Aromatic Acetylenic Alcohols and Vinyl Ethers: Synthesis from Phenylacetylene, Aniline, and Acetylene

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ABSTRACT

The aim of research work is opening of physical out physical characteristics of synthesis of new aromatic acetylenic alcohols and their vinyl ester on the base local raw material and waste, and also elaboration of new industrial technologies. Investigation of synthesis of aromatic acetylenic alcohols with high yields with using of different method at using of phenylacetylene ower croton aldehydes and ketones (acetone, methyl ethyl ketone, methyl isopropyl ketone, acetophenone and pinokalin) in the presence of different catalysts; carring out of chemical and structural analysis's and on the base of chemical theories and laws the scientifical basing of effectivity of aromatic acetylenic alcohols synthesis by different methods. Determination of optimal conditions of aromatic acetylenic alcohols vinylation by acetylene in the presence of catalytical systems MOH+DMSO+DMP, CsF-MOH-DMSO and MOH/Cactiv.. Determination the most anticorrosion action of aromatic acetylenic alcohols against microorganism cause biocorrosion of metal and steel equipment of processing of oil and gas, elaboration of improvement methods of investigations of preparates on the base of vinyl ester aromatic acetylenic alcohols for extraction of sulfer-containing compound in products of processing of oil and gas.

KEYWORDS: aromatic acetylenic alcohols, vinyl esters, catalysts and solvents, technological processes, bacterium and fungous, sulfer and it's compounds.

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% [1]. 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 [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].

To date, the introduction of the world chemical industry in modern technology synthesis of new types of organic compounds, based on their creation of polymeric and plastic materials with unusual properties, solvents, fungicides, stimulants, antibiotics, hormones, adhesives and paints is perspective task. Synthesis based on tabor reactions, Favorsky, Grignard-Iosicha and diazotization new aromatic acetylene alcohols (AAA), and vinyl esters (VE), the development of highly effective mechanisms for increasing the yield of the product, the creation of eco-friendly, non-waste resource-saving technologies, the structure of the establishment and properties of aromatic acetylene alcohols, and vinyl esters of modern physicochemical methods to obtain their chemical-based corrosion inhibitors, biocides against biological corrosion processes, ion exchangers for scaling and defoliyants for use in agriculture is promising [4-6].

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 Et_2O+PhMe+Hex, $TiCl_4/Me_2S$, $Et_3N/Zn(OTf)_2$, $Ti(O\textit{i}Pr)_4$ and $Cl_2Ti(OPh)_2$ at synthesis of aromatic acetylenic alcohols; using of waste of production at extraction oil and gas and chemical industry for aromatic acetylenic alcohols production and their vinyl ester; elaboration and obtain of pharmaceutical products on the base of aromatic acetylenic alcohols (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 [7-12].

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. Phenylacetylene 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^{-1}; 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^{1}H structure has been determined with the help of spectrometer Bruker DPX 400 (working frequency 400.13 millihertz, solvent $CDCl_3$, inner standard – GMDS).

Reagents and Chemicals: phenylacetylene (PhA), acetone, methylethylketon, methylpropylketon, methylisopropylketon, pinokalin, acetophenon, crotonic aldehyde, aniline, acetylene; magneous-organic compounds, catalysts and solvents- methyl,ethyl, isopropyl and isoamil alcohols, diethyl esther (DEE), tetrahydrophuran (THP), dimethyl silfoxide (DMSO), dimethyl pharmamide (DMP).

Synthesis of aromatic acetylene alcohols of the methods Favorski: Powdery KOH of 5,6 g (0,1 mole) is placed into the three-necked flask in volume of 500 ml, supplied with a mechanical mixer, the reverse refrigerator and a drop funnel, and at once THP of 200 ml is added, in the flask cooled a mix of ice and salt to temperature -5 °C and through a drop funnel within 1 hour PhA of 10,2 g (0,1 mole) is added and 0,1 mole of dissolved crotone aldehyde in 25 ml of DEE then a mix is left for a night. The reactionary mix is hydrolyzed at cooling by ice water, the ether bed and ether extractions are dried over potash and subjected to distillation at the presence of hydroquinone 19 g (70,4 %) 1-phenylhex-4-en-1-yn-3-ol $T_{boil.}$ = 153 °C is allocated (released). The obtained spirit is dissolved in benzene, acetone, chloroform and other organic solvents, but it is badly dissolve in water [13].

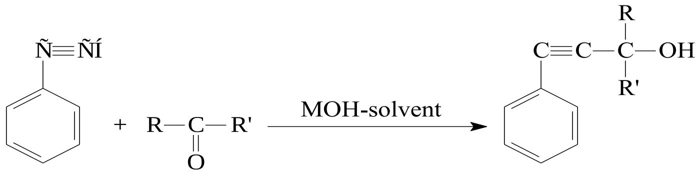
In the similar way 2-methyl-4-phenylbut-3-yn-2-ol (81,4 %) is synthesized from 10,2 g (0,1 mole) of PhA and 5,8 g (0,1 mole) of acetone, $T_{boil.}$ = 147 °C., 3-methyl-1-phenylpent-1-yn-3-ol (72,1 %) is synthesised from 10,2 g (0,1 mole) of PhA and 7,2 g (0,1 mole) of methyl ethyl ketone, $T_{boil.}$ = 160-162 °C., 3,4-dimethyl-1-phenylpent-1-yn-3-ol (65,3 %) is synthesised from 10,2 g (0,1 mole) of PhA and 8,6 g (0,1 mole) of methyl isopropyl ketone, $T_{boil.}$=137 °C., 3,4,4-trimethyl-1-phenylpent-1-yn-3-ol (57,6 %) is synthesised from 10,2 g (0,1 mole) of PhA and 10,0 g (0,1 mole) of pinokaline, $T_{boil.}$=134 °C., 2,4-diphenylbut-3-yn-2-ol (85,3 %) is synthesised from 10,2 g (0,1 mole) of PhA and 12,0 g (0,1 mole) acetophenone, $T_{boil.}$ =183-185 °C [14].

Characterization of the 2,4-diphenylbut-3-yn-2-ol, 85,3 percent yield isolated after 8 h, determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane, 254 nm). ^{1}H NMR ($CDCl_3$) □□1,87 (s, 3H), 2,52 (br, 1H), 7,32 (d, J=7,6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 33,5: 70,6: 85,1: 92,6: 122,7: 125,2: 126,3: 127,9: 128,5: 128,7: 131,9.

Methods homogeneous - catalytic vinylation of aromatic acetylene alcohols with acetylene: First of all 4,62 g CsF 3,76 g. alkali (for analyze $2KOH\cdot H_2O$, ~15% H_2O with pure grade) and 150 ml., solvent (DMSO 0,2% H_2O 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 temperature120 °C. Having been cooled the mixture is hydrolyzed and it is extracted, organic part is separated and dried with the help of $MgSO_4$. 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 [15, 16].

RESULTS AND DISCUSSION

Synthesis aromatic acetylene alcohols of the MOH-solvent catalytic systems: By action of acetone, methylethylketone, methylpropylketone, diethylketone, methylisopropyl-ketone, pinokaline, acetophenone and croton aldehyde of PhA were obtained by method Favorski fallowing 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 carring out reactions [14, 17]:



Where: $RR'= -CH_3$; $R= -CH_3$, $R'= -C_2H_5$; $R= -CH_3$, $R'= -C_3H_7$; $RR'= -C_2H_5$; $R= -CH_3$, $R'=$ *izo* $-C_3H_7$, $R= -CH_3$, $R'= -C(CH_3)_3$; $R= -CH_3$, $R'= -C_6H_5$, $R= -H$, $R'= -CH=CHCH_3$, *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 (table 1).

At duration of reaction 8 h PhA and ketene interacted between themrelf 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 alcoholyat of potassium hydrolyzed owing to which high yield of AAA were reacted.

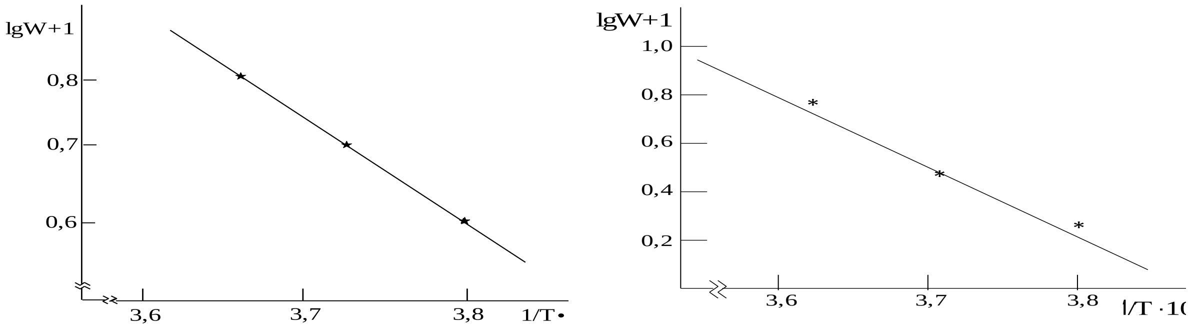
At THP in comparison with DEE of medium increased and it using active complexes were formed; constant of reaction rate has increased and in result of transmition of KOH in solutions favorable homogeneous catalytical conditions for formation of active centers and correspondently to increasing of yields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

Table-1: Influence of temperature, duration of reaction, nature of catalysts and solvents on yields of aromatic acetylene alcohols

Catalyst	Duration of reaction, h	Yields of aromatic acetylene alcohols, %													
		I	II	III	IV	V	VI	VII	I	II	III	IV	V	VI	VII
		solvent DEE							solvent THP						
Temperature, -10 °C															
LiOH	6	19,0	16,5	16,0	15,2	14,8	13,0	24,3	25,5	22,5	21,0	19,0	17,3	15,2	29,6
	8	22,3	19,0	18,5	18,0	17,6	15,8	26,2	29,1	26,6	25,3	24,5	23,2	20,3	37,2
	10	20,0	17,3	17,2	17,1	16,0	15,0	24,8	28,3	24,4	23,1	22,2	21,0	18,7	37,0
NaOH	6	26,2	24,0	22,8	22,2	21,0	18,3	31,0	31,6	30,6	29,8	26,0	28,7	25,3	36,7
	8	29,8	28,0	27,6	27,4	26,0	25,6	39,5	36,0	34,4	34,2	33,6	33,0	31,0	43,8
	10	27,3	26,3	26,0	25,3	24,6	22,5	38,0	35,3	32,7	32,0	31,4	30,9	27,4	41,3
KOH	6	51,3	53,7	48,7	46,5	44,0	39,6	61,2	64,1	56,6	52,0	48,8	46,3	43,2	65,0
	8	66,6	57,6	52,3	50,0	48,6	46,2	69,0	68,4	61,1	58,8	55,8	53,7	47,0	71,3
	10	56,2	54,0	52,2	48,7	46,5	43,3	63,3	67,6	60,0	56,0	54,0	52,0	45,8	70,7
Temperature, 0 °C															
LiOH	6	34,0	31,4	28,8	25,3	24,4	22,0	32,6	37,8	33,5	32,2	31,0	28,4	26,5	39,4
	8	39,4	33,5	32,4	32,1	30,0	24,6	42,4	42,6	36,0	35,2	34,7	34,0	29,6	46,4
	10	33,4	28,5	27,4	27,0	26,7	23,4	38,0	40,3	34,4	34,0	32,9	32,7	29,1	45,5
NaOH	6	41,1	42,4	39,2	36,5	35,8	30,0	45,0	46,8	43,0	42,1	40,3	39,0	36,5	49,7
	8	48,6	45,0	42,0	42,3	41,1	37,4	52,4	52,4	50,5	48,1	47,7	47,3	43,2	55,8
	10	37,5	35,7	34,2	33,2	33,0	32,5	49,0	51,1	49,3	47,0	46,0	45,8	41,3	54,2
KOH	6	69,5	65,1	58,2	56,6	49,5	45,1	70,2	73,3	67,6	62,2	58,3	55,3	51,3	78,4
	8	74,1	66,2	65,0	63,1	62,3	54,1	78,3	81,4	72,1	69,0	66,8	65,3	57,6	85,3
	10	61,8	55,5	54,2	54,0	53,2	48,8	75,2	80,0	71,3	68,2	65,0	64,0	55,7	83,8
Temperature, 10 °C															
LiOH	8	24,8	22,2	21,5	21,0	20,3	18,5	26,8	31,7	29,4	29,0	28,3	27,0	22,2	35,4
	10	23,0	21,1	19,5	18,0	17,3	16,8	24,6	30,1	28,2	27,0	26,0	25,3	20,7	34,8
NaOH	6	31,0	28,7	26,9	25,3	24,7	22,4	41,0	34,4	31,1	30,7	30,5	30,3	28,3	38,5
	8	33,0	30,6	29,0	27,0	26,8	24,2	43,1	39,2	37,4	37,0	36,4	36,0	31,0	47,7
	10	32,2	29,3	27,7	26,8	25,0	23,6	42,2	37,9	35,3	35,0	34,7	34,5	31,3	46,8
KOH	6	58,5	43,5	42,1	40,1	39,4	41,3	62,0	61,1	52,3	51,7	51,1	49,2	46,3	70,0
	8	71,5	47,9	46,6	46,0	45,5	44,1	58,3	73,0	64,7	62,8	59,0	56,2	52,0	76,8
	10	66,0	45,0	44,8	44,4	44,2	43,2	56,0	72,2	63,1	61,0	57,0	55,5	51,1	76,2

With increasing of number of such particles have nucleophilic interactions; instability of acetylenids and alcoholyats increased and correspondently yields of AAA have increased. Also at carring out of process at 0 °C, ionical bonds in molecules of alcoholyats 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.



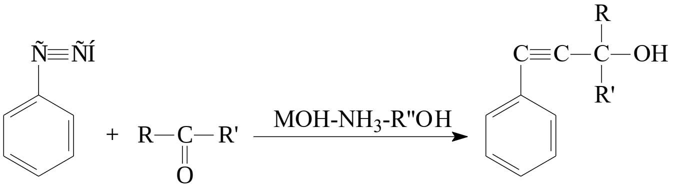
a *в*

a) For synthesis of 2-methyl-4-phenylbut-3-yn-2-ol; в) For synthesis of 3-methyl-1-phenylpent-1-yn-3-ol
Fig-1: Dependence of lg W from 1/T.

Kinetics of synthesize of AAAs 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 [18].

In results of experiments by synthesis of AAAs 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.

Synthesis aromatic acetylene alcohols of the MOH–NH$_3$–ROH catalytic systems: Synthesis of AAAs in homogeneous conditions in the presence of liquid NH$_3$ has been investigated. Process was carried out in suspension of KOH during 30-120 min at pressure 30 atm. and interval of temperature from -10 to -50 °C with using ethyl, isopropyl and isoamil alcohols and it was carried out according to following scheme [19]:



Where: M= Li, Na, K; R"= –Me, –Et, –^{i}Pr, – ^{i}Am.

Influence of ratio of quantities (in moles) of initial compounds on the formation of AAAs was investigated.

Table-2: Influence of catalyst and nature of solvent on yield of aromatic acetylene alcohols (duration reaction 90 min., temperature -20 °C)

Solvent	Catalyst	Yields of products, %						
		I	II	III	IV	V	VI	VII
CH_3OH	NaOH	88,8	84,6	83,0	77,8	71,6	69,6	92,0
	KOH	94,6	91,2	87,0	85,3	77,6	74,3	96,3
C_2H_5OH	NaOH	86,0	82,0	77,0	74,2	69,6	66,8	87,3
	KOH	88,2	85,0	82,2	78,2	71,0	70,2	93,0
izo-C_3H_7OH	NaOH	76,0	72,0	70,0	66,5	62,2	61,0	79,0
	KOH	83,0	79,5	76,8	72,6	67,7	65,1	87,3
izo-$C_5H_{11}OH$	NaOH	66,4	61,1	58,0	56,3	51,3	49,8	68,4
	KOH	68,0	64,2	62,3	59,3	55,0	53,4	75,0

As shown from fig.2 from investigated alcohols methanol is the most active in reaction owing to fact that it is strong protonational solvent forming hydrogen bonds; removing H^+ connected with OH-group of catalyst with formation in system free radicals which are very active and strong reductors and have promoted formation of large quantity alcoholayts of AAA in result of which rate of reaction increased. Influence of quantity (mole) of initial reagents that is their molar ratios on yields of AAA was investigated.

Table-3: Influence of mole ratio of reagents on yields of aromatic acetylene alcohols (duration of reaction 90 min, temperature -20 ºC, solvent - methanol)

Mole ratio (mole)			Yields of products, %						
RCOR'	NH_3	$C_6H_5C{\equiv}CH$	I	II	III	IV	V	VI	VII
1	1	1	62,3	56,4	54,2	51,2	47,6	45,0	71,3
1	3	1	76,9	72,0	69,2	68,0	61,3	58,3	79,5
1	6	1	86,5	84,0	82,0	79,5	75,0	72,0	89,5
1	6	3	94,6	91,2	87,0	85,3	77,6	74,3	96,3

As shown from table 3 at surplus of NH_3 in comparison with ketons in 6 times and 2 times with PhA yields of AAA approached to maximum and by product- minimum. With increasing of number of carbon atoms and branching in molecule of keton yields of products were decreased: acetophenon with phenyl radical in it's molecule has shown yield at synthesis of compounds VII. Cause of high yield is a high constant of dissociation of it's molecules owing to presence in it's molecule phenyl group with strong induction effect.

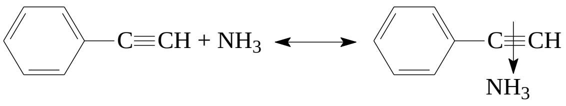
From data of investigation it is shown that at synthesis of AAA in presence of NH_3 in comparison with system KOH-THP yields of products (%) were increased: I- 81,4 from 94,6; II- 72,1 from 91,2; III- 69,0 from 87,0; IV- 66,8 from 85,3; V- 65,3 from 77,6, VI- 57,6 from 74,3 and VII- 85,3 from 96,3.

At synthesis of AAA influence of liquid NH_3 is concluded in following [20]:
NH_3 has acted on triple bond of PhA and correspondently has increased mobility of hydrogen atom in it's molecule in result of which atoms of metals in alkalies displaced it with formation of phenylacetylenid;

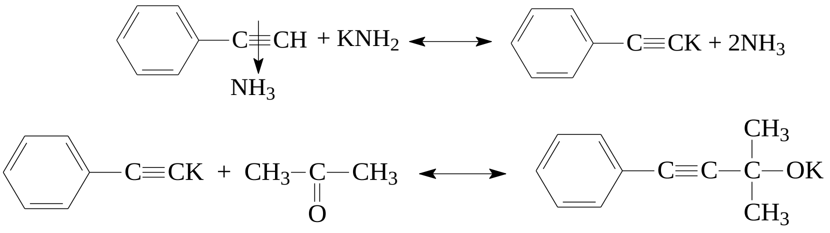
NH_3 has supplanted OH- group from molecules alkalis and has formed catalytically active MNH_2 which interested with PhA forming phenylacetylenid:based on results of scientifical investigations and presented date in scientifical literature by synthesis of acetylenic alcohols with using of different organical compounds particular on the base of investigation, theoretical regulates and conclusions of such sciences as Yin Ngai Sum, Shuai Pu, K.A.Tanaka, R.W.Wannort, J. Brandshma, B.A.Trophimov and O.N.Temkin mechanisms of reactions of synthesis AAAs have been proposed. As example mechanisms of reaction of Ph A with acetone are presented [21-28].

First mechanism of reaction. From low presented scheme it is shown that at obtain of AAAs NH_3 preliminary has reacted with catalyst-KOH, NaOH or LiOH with formation for example KNH_2 processing by high catalytical activity [29].

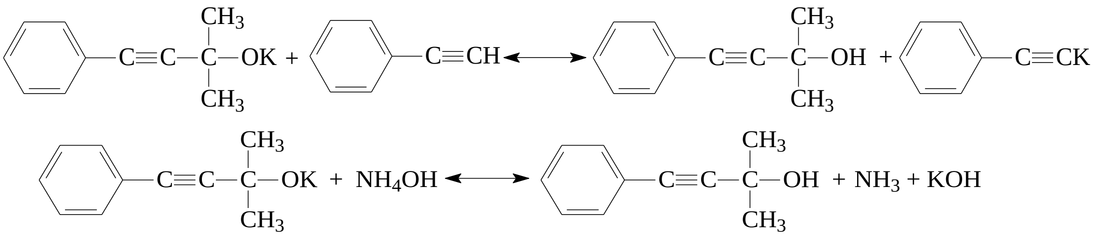
$$KOH + 2NH_3 \longleftrightarrow KNH_2 + NH_4OH$$



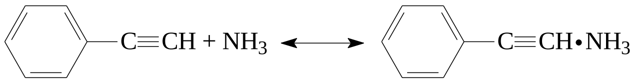
In result of phase orientation of triple land of PhA molecule with NH_3 by-product was formed. Triple band in molecule of KNH_2 owing to NH_3 light reactes with PhA with formation of phenylacetylenid of potassium:



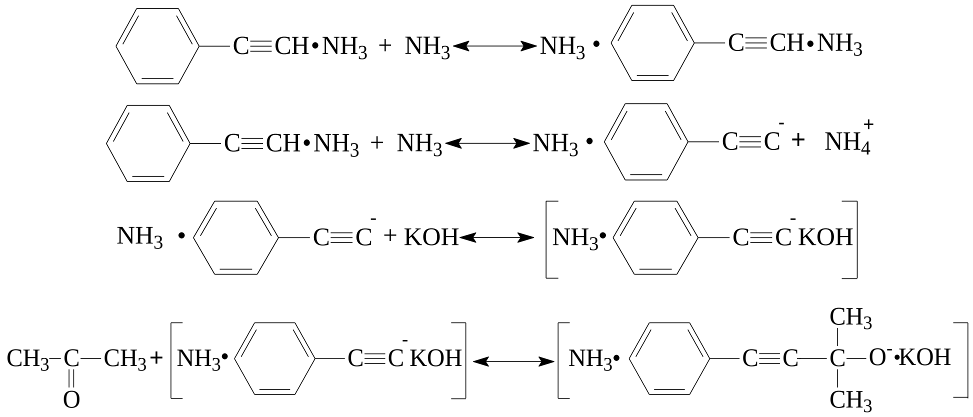
Owing to active mobility of potassium atom in molecule of PhA under action of oxygen atom of acetone molecule it has transmited in alcoholyat of AAA:



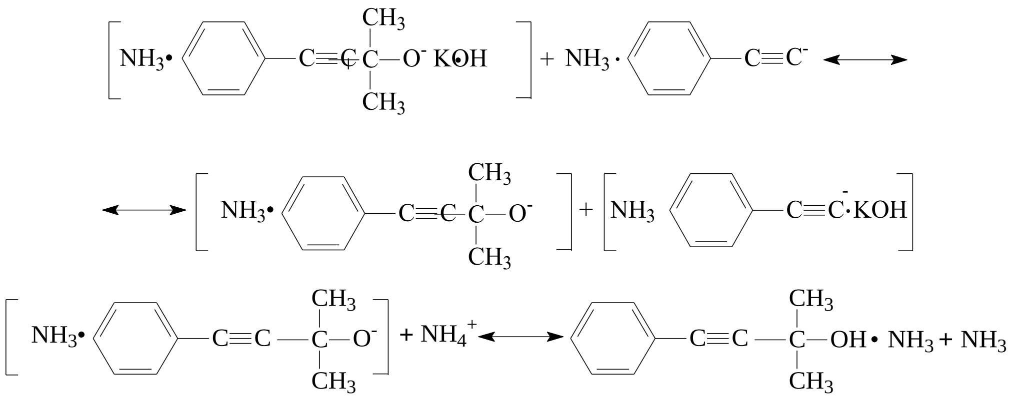
Forming intermediate product that is alcohalyat at the same time has reacted with potassium salt of PhA and hydroxide of ammonia with formation of 2-methyl-4-phenylbuthin-3-ol-2. Second mechanism of reaction:



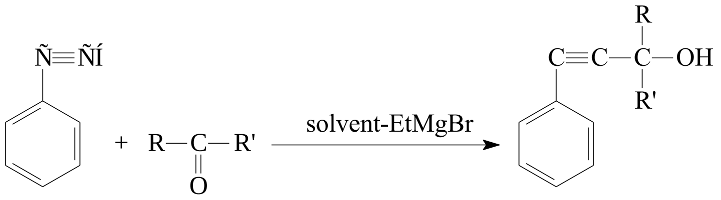
Radical mechanism was proposed and scheme of synthesis of AAA-2-methyl-4-phenylbutine-3-ol-2 in presence of liquid NH_3 has presented [30]:



Physico-chemical methods were determined comporition and structure of base product 2-methyl-4-phenylbutine-3-ol-2 and by products:



Synthesis of aromatic acetylene alcohols of the magnesium - organical compounds: Reaction was carried out owing to breaking of bond >C=O of carbonylic group of aldehydes or ketons. Of electronic density is displaced to oxygen atom owing to witch on carbon atom density of positive charge has increased and on oxygen atom-density of negative charge owing to which carbonylic group has undergone to polarization. In result of this atom of carbon of carbonylic group has become electrophonic and react with nucleophylic reagents. Such on the base of aldehydes and ketons by method of Grignard-Iocich were synthesized AAA. As example low scheme of synthesis of AAA from PhA and any keton is presented [31]:



Where: solvent– DEE and THP.

Synthesis of AAAs on the base of magnesium- organical compounds was carried out at temperature 0-10 ^oC in solution of DEE and THP during 2-h. Initial compounds were taken in equimolecular ratio (table 4).

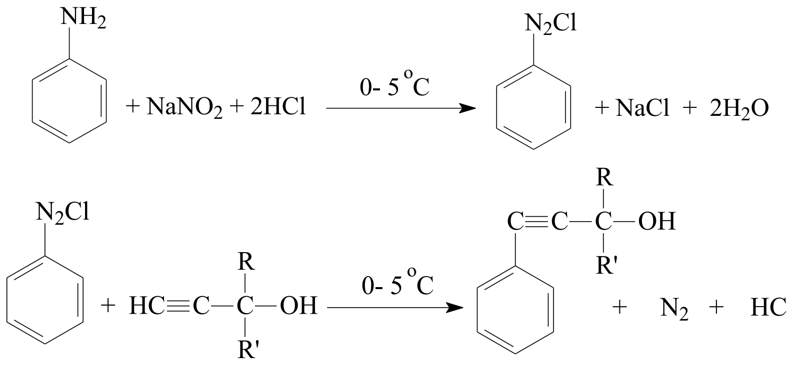
At carring out of process in solution of THP the yield of product was higher than in solution of DEE. Course of this cause by fact that THP has implemented function not only of solvent but also of additional catalyst. At carring out of process during 2 h condensation of aldehydes and ketons is carried out or in result of enolisation initial reagents don't fully undergo to reaction in result of which yields of AAAs is decreased.

Table-4: Synthesis of aromatic acetylene alcohols by methods Grignard-Iocich

Duration of reaction, h	Yields of products, %							
	I	II	III	IV	V	VI	VII	VIII
Solvent - DEE								
2	75,0	68,4	64,4	61,3	56,4	53,0	50,0	64,3
4	78,6	71,8	69,6	65,2	60,6	55,9	54,7	68,0
6	67,3	62,4	57,0	54,8	52,4	45,2	42,7	58,6
Solvent - THP								
2	87,4	83,5	82,0	76,0	74,5	69,3	66,0	79,0
4	89,6	85,0	80,0	78,2	75,2	71,0	68,7	81,2
6	82,2	77,6	73,0	71,3	69,5	63,2	57,3	70,6

At carring out of reaction during 6 h owing to formation of such compounds as dipnon, there phenylbenzol, mezithylenoxide and some other intermediate compounds yield of obtained compound (product) is decreased. At duration of reaction 4 h in solution of THP AAAs were obtained with high yields (%): I= 89,6; II= 85,0; III= 80,0; IV= 78,2; V= 75,2; VI= 71,0; VII= 68,7 ва VIII= 81,2.

Synthesis of aromatic acetylene alcohols of the reaction diazotizations: AAAs were synthesized by method of Favorski and Grignard-Iocich and in the first time by diazotization of aniline and following reaction of obtained $C_6H_5\text{-}N_2Cl$ with AA were obtained correspoded AAA according to following scheme [32]:



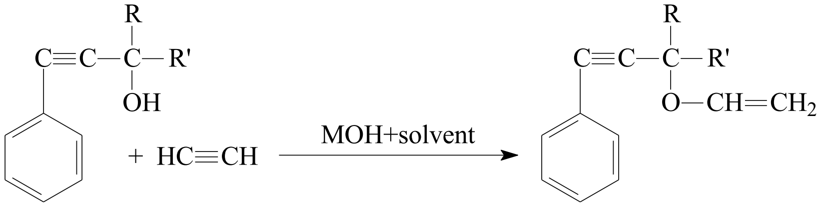
Where: $RR' = -CH_3$; $R = -CH_3$, $R' = -C_2H_5$; $R = -CH_3$, $R' = -C_3H_7$; $RR' = -C_2H_5$; $R = -CH_3$, $R' =$ *izo* $-C_3H_7$, $R = -CH_3$, $R' = -C(CH_3)_3$; $R = -CH_3$, $R' = -C_6H_5$, $R = -H$, $R' = -CH{=}CHCH_3$.

Reaction was carried out at low temperature 0-5 ^oC, 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 AAAs have been synthesized by following yield (%): I = 70,0; II = 59,0; III = 58,1; IV = 57,5; V = 56,2; VI = 52,7; VII = 73,4; VIII = 54,5.

On the base of carried out scientifical investigations number of relative effectivity of elaborated method of synthesis of AAA: daizotation < Grignard-Iocich < Favorski was determined.

It is necessary to note that at diazotation and method of Favorski acetophenon, contain-ning in it' molecule phenylic radical, were characterized by high yields of products. In method of Grignard it was observed reverse effect: acetophenon in water didn't soluble and a it's condensation dipnon and threephenylbenzol, were formed, which with HCl in solution have formed has carried out to decreasing of yield of product VII. 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 [33].

Synthesis vinyl ethers aromatic acetylene alcohols of the MOH–solvent catalytic systems: In composition of molecules of AAAs berides aromatical cycle and triple bound there is OH group in which there is mobile activ atom of hydrogen which is responsible for vinylation reaction of synthesized AAAs by acetylene in different conditions [34]:



Where:M– Li, Na, K; solvent– DMSO and DMP

Process was carried out in solutions of DMSO and DMP at duration 4-10 h and temperature 80-140 °C in presence of NaOH and KOH.

Carring out of vinylation in solution of DMSO was more selective in comparison with using of DMP. In molecule of DMSO there is common electronic pare: so being in alcolholyats system acetylenydes and easily dissolves the catalysts of the process and makes the stable with the MOH forms the main system and increases their mainly due to the number of additional substances is reduced, the efficiency of formation VE AAA increases.

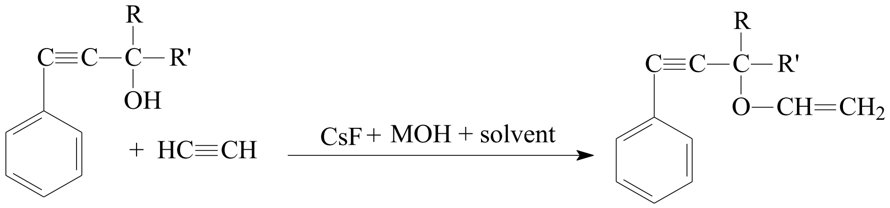
In process at first AAA with MOH have formed intermediate compounds- alcoholyats which reaction with acetylene with formation of VE. At using catalysts with high base KOH (quantity catalyst 10%) maximal yield of VE AAA was determined. At this alcoholyat of potassium in comparison with such of Na and Li is the most active and correspondently in it's presence yields of VE were high.

Table-5: Influence of quantity of catalyst KOH on yields of vinyl ethers aromatic acetylene alcohols (solvent DMSO, temperature 120 °C, duration of reaction 8 h.)

Catalyst KOH, %	Yield of products, %							
	I	II	III	IV	V	VI	VII	VIII
5	48,6	44,2	43,2	42,6	41,2	37,5	56,7	44,0
10	58,4	53,0	51,0	48,7	47,8	42,5	62,4	55,7
15	53,0	48,0	46,2	45,6	44,4	39,6	58,0	46,5

At reaction of vinylation AAAs at optimal conditions: temperature 120 °C, solvent DMSO, catalyst KOH, duration of reaction 8 h.yields of forming VE AAA is high and by- products and resin-compound were formed with low yields.

Synthesis vinyl ethers aromatic acetylene alcohols of the CsF-MOH–solvent catalytic systems: Reaction of AAAs with acetylene in homogeneous conditions at using of high-base catalytical system MeOH-CsF-DMSO was investigated according to following scheme [35]:



Where:M– Li, Na, K; solvent– MeOH, EtOH, ^{i}PrOH, ^{i}AmOH.

Analysis of obtained data has shown that yields of VE AAAs at using of used catalytical systems were distributed according to following number:LiOH·CsF < KOH·CsF < NaOH·CsF and also at increasing of temperature from 80 to 120 °C a high increasing of their yields was ob serves.

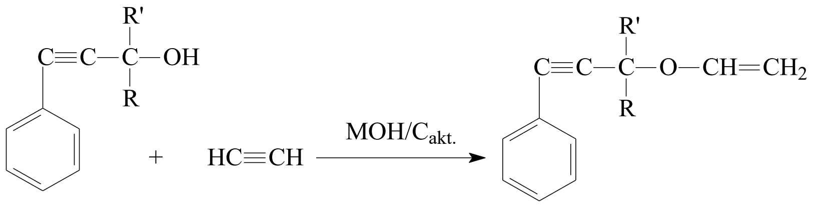
Vinylation of AAAs in the presence of high- base system is characterized by high velocity. At this hydrogen atom of acetylene has stereos- and regeoselectivity owing to which process of exchange has carried out lightly. In systems MeOH-CsF-DMSO during of reaction solvates of metals are formed active metal is conversed in complex with formation of catalytically active centers and increasing of function of catalysts.

Table-6: Influence of catalyst nature and temperature of yields of vinyl ethers aromatic acetylene alcohols (duration of reaction 6 h., solvent - DMSO)

Catalyst	Temperature, °C	Yield of products, %						
		I	II	III	IV	V	VI	VII
LiOH·CsF	100	58,1	49,0	48,0	47,1	46,6	42,9	59,4
KOH·CsF	100	64,0	57,4	55,3	52,0	52,0	40,7	66,4
	120	65,1	58,3	57,0	56,3	55,7	49,6	67,3
NaOH·CsF	80	77,3	74,2	74,0	73,5	73,2	67,3	79,6
	100	86,4	84,8	82,1	81,0	77,1	72,3	88,0
	120	87,5	86,0	83,4	82,2	79,7	75,0	89,5

The catalytic activity of the system and the formation of CsOH NaF its relative low solubility can be attributed to property of high basicity. In systems LiOH and is high in the system they are in ionic form and equilibrium is established. This CsOH not completely free and inactive, it acts as a catalyst function as catalytically LiOH+CsOH+LiF+CsF system.

Synthesis vinyl ethers aromatic acetylene alcohols of the MOH/C$_{act.}$ catalytic systems: Synthesis of VE AAAs on the base of local raw material-acetylene by heterogeneous-catalytical method is presented by following scheme [36]:



Where:M– Li, Na, K.

Influence of nature of catalysts and molar ratio of initial components was investigated. Systems such as NaOH/C$_{activ.}$ and KOH/C$_{activ.}$ were used as catalysts. Reactions were carried out at 200 °C during 3 h.(table 7).

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 π– complex transform mating in compound which has reacted with molecules of alcohols with formation of VE. By alcoholyats AAAs don’t saturated by acetylene than catalysts reagated with molecules of AAA what is prevented carring out of reaction and is a cause of decreasing of VE yields.

Process of interaction of AAAs 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 alcoholyat 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 before25-30 mass.% yields of forming products didn’t changed practically.

Table-7: Influence of nature of catalysts and molar ratio of initial components of yields of vinyl ethers aromatic acetylene alcohols (quantity of catalyst – 20%)

AAA:HC≡CH molar ratio	Yields of product, %							
	I	II	III	IV	V	VI	VII	VIII
	Catalyst – KOH/C$_{акт}$							
3:1	3:1	28,6	25,4	24,2	22,5	21,2	18,4	31,0

1:1	1:1	58,4	55,2	52,0	51,1	49,3	42,4	63,8
1:3	1:3	84,7	82,3	81,0	79,5	77,7	74,4	87,3
1:5	1:5	86,2	84,1	82,4	80,6	79,3	76,2	88,9
	Catalyst− NaOH/$C_{activ.}$							
1:1	1:1	52,3	47,6	46,2	45,0	43,0	38,4	60,0
1:3	1:3	82,3	79,6	76,5	75,1	74,2	71,0	84,7
1:5	1:5	83,9	81,2	79,2	77,5	75,6	73,9	86,0

At carring out of vinylation of AAAs by acetylene by heterogeneous method in the presence of catalyst KOH/$C_{activ.}$ (20 mass.%) VE AAAs were obtained with high yields %: I=84,7; II=82,3; III=81,0; IV=79,5; V=77,7; VI=74,4; VII=87,3.

Advantages of geterogenno-catalytical synthesis in comparasion with gomogeneous-catalytical were determined. It is necessary to note that geterogeneous-catalytical method of synthesis of VE AAAs is more economically cheaper, ecologically safety and at this quantities of by products were increased.

Table-8: Some physico-chemical characteristics of synthesized aromatic acetylene alcohols and their vinyl ethers

No	Brutto formula	Molecular mass, g/mole	$T_{b,}$ ˚C	n_d^{20}	d_n^{20}
I	$C_{11}H_{12}O$	160	145-147	1,9320	1,4560
II	$C_{12}H_{14}O$	174	160-162	1,4887	1,1658
III	$C_{13}H_{16}O$	188	168-170	1,5126	1,1261
IV	$C_{13}H_{16}O$	188	174-175	1,5333	1,0765
V	$C_{13}H_{16}O$	188	178-180	1,5400	1,0010
VI	$C_{14}H_{18}O$	202	187-188	1,5360	1,9223
VII	$C_{16}H_{14}O$	222	191-192	1,0221	1,1280
VIII	$C_{12}H_{12}O$	172	153-155	1,4031	1,1784
I VE	$C_{13}H_{14}O$	186	152-154	1,3628	1,1958
II VE	$C_{14}H_{16}O$	200	147-149	1,2531	1,1850
III VE	$C_{15}H_{18}O$	214	155-156	1,3800	1,2008
IV VE	$C_{15}H_{18}O$	214	158-160	1,4283	1,2843
V VE	$C_{15}H_{18}O$	214	163-166	1,4302	1,2960
VI VE	$C_{16}H_{20}O$	228	168-169	1,4387	1,3502

Elaboration of technologies of obtain of acetylene alcohols and their vinyl ethers: For the first time AAAs on the base magneous- organical compound (by method of Grignard-Iosich) have been synthesize : technological process consist from following stages: at first in saturator mixture of ethyl bromide and magneous that is reactive Iosich, than mixture from saturator is carried out to buffer saturator were solvent THP is added and at this catalytical system is formed for interaction of PhA with ketones after which mixture from saturates is cooled by liquid NH_3 and is carried out in reactor. PhA and ketones in equimolecular quantities is mixed during 4 h.

THP in process has implemented function not only solvent but also of catalyst. At this temperature in reactor must be 0- 5 ^oC. After completion of reaction mixture is hydrolyzed in hydrolyzer by icy water and dilute HCl is added for dissolution of deposit. Forming solution is pawed in extractor where is extra gated by diethyl ether. Ether part is and is directed in rectification column. Remaining water part is extracted of wise by ether and ether's part is dried by waterless Na_2SO_4 and than is directed in column where AAA is extracted.

In rectification column intermediate and by- products are isolated by physico-chemical methods. Resin-line products– residue in column is washed by DEE and solid layer was rendered harmless at temperature 400 ^oC [37].

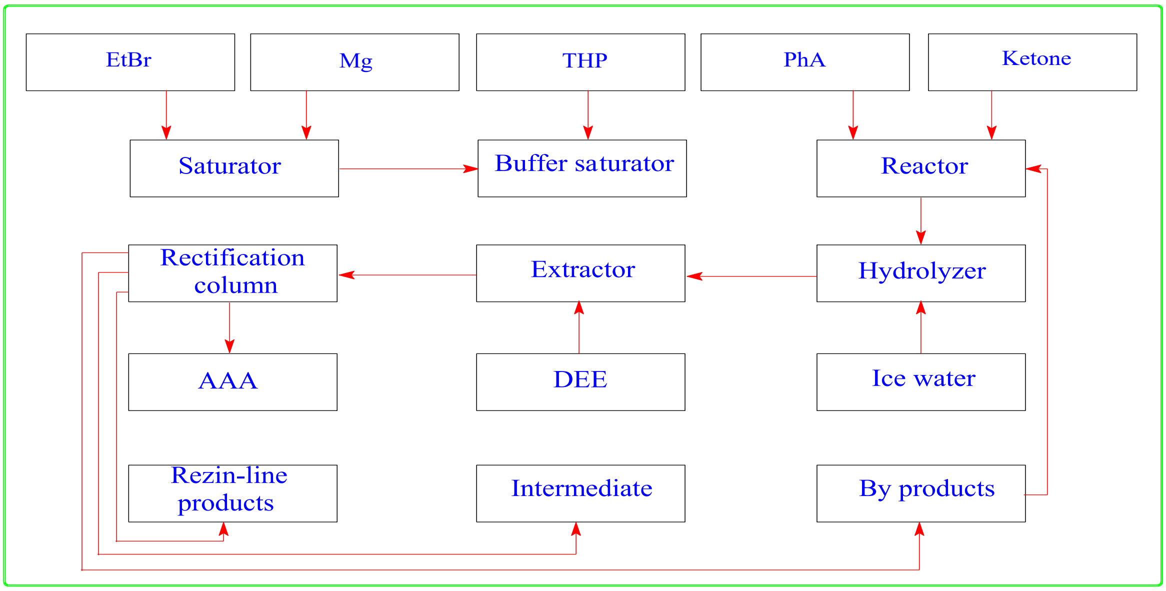


Fig-2: Principal technological scheme of obtain aromatic acetylene alcohols with using of magnesium compounds

VE AAAs for the first time were obtained on the base of local raw material on the «Navoiazot» and at this using of catalytical systems MOH/$C_{activ.}$ has allowed to obtain products with high yields. At production of VE AAAs by catalytical method first in reactor from quartz glass is prepared catalytical system from activated coal and KOH and than AAA is delivered in reactor through dozator and vinylating agent- acetylene from gasholder. All this is first stage of technological process and at this temperature is controlled by thermopair and pressure- by manometer. In following stage formed solution of AAA and VE are extracted by DEE and extract is directed in rectificated column. Then rectification was carried out at which division of it's on fraction was carried out [38].

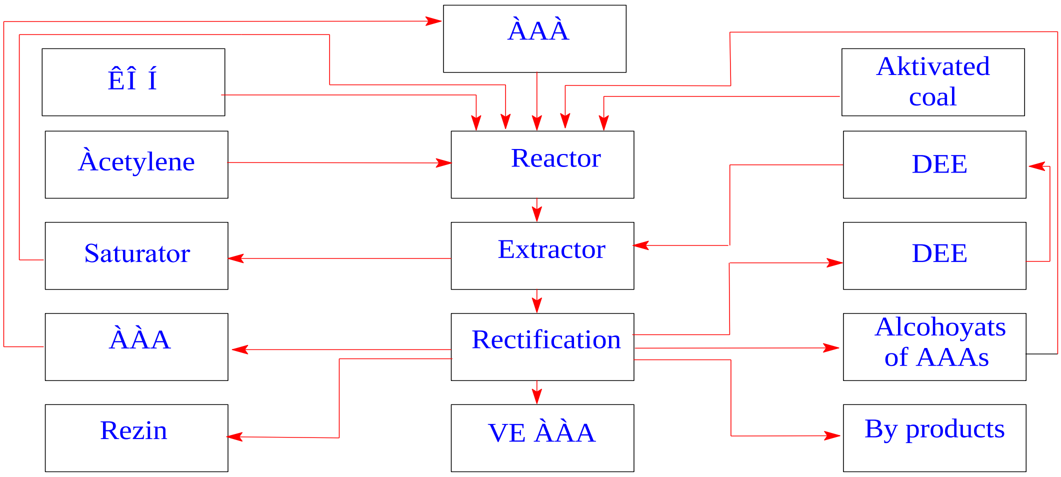


Fig-3: Principal technological scheme of obtain vinyl ethers aromatic acetylene alcohols by heterogeneous catalytical method

At production of VE AAAs forming by products have been division by physico- chemical methods and thermos part of them was directed for repeat using and remain part was utilized.

Using of aromatic acetylene alcohols and their vinyl ethers: Biological properties of synthesized AAAs against microorganisms-bacterium's and fungous inducing of biocorrossion of steel and metallic constructions, equipment using at storing and processing of oil and gas [39]. 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 Desulfovibrio and Desulfotmaculium. It was determined that from synthesized AAAs compounds VII, I and III are very active biocides against bacterium's and funguses containing in products of oil-processing [40].

In system «Mubarekneftegaz» and deposits «Urtabulak», «Dengizkul» and «Khauzak» it was determined that content of sulfur and it's 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 AAAs by isolation of H_2S from oil and gas have been investigated [41].

In result of caring out investigations on the base of local raw materials have been elaborated phosphorous-containing AAAs 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 and NH_3+KOH+CH_3OH obtained on the basis of local raw materials and industrial waste serve to improve aromatic acetylene alcohol production technology. Systematization process for producing aromatic acetylene alcohol based phenylacetylene, aniline and organo-magnesium compounds is essential. Expediency effective catalyst compositions with nanostructures based impregnating alkali activated carbon of different sizes during vinylation of aromatic acetylene alcohols homogeneous and heterogeneous catalytic methods. Applications aromatic acetylene alcohols 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. The use of vinyl esters of aromatic acetylenic alcohols for complex allocation of sulfur compounds from the oil, petroleum products and natural gas reduces the amount of sulfur compounds to 42-55%.

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