

## SYNTHESIS OF AROMATIC ACETYLENE ALCOHOLS AND THEIR VINYL ETHERS BY VARIOUS METHODS

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### ABSTRACT

Investigation of synthesis of aromatic acetylenic alcohols with high yields with using of different method at using of phenylacetylene (PhA) over some aldehydes and ketones in the presence of different catalysts, carrying out of chemical and structural analysis's and on the base of chemical theories and laws the scientific basing of effectivity of aromatic acetylenic alcohols synthesis by different methods. Determination of regularities of carrying out of reaction of aromatic acetylenic alcohols and vinyl ester and influence at this temperature, duration of reaction, nature of catalysts and solvents, initial concentration of reagents, their molar ratios and nature; determination of kinetics and mechanisms on the base of theoretical regulative and physic-chemical properties. Using of quatitave- chemical calculations with using of modern computer programs and on base of practical data. Investigation of energo- and resurso-saving, economically effective, paying, ecologically pure technology of aromatic acetylenic alcohols and vinyl ester production.

**Keywords:** PhA, aldehydes, ketones, alcohols, vinyl esters, catalysts, solvents.

### INTRODUCTION

Currently, the global diversification of oil and gas industry, including the introduction of innovative technologies in the petrochemical or heavy organic synthesis in modern conditions is 62-67%. Chemical processing of oil and gas as well as obtaining on the basis of thin organic synthesis products and materials for agriculture, chemical, pharmaceutical, textile, energy, automotive and aircraft industries is highly effective [1, 2].

In the years of independence the Republic pays great attention to the development of scientific research in the field of chemical industry new products and sales, and achieved certain results of a wide range of measures to meet domestic import-substituting chemicals needs [3].

In world for synthesis of aromatic acetylenic alcohols and their vinyl ester, management of their physic-chemical properties, broadening of ranges of their using and elaboration of technologies of their production investigation are carried out by following priorital directions: using of nanocatalysts  $\text{Et}_2\text{O}+\text{PhMe}+\text{Hex}$ ,  $\text{TiCl}_4/\text{Me}_2\text{S}$ ,  $\text{Et}_3\text{N}/\text{Zn}(\text{OTf})_2$ ,  $\text{Ti}(\text{OiPr})_4$  and  $\text{Cl}_2\text{Ti}(\text{OPh})_2$  at synthesis of aromatic acetylene alcohols (AAA). Using of waste of production at extraction oil and gas and chemical industry for AAA production and their vinyl ester. Elaboration and obtain of pharmaceutical products on the base of AAA (antibiotics, vitamins, ant bactericidal biocides); elaboration biologically- activ compounds, new cross-linking agents and on base of vinyl ester polymers, resins, rubbers, nonmaterial's for molecular electronics [4-9].

## MATERIALS AND METHODS

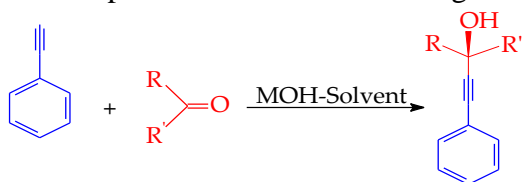
### Experimental Section:

All reactions were carried out under atmosphere condition and monitored by thin layer chromatography (TLC). Column chromatography purifications were performed using silica gel. All solvents were dried and degassed by standart methods and all ketones and alkalis were purchased from Aldrich. Ph was purchased from Acros. Optical rotations were measured with a HORIBA SEPA-200 high sensitive polarimeter. Enantoimeric excess (ee) determination was carried out using HPLC with a Diacel Chiralcel OD-H column on an Agilent HP-1100 HPLC instrument; solvent, 95:5 hexane/isopropanol; flow rate 1 mL min<sup>-1</sup>; 254 nm UV detection. PMR spectra of the structure of synthesized compounds have been studied in the spectrometer Jeol FX-90Q (90 millihertz), and IR structure has been studied in the spectrophotometer Bruker JFS25. In the room temperature NMR<sup>1</sup>H structure has been determined with the help of spectrometer Bruker DPX 400 (working frequency 400.13 millihertz, solvent CDCl<sub>3</sub>, inner standard – GMDS).

## RESULT AND DISCUSSION

### Synthesis AAA of the MOH-solvent catalytic systems

By action of acetone, methylethylketone, methylpropylketone, diethylketone, methylisopropylketone, pinokaline, acetophenone and croton aldehyde of phenylacetylene were obtained by metod Favorsky falloving AAA: 2-methyl-4-phenylbut-3-yn-2-ol (I), 3-methyl-1-phenylpent-1-yn-3-ol (II), 3-ethyl-1-phenylhex-1-in-3-ol (III), 3-ethyl-1-phenylpent-1-yn-3-ol (IV), 3,4-dimethyl-1-phenylpent-1-yn-3-ol (V), 3,4,4-trimethyl-1-phenylpent-1-yn-3-ol (VI), 2,4-diphenylbut-3-yn-2-ol (VII) and 1-phenylhex-4-en-1-yn-3-ol (VIII) and also was proposed law-presented scheme of carrying out reactions [10]:



Where:  $RR' = -Me$  (I);  $R = -Me, R' = -Et$  (II);  $R = -Me, R' = -Pr$  (III);  $RR' = -Et$  (IV);  $R = -Me, R' = ^iPr$  (V),  $R = -Me, R' = -^nBu$  (VI);  $R = -Me, R' = -Ph$  (VII),  $R = -H, R' = -CH=CHCH_3$  (VIII).

$M = Li, Na, K$ ; Solvent- DEE, THP.

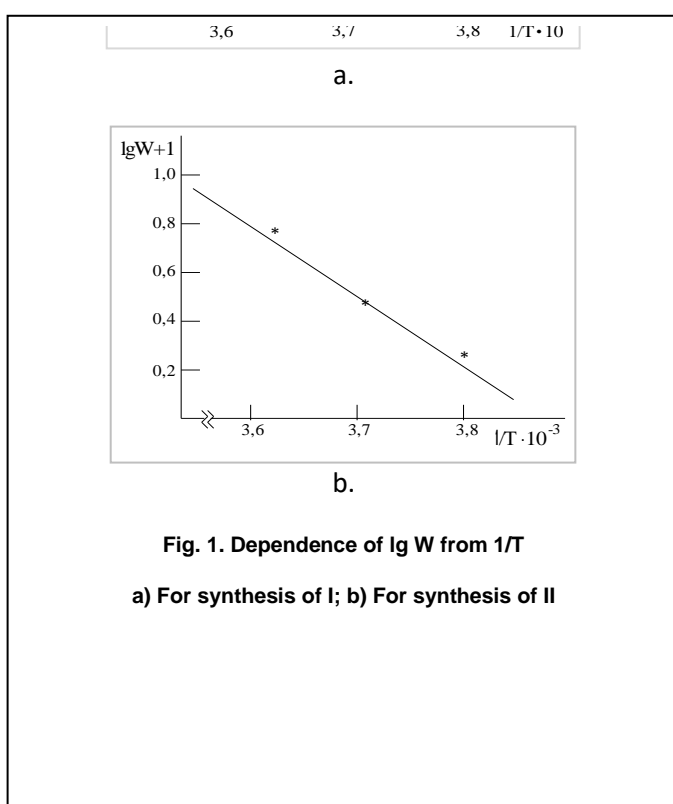
For achievement of high yields of AAA it was systematically investigated influence of different factors – temperature, duration of reaction, nature of solvents and catalysts, mole ratio of initial compounds.

At duration of reaction 8 h PhA and ketons interacted between themself laugh rapidly with formation of AAA with high yield. At increasing duration of reaction before 10 h partial oligomerization, condensation of initial compounds and polymerization of PhA have decreased yields of products. KOH in comparison with LiOH and NaOH have possessed high base properties and forming alcoholat of potassium hydrolyzed owing to which high yield of AAA were reacted.

At THP in comparison with DEE of medium increased and it using active complexes were formed; constant of reaction rate has increased and in result of transmittion of KOH in solutions favorable homogeneous catalytical conditions for formation of active centers and correspondently to increasing of yields of products.

Owing to that electronical pairs of oxygenation of DEE are placed in one plane, and at THP the negative charge in delocalization state in cycle catalitical activity of KOH has increased owing to which hydrolysis of acetate, acetylenides and alcoholysats forming during of reaction was increased.

At carring out of difficulty of formation of MOH suspension formation of catalytically active centers and interaction of molecules of reagent were decreased what carried out to decreasing of reaction rate and yields of products. Ar temperature 0 °C velocity of moving of molecules of initial compounds and solvent was increased and they with alkalis have formed active particles with high energy. With increasing of number of such particles have nucleophilic interactions; instability of acetylenids and alcoholysats increased and correspondently yields of AAA have increased. Also at carring out of process at 0 °C, ionic bonds in molecules of alcoholysats and acetylenides are destructed with formation of cations what is promoted to increasing of reaction of PhA with ketons.



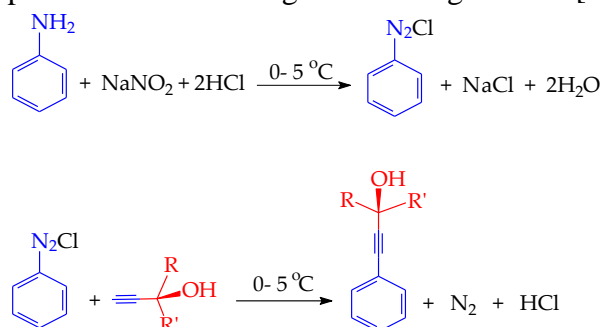
At increasing of temperature to 10 or 20 °C yields of products were decreased owing to partial polymerization of AAA with formation of compounds; catalysts, solvent and ketones have interacted forming by-products-acetates, polyacetates, vinyl alcohols: on the base of obtained data optimal parameters of positive influence of solvent and catalyst on yield of AAA have been determined.

Kinetics of synthesise of AAA has been investigated and by obtained data on the base of lgW-T by method of Arrhenius (fig.1) values of Are energy of activation of reactions was calculated (for I=10,06 kcal/mole; II=9,16 kcal/mole) were calculated.

In results of experiments by synthesis of AAA the optimal conditions have been determined at which reaction was carried out in presence of KOH in solution of THP, temperature 0 °C and duration 8 h (I- 81; II- 72; III- 69; IV- 67; V- 65; VI- 58; VII- 85).

### Synthesis of AAA of the reaction diazotizations:

AAA were synthesized by method of Favorsky and Grignard-Iocich and in the first time by diazotization of aniline and following reaction of obtained  $C_6H_5-N_2Cl$  with AA were obtained corresponded AAA according to following scheme [11]:



Reaction was carried out at low temperature 0-5 °C, nitric acid and aniline were take in equimolar quantities and the mineral acid is taken in an excess, because, if it is taken in smaller amounts by-products are formed, for example diazoaminobenzene and aminoazobenzene. According to results of investigation corresponding AAA have been synthesized by following yield (%): I = 70; II = 59; III = 58; IV = 57; V = 56; VI = 53; VII = 73; VIII = 54.

On the base of carried out scientific investigations number of relative effectivity of elaborated method of synthesis of AAA: daizotation < Favorsky was determined.

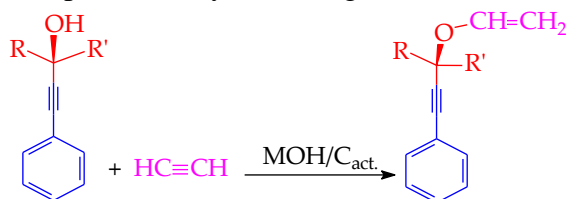
It is necessary to note that at diazotation and method of Favorsky acetophenon, containing in it' molecule phenylic radical, were characterized by high yields of products. By the nature of the radicals at a carbon atom of the carbonyl group was ditremined a number of efficiency of aldehydes and ketones in the reaction with PhA: acetophenone < pinokalin < methylisopropyl < croton aldehyde < diethylketone < methylpropylketone < methylethylketone < acetone.

TABLE 1 Some Physic- Chemical Characteristics Of Synthesized AAA

No	Brutto formula	Mol. mass, g/mole	T <sub>b</sub> , °C	n <sup>20</sup> <sub>d</sub>	d <sup>20</sup> <sub>n</sub>
I	C <sub>11</sub> H <sub>12</sub> O	160	145	1,932	1,456
II	C <sub>12</sub> H <sub>14</sub> O	174	160	1,488	1,165
III	C <sub>13</sub> H <sub>16</sub> O	188	168	1,512	1,126
IV	C <sub>13</sub> H <sub>16</sub> O	188	174	1,533	1,075
V	C <sub>13</sub> H <sub>16</sub> O	188	178	1,540	1,001
VI	C <sub>14</sub> H <sub>18</sub> O	202	187	1,536	1,922
VII	C <sub>16</sub> H <sub>14</sub> O	222	191	1,022	1,128
VIII	C <sub>12</sub> H <sub>12</sub> O	172	153	1,403	1,178

**Synthesis VE AAA of the MOH/C<sub>aktiv.</sub> catalytic systems:**

Synthesis of VE AAA on the base of local raw material-acetylene by heterogeneous-catalytical method is presented by following scheme [12, 13]:



Influence of nature of catalysts and molar ratio of initial components was investigated. Systems such as NaOH/C<sub>aktiv.</sub> and KOH/C<sub>aktiv.</sub> were used as catalysts. Reactions were carried out at 200 °C during 3 h. (table 2).

With increasing of acetylene content it's diffusion to surface of catalyst has increased and at this at first physical and then chemical adsorption have carried out. Adsorptive molecule of acetylene has formed with active center of catalyst  $\pi$ -complex transform mating in compound which has reacted with molecules of alcohols with formation of VE. By alcoholysats AAA don't saturated by acetylene than catalysts reagated with molecules of AAA what is prevented carrying out of reaction and is a cause of decreasing of VE yields.

TABLE 2 Influence Of Nature Of Catalysts And Molar Ratio Of Initial Components Of Yields Of VE AAA

(Quantity Of Catalyst – 20%)

AAA:HC≡CH molar ratio	Yields of product, %						
	II	III	IV	V	VI	VII	VIII
Catalyst – KOH/C <sub>акт</sub>							
1:1	58	55	52	51	49	42	64
1:3	85	82	81	79	78	74	87
1:5	86	84	82	81	79	76	89
Catalyst – NaOH/C <sub>актив.</sub>							
1:1	52	48	46	45	43	38	60
1:3	82	80	76	75	74	71	85
1:5	84	81	79	77	76	74	86

Process of interaction of AAA with acetylene at their ratio 1:3 was carried out at 200 °C and duration 3 h. With increasing of KOH quantity in system it was observed increasing of potassium alcoholysat content which has formed active form of catalyst which has reacted with acetylene with formation of VE with high yield and at this quantity of resin compounds has decreased. At content of KOH 10-20 mass.% in catalysts yields of VE sharply increasing and at following their increasing before 25-30 mass.% yields of forming products didn't changed practically.

At carrying out of vinylation of AAA by acetylene by heterogeneous method in the presence of catalyst KOH/C<sub>aktiv.</sub> (20 mass.%) VE AAA were obtained with high yields (%): I=85; II=82; III=81; IV=79; V=78; VI=74; VII=87.

Advantages of heterogeno-catalytical synthesis in comparison with homogeneous-catalytical were determined. It is necessary to note that heterogeneous-catalytical method of synthesis of VE AAA is more economically cheaper, ecologically safety and at this quantities of by products were increased.

#### **Using of aromatically acetylenes alcohols and their vinyl ethers:**

Biological properties of synthesized AAA against microorganisms-bacterium's and fungus inducing of biocorrosion of steel and metallic constructions, equipment using at storing and processing of oil and gas. In result of investigations it was determined that destruction of oil induced in general such microorganisms as Micrococcace, Pseudomonace, Rhodococcace, Thiobacillus, Acinetobacter sp. and families Vibrionace, Gallionella and Vibrionace induced a aerobic corrosion. Microorganism induced anaerobic corrosion are attributed to families Desulfobivrio and Desulfotomaculum. It was determined that from synthesized AAA compounds VII, I and III are very active biocides against bacteriums and fungus containing in products of oil-processing.

In system "Mubarekneftegaz" and deposits "Urtabulak", "Dengizkul" and "Khauzak" it was determined that content of sulfur and its compounds is equaled 4,5-5,0%, in deposits "Karakum", "Pamuk", "Alan", "Zevarda" and "Kukdumalak" their content is equaled from 0,08 to 0,1%. Properties of VE AAA by isolation of H<sub>2</sub>S from oil and gas have been investigated.

In result of carrying out investigations on the base of local raw materials have been elaborated phosphorous-containing AAA and their VE which were proposed to use as inhibitors of salt-deposits on metallic constructions at processing of oil and gas.

#### **CONCLUSION**

Applied catalytic system KOH+THP obtained on the basis of local raw materials and industrial waste serve to improve AAA production technology.

Expediency effective catalyst compositions with nanostructures based impregnating alkali activated carbon of different sizes during vinylation of AAA heterogeneous catalytic methods.

Applications AAA as corrosion protection of biocides in the biological corrosion of steel and metal industry equipment Oil and gas leads to a 80-82% disinfection of bacteria and fungi and improve the performance properties of metal equipment.

#### **ACKNOWLEDGEMENT**

The authors are thankful to Ministry of Higher and Secondary Specialized Education Republic of Uzbekistan and Tashkent Chemical-Technological Institute for their financial support. The authors are also thankful to the Chairman of the Department of Chemistry Chirchik State Pedagogical Institute.

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