives thereof, due to their high reactivity and availability is widely used in organic synthesis. Organometallic compound first synthesized by E. Franklin. M. Barbe is shifted synthesized organometallic compounds [1, 2]. French scientist B. Grignard reaction of alkyl halides with anhydrous magnesium metal powder mixed synthesized organometallic compounds (reagent Grignard) and developed the conditions of their application to various organic syntheses. New stable compounds by reaction with alkynes reagent Grignard synthesized J. Iotzich [3, 4]. The high reactivity of C $\equiv$ C- and C-H bonds in alkynyl makes them participants in the diverse reactions that form the basis of section synthetic organic and industrial chemistry [5, 6].

Recently, scientific investigations on the creation of ecological safety and waste less technologies, also, on the synthesis of economically cheap chemical preparations with higher yield and to introduce them into the practice have been carried out [7]. Homogenous-catalytic vinylation reaction on the basis of aromatic acetylene alcohols (AAA) MeOH-DMSO (MeOH- LiOH, NaOH and KOH) has been carried out and it was exposed that vinyl ethers (VE) synthesized desirable in the interval of 40-60% [8].

The gained results show that as LiOH, NaOH and KOH are used in the system of CsF-MOH-DMSO as MOH, in each particular state the yield of product goes through maximum while the temperature is rising. It has been determined the increase of AAA on the series LiOH·CsF < KOH·CsF < NaOH·CsF in the selected catalytic systems. As temperature rose from 80 to 120 °C, the yield raised appreciably.

The selectivity of temperature 100°C state has been meant as the highest system for the process. It can be explained that catalytic activity of presented system with the formation of CsOH and NaF in the system and its less solubility with the higher base-property of CsOH. In LiOH and KOH systems, the solubility of the formed LiF and NaF is higher, and in the system they are existed in the state of ion in the system, the balance specifies. Hereon, CsOH couldn't perform completely activity. Owing to this LiOH+CsOH+LiF+CsF system is in charge of catalyst.

When industrial implementation of heterogeneous catalytic processes have to adjust the speed and direction of chemical reactions, the mechanism of which is known only in the most general terms, and the

catalysts are complex solids, properties which are still not fully understood, and that may include almost all the elements of the periodic the periodic system [9, 10].

In this study of heterogeneous catalytic process to synthesize certain vinyl esters of aromatic acetylenic alcohols in relatively high yields in the presence of MOH (MOH- LiOH, NaOH and KOH) systems impregnated activated carbon. The active component of the catalyst used hydroxides of sodium and potassium. The process carried out at different temperatures and reaction time.

### Experimental Section:

PMR spectra of the structure of synthesized compounds have been studied in the spectrophotometer Jeol FX-90Q (90 millihertz), and IR structure has been studied in the spectrophotometer Bruker JFS-25. In the room temperature NMR<sup>1</sup>H structure has been determined with the help of spectrophotometer Bruker DPX - 400 (working frequency 400.13 millihertz, solvent - CDCl<sub>3</sub>, inner standard - GMDS). The content of mixture has been analyzed GLCh with the help of device LXM-80 (gas - carrier - helium, (column) geysir 3000×3 mm, 1% solution of liquid phase polyethylene glycol in NaCl).

Phase structure of synthesized AAA molecules, distribution of charges and electron density in the molecules, quantum - chemical granularity of compounds have been determined with the help of quantum-chemical half-empiric PM3 of STAT program Hyper Chem Activation 7,0 packet and the processes have been mathematical modeled, also AAA physical-chemical value (amount), including boiling and liquefaction temperatures, density, specific refraction indexes, their solubility in water or in which solutions and acceptable poisonous degrees have been investigated [11].

### Material and Methods

To study the synthesis of AAA and vinylation used styrene, bromo, phenylacetylene (PhA), acetone, methyl ethyl ketone, methyl isopropyl ketone, pinokalin, acetophenone, croton aldehyde, ethyl benzene, dimethylsulfoxide (DMSO), dimethylformamide (DMFA), diethylether (DEE), benzene, chloroform, hydroquinone, cesium fluoride, tetrahydrofuran (THF), acetylene, alkalis, salts and others.

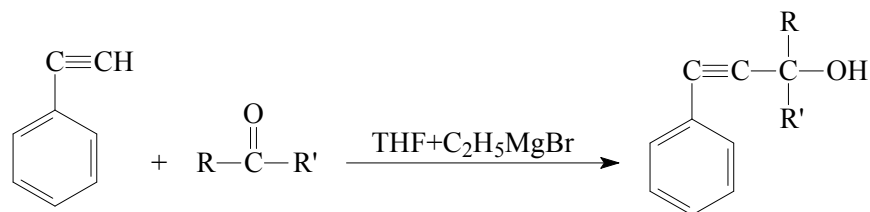
#### *Methods homogeneous- catalytic vinylation of AAA with acetylene*

First of all 4,62 g CsF, 3,76 g. alkali (for analyze 2KOH·H<sub>2</sub>O, ~15% H<sub>2</sub>O with pure grade) and 150 ml., solvent (DMSO 0,2% H<sub>2</sub>O of chemical pure grade) are poured into a 500 - millimeter - flask that mechanic stirrer, thermometer and reverse cooler are installed in, and heating under the temperature of 100 °C, it is prepared suspension. Product suspension is cooled to the temperature of 30- 35°C. It is saturated with acetylene for 30 minutes, then as acetylene is running, ether solution (0,1 mole) is sent to the system for 6 hours at temperature 120°C. Having been cooled the mixture is hydrolyzed and it is extracted, organic part is separated and dried with the help of MgSO<sub>4</sub>. The mixture purified from water is refined of ether through distillation in common situation, then vacuum distillation is fulfilled. In this case aromatic acetylene alcohol, its vinyl ether, secondary and interval products are rectified and refined [12].

### Result and Discussions:

**Synthesis AAA.** In reaction Grinyara- Iotsicha using croton aldehyde and ketones (acetone, methyl ethyl ketone, methyl isopropyl ketone, pinokaline and acetophenone) PhA by their interaction with the organomagnesium compound synthesized in the following respective compounds AAA- 1-phenyl-3-methylbutyn-1-ol-3 (I) 1-phenyl-3-methylpentyn-1-ol-3 (II) 1-phenyl-3,4-dimethylpentyn-1-ol-

3 (III), 1-phenyl-3,4,4-trimethylpentyn-1-ol-3 (IV) 1,3-diphenylbutyn-1-ol-3 (V) and 1-phenylgekcyn-4-in-1-ol-3(VI). The scheme of the reaction has been offered as following[13].



here: R= -CH<sub>3</sub>, R'= -CH<sub>3</sub>; R= -CH<sub>3</sub>, R'= -C<sub>2</sub>H<sub>5</sub>; R= -CH<sub>3</sub>, R'= *izo* -C<sub>3</sub>H<sub>7</sub>, R= -CH<sub>3</sub>,  
R'= -C(CH<sub>3</sub>)<sub>3</sub>; R= -CH<sub>3</sub>, R'= -C<sub>6</sub>H<sub>5</sub>, R= -H, R'= -CH=CH-CH<sub>3</sub>.

Synthesis process AAA method Grinyara- Iotsicha conducted at a temperature range -5-10 °C in the presence of solvents DEE and THF. The starting materials were taken in equimolar amounts. The results are shown in the table 1.

**Table1** Influence of the nature and duration of the reactions solvent on the yield of AAA (temperature 0–5 °C, starting materials in an equimolar ratio)

AAA	Products, %			
	solvent DEE		solvent THF	
	AAA	intermediate and auxiliary connections	AAA	intermediate and auxiliary connections
Duration of reaction, 2 hour				
I	75,0	18,3	87,4	6,5
II	68,4	23,4	83,5	10,2
III	56,4	29,5	74,5	15,3
IV	53,0	34,7	69,3	18,4
V	50,0	39,6	66,0	21,0
VI	64,3	26,4	79,0	14,1
Duration of reaction, 4 hour				
I	78,6	13,2	89,6	4,5
II	71,8	17,4	85,0	7,6
III	60,6	21,6	75,2	13,0
IV	55,9	25,0	71,0	15,5
V	54,7	28,0	68,7	18,2
VI	68,0	20,0	81,2	12,2
Duration of reaction, 6 hour				
I	67,3	24,8	82,2	11,4
II	62,4	27,0	77,6	17,0
III	52,4	37,0	69,5	18,4
IV	45,2	41,6	63,2	21,0
V	42,7	44,0	57,3	23,7
VI	58,6	35,6	70,6	17,4

here: I- 1-phenyl-3-methylbutyn-1-ol-3;

III- 1-phenyl-3,4-dimethylpentyn-1-ol-3;

V- 1,3-diphenylbutyn-1-ol-3;

II- 1-phenyl-3-methylpentyn-1-ol-3;

IV- 1-phenyl-3,4,4-trimethylpentyn-1-ol-3;

VI- 1-phenylgekcyn-4-in-1-ol-3.

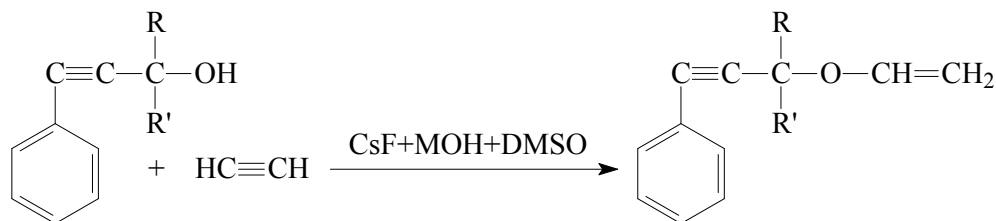
The table shows that when using THF as solvent, increasing the reaction time from 2 to 4 hours, an increase yield. However, with increasing duration of synthesis up to 6 hours, a sharp fall of efficiency AAA exit. The table shows that when the reaction is carried out in solvents DEE and THF in AAA is formed with a high yield. For example, with a reaction time 4 hours temperature -5- 0 °C in a solvent DEE, yield AAA: I- 78,8; II- 71,8; III- 60,6; IV- 55,9; V- 54,7 and VI- 68,0%, and in case of replacement solvent THF respectively 89,6; 85,0; 75,2; 71,0; 68,7 and 82,2%. Comparing the reaction results in different solvents shows that the average selectivity output y THF solvent by 13,0% more than the DEE. This reaction is due to the greater polarity of THF molecule compared to DEE.

The reaction carried out in THF, AAA negligible amount of by-products and intermediates. Solubility Iotsicha reagent in THF solution is very high; it creates a comfortable environment for the last phase of collision with aldehydes and ketones. Halogen AAA salt formed during the reaction is hydrolyzed, THF serves as a catalyst and, disaggregated electron pairs in its molecule solvation salts promote conversion AAA. THF relatively low solubility in water than DEE forms with water an unstable tetramethylglycol in weakly acidic medium and forms tetrametilenhloridrin acid as a byproduct. This reduces the amount of alkoxides formed by reacting a basic salt AAA and provides the basis for the synthesis of alcohols in high yield.

To explore possible areas of application of the synthesized compounds was studied their microbiological activity against the biological corrosion of pipelines of the oil industry in the laboratory together with the staff of the Institute of Microbiology, Academy of Sciences of Uzbekistan [14]. AAA obtained possess microbiological activity, among the compounds studied V, I and II have active antibacterial properties against bacteria *Pseudomonas*, *Arthrobacterchroococcum*, *Micrococcus album*, *Micrococcus sulfurous*, *Desulfovibrio vulgaris*, *Acinetobacter*, *Rhodococcuseruthropolis*, *Rhodococcusluteus*, *Rhodococcusterrae*, *Basillus sp.* isolated from samples of oil field pipelines[15].

### Synthesis VE AAA.

Hence, vinylation reaction on the basis of AAA acetylene with higher base-catalytic system, The scheme of the reaction has been offered as following:



here: R= -CH<sub>3</sub>, R'= -CH<sub>3</sub>; R= -CH<sub>3</sub>, R'= -C<sub>2</sub>H<sub>5</sub>; R= -CH<sub>3</sub>, R'= *izo* -C<sub>3</sub>H<sub>7</sub>, R= -CH<sub>3</sub>, R'= -C(CH<sub>3</sub>)<sub>3</sub>; R= -CH<sub>3</sub>, R'= -C<sub>6</sub>H<sub>3</sub>, MOH= LiOH, NaOH, KOH.

It has been observed the relatively maximum yield synthesis of VE AAA in the presence of MeOH-CsF-DMSO with higher base-system on the experiment's results.

The gained results show that as LiOH, NaOH and KOH are used in the system of CsF-MOH-DMSO as MOH, in each particular state the yield of product goes through maximum while the temperature is rising. It has been determined the increase of AAA on the series LiOH·CsF<KOH·CsF<NaOH·CsF in the selected catalytic systems. As temperature rose from 80 to 120 °C, the yield raised appreciably.

**Table 2. The influence of nature and temperature of catalysts on the yield of VE AAA (duration of reaction is 6 hours, solvent DMSO)**

Catalyst	Temperature, °C	I	II	III	IV
LiOH·CsF	80	44,3	38,2	33,3	56,0
	100	49,0	46,6	42,9	59,4
	120	51,1	48,4	46,3	58,0
KOH·CsF	80	49,6	45,2	40,2	57,4
	100	57,4	52,0	40,7	66,4
	120	58,3	55,7	49,6	67,3
NaOH·CsF	80	74,2	73,2	67,3	79,6
	100	84,8	77,1	72,3	88,0
	120	86,0	79,7	75,0	89,5

here: I- VE 1-phenyl-3-methylpentyn-1-ol-3; II- VE 1-phenyl-3,4-dimethylpentyn-1-ol-3;  
III- VE 1-phenyl-3,4,4-trimethylpentyn-1-ol-3; IV- VE 1,3-diphenylbutyn-1-ol-3.

The selectivity of temperature 100°C state has been meant as the highest system for the process. It can be explained that catalytic activity of presented system with the formation of CsOH and NaF in the system and its less solubility with the higher base-property of CsOH. In LiOH and KOH systems, the solubility of the formed LiF and NaF is higher, and in the system they are existed in the state of ion in the system, the balance specifies. Hereon, CsOH couldn't perform completely activity. Owing to this LiOH+CsOH+LiF+CsF system is in charge of catalyst.

It has been observed, vinylation process on the AAA higher base-system, reaction undergoes under top level along with the formation of polycomponent mixtures on the some stages. Herein, moving hydrogen of acetylene goes on base of stereo-regioselectivity, also its exchanging process does easily. Although investigations on the vinylation process of organic compounds including members of various classes hydroxyl group containing in their molecules have been carried out for years, reaction mechanism hasn't enough researched scientifically yet. At present having formed catalytic active center, reactions being carried out in the system MeO–CsF–DMSO, formation of metal solvates and having become interval metal complex possessing active center, counterbalances the function of catalyst.

As the result of investigation, it has been determined that duration of reaction appreciably influences on the product yield. Including when the process lasted for 6 hours, it was observed vinyl ethers emerge with top yield in all selected systems.

When the process lasted 8 hours, it was observed the yield of product decrease on the consequence of polycomponent mixtures formation, dimerization of acetylene and polymerization of VE (Table 3).

**Table 3** The influence of nature and temperature of catalysts on the yield of VE AAA (Temperature 100 °C, solvent DMSO)

Catalyst	Duration of reaction, hour	I	II	III	IV
LiOH·CsF	4	43,8	39,0	36,8	54,8
	6	49,0	46,6	42,9	59,4
	8	42,4	37,8	34,1	52,2
KOH·CsF	4	48,4	46,3	44,4	62,0

	6	57,4	52,0	47,0	66,4
	8	47,2	42,2	40,1	58,4
NaOH·CsF	4	78,2	73,0	67,7	79,8
	6	84,8	77,1	72,3	88,0
	8	73,4	70,8	65,5	76,3

here: I- VE 1-phenyl-3-methylpentyn-1-ol-3; II- VE 1-phenyl-3,4-dimethylpentyn-1-ol-3;  
III- VE 1-phenyl-3,4,4-trimethylpentyn-1-ol-3; IV- VE 1,3-diphenylbutyn-1-ol-3.

It has been determined that the yield of product emerge at very maximum: I=84,8%; II=77,1%; III=72,3% and IV=88,0% in the interval of catalysts LiOH·CsF, KOH·CsF as NaOH·CsF is used. We can explain the exact higher yield of VE quantity in NaOH·CsF state than in KOH·CsF state as stated below:

– as the result of fusing of sodium hydroxide in DMSO solution, exchanging reaction with CsF goes to the end, forming CsOH quantity relatively more, forms metal complex possessed active catalytic center and it just reacts with acetylene easily;

– new higher state is observed in potassium hydroxide too, but formation of potassium and cesium alcoholate two kinds of catalysate have been formed in the system of AAA active centre, in the account of being difficult to separate them from each other, quantity of additional products form relatively more, and this demands extra product alongside with complication of acetylene combination. As a result, in order to increase the yield of product it leads to continue the process longer, to use extra acetylene and solvent, to increase economical expense. For these reasons the cost of VE rises in price;

– because of being higher of the solubility degree of KF than NaF, having formed interval compound with DMSO, KF causes quantity of CsOH to be less.

## Conclusions

Also synthesize AAA reacting phenylacetylene and crotonaldehyde and ketones based organomagnesium compounds. Scientifically proven influence of various factors-the molar ratio of the starting materials, temperature, prodolzhitelnosti reaction and the nature of the solvent on the yield of the product itself. The kind's promozhutochnyh and dopolnitelnyh compounds and their education. The optimal conditions for the synthesis of a high yield in the process. Determined purity, structure, elemental composition, quantum chemical and physical constants of the synthesized compounds.

The optimal conditions for the synthesis of AAA: equimolar ratio of the starting materials; temperature - 5- 0°C, the solvent THF, the reaction time of 4 hours. In this case it has been determined that very maximum yield of product is I synthesized AAA – I- 89,6; II- 85,0; III- 75,2; IV- 71,0; V- 68,7 and VI- 81,2%.

On the basis of experimental studies identified the following series of reactions reactivity of ketones Grinyara- Iotsichaacetophenone <pinokalin <methylisopropylketone <crotonaldehyde <ethyl ketone <acetone.

To sum up, it has been observed the decrease in vinyl ethers productivity owing to the formation of acetylenes reacting with metals and their hydrolysis, the increase of alcoholates stability formed by joining AAA containing ethyl, isopropyl and triple radicals with metals.

Conclusion, in order to synthesize VE AAA with higher yield 6 hour's process at 100 °C temperature in the system of NaOH–CsF–DMSO has been chosen. In this case it has been determined that very maximum yield of product is I=84,8%; II=77,1%; III=72,3% and IV=88,0%.



Quantum-chemical and molecular-dynamical calculations of molecules of different vinyl ethers aromatic acetylenic alcohols carried out; also the vinylation process was modulated and the mechanisms of formation new compounds were proposed. Biological activity of vinyl ethers was determined and also technological regalement of their synthesis was elaborated.

In JSC "Navoiyazot-Uzbekistan" the plant for their synthesis has been constructed and also the test samples of vinyl ether 1-phenyl-3-methylbutyn-1-ol-3 it's were obtained and also the technological regalement and economical effect of there synthesis was elaborated.

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