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Synthesis of Aminocompounds

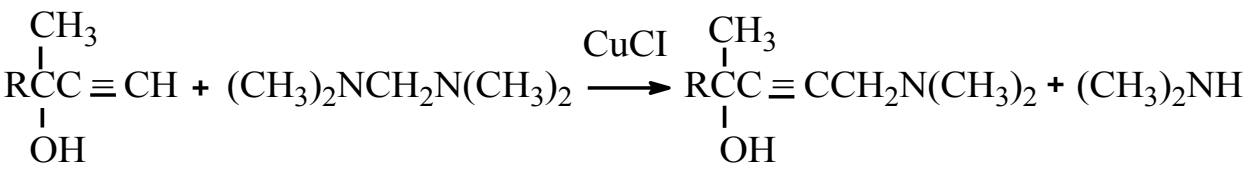
Kultaev Kuzibay Kazakbaevich
Tashkent state pedagogical university named after Nizami, faculty of Natural Sciences, department of "Chemistry and Methods of its Teaching", associate professor of the department

Abstract: In the article formation of aminoalcohols and aminocompounds by Mannich reaction from acetylenic alcohols and phenylacetylene have been investigated. Acetylenic alcohols were synthesized by the reaction A.E. Favorsky and phenyl-acetylene was obtained from styrene. The influence of various factors (temperatu-re, catalyst, time and nature of solvents) on the yield of aminoalcohols was studied. A theoretical analysis of the mechanism of formation of acetylenic aminoalcohols is given. The physicochemical properties of the synthesized aminoalcohols and their yields were determined. The chemical structure of aminoalcohols has been confirmed by IR and PMR spectrums.

Keywords: catalyst, Mannich reaction, N-hydroxymethylamine, condensation reaction, IR spectrum, valent vibrations, deformational vibrations.

Mannich reaction has alloved to synthesise physiologically active compo-unds and aminoalcohols [1] which are used in industry as adsorbents at purifyca-tion of gases; compounds strengthening process of vulcanization of synthetic and natural rubbers; inhibitors of metals corrosion. also they are used for formation of coverings on metallic surfaces and increasing of corrosion stability of different metals [2,3]. Aminoalcohols obtained on of base of acetylene, phenylacetylene and acetylene alcohols are very important compounds because on their base pesti-cides, medical preparates, bactericides, stimulants and inhibitors are obtained [4- 7]. Many chemists are interested in the synthesis of compounds containing differ-rent functional groups in their molecules and investigation of their different pro-perties. Aminoalcohols containing in their composition triple bond have theore-tical and practical importance. Aim of this investigation is synthesis of aminoal-cohols and aminocompounds on the base of tertiary acetylenic alcohols and phe-nylacetylene and invertigation of physicochemical properties of obtained com-pounds and obtaine on their base biologically active substances. Acetylenic alco-hols have been synthesized by reaction of A.E. Favorsky [8] and phenylacetylene was obtained by bromination of styrene [9]. Synthesis of aminoalcohols by Man-nich reaction from acetylenic alcohols and phenylacetylene.

Aminoalcohols are synthesized by two methods: breaking of diamines and the Mannich reaction. Yields of aminoalcohols obtaind by breaking of diamines were equaled 84-96% [10]. Reaction was carried out at 80 ° C and normal pres- sure during 3-5 hours without using solvent. Scheme of obtaine compounds can be presented as following :



where : $R = -C_2H_5$; $- C_4H_9$; $-C_6H_{13}$

Acetylenic alcohols and phenylacetylene have possesed by enough acidic properties owing to presence of mobile hydrogen atom at triple bond. Ions metals such as Cu^{+}, Cu^{2+} and Ag^{+} can substitute hydrogen atom. Intermediate metal -organic compounds have transformed in aminoalcohols by Mannich reaction with paraformaldehyde and secondary amines. In this reaction n-dioxane was used as solvent and salts Cu_2CI_2 and $Cu(CH_3COO)_2$ were used as catalysts. This reaction for obtaine acetylene derivatives can be presented schematically as follows:

$$RR'CC \equiv CH + CH_2O + HNR''R''' \longrightarrow RR'C(OH)C \equiv CCH_2NR''R''' + H_2O$$

$$C_6H_5C \equiv CH + CH_2O + HNR''R''' \longrightarrow C_6H_5C \equiv CCH_2NR''R''' + H_2O$$

where : $R = R' = -CH_3$: $R = -CH_3$, $R' = -C_2H_5$; $R = -H$, $R' = -C_3H_7$

$R'' = R''' = -CH_3$; $R'' = R''' = -C_2H_5$; $R'' = R''' = -C_4H_9$; $R'' = R''' = -C_5H_{10}$

It was determined that yield of aminoalcohols has depended on following fac-tors: a) temperature. At temperature 35-45 °C rate of reaction was low but at 45-85 ° C yield of aminoalcohols was equaled 50-55% and at 85-100 ° C it's yield was equled 66-80%. From fig. 1 it is shown that yield of aminoalcohol has increased with increasing molecular mass of secondary amine. At using heterocyclic amines such as pyperidine and morpholine yield of aminoalcohols was equaled 50-64%.

Table 1. Dependence on yield of reaction from temperature

Tempera-ture, °C	30	40	50	60	70	80	90	100	120
Name of substance					Yield of reaction,%				
5-N-diethyl -amino-2-methyl pentin-3-ol-2	-	23	30	40	50	59	62	65	60
5-N-dibutyl amino-2-methyl pentin-3-ol -2	18	27	38	45	55	63	70	73	70
5-N-pyperidil-2-methylpentin-3-ol-2	-	-	25	33	40	49	54	60	54

1. $(CH_3)_2COHC \equiv CCH_2N(C_2H_5)_2$ (5-N-diethylamino-2-methylpentin-3-ol-2)
2. $(CH_3)_2COHC \equiv CCH_2N(C_4H_9)_2$ (5-N-dibutylamino-2-methylpentin-3-ol-2)
3. $(CH_3)_2COHC \equiv CCH_2NC_5H_{10}$ (5- N-pyperidil -2-methylpentin-3-ol-2)

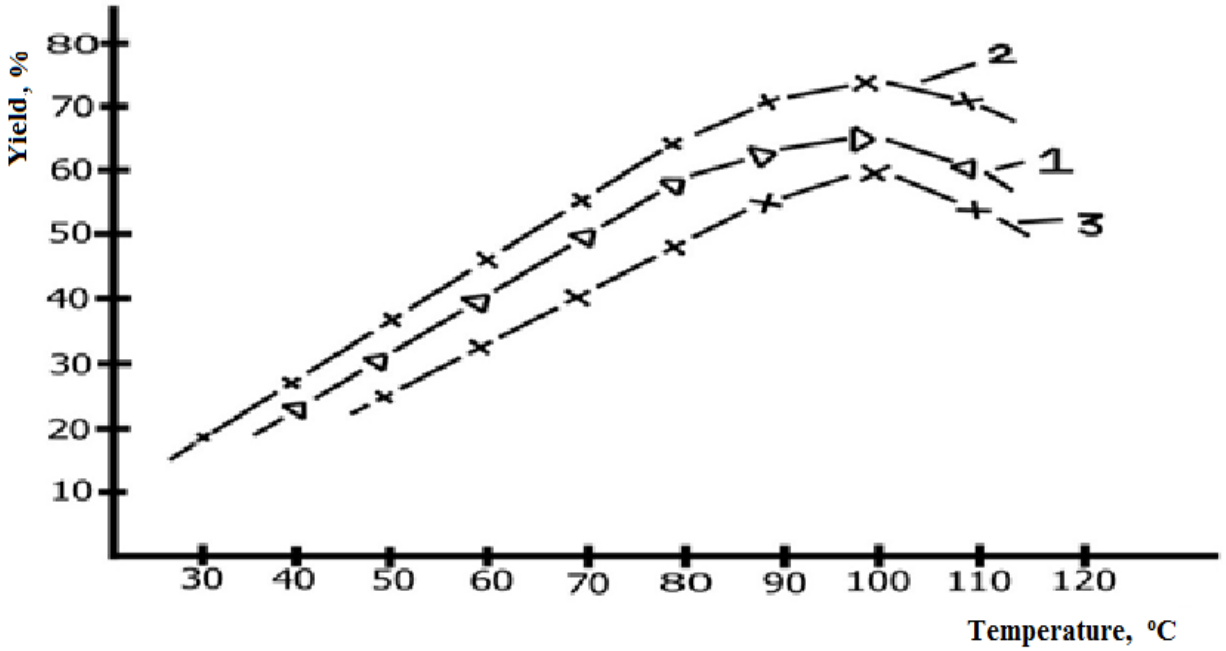


Fig.1. Dependence of aminoalcohols yield from temperature

b) nature of catalysts. Influence of nature of catalysts on yield of acetylenic aminoalcohols was investigated. Results, obtained in presence of withoutoxygen and oxygen salts of d-metal namelly of Cu^{+} and Cu^{2+} used as catalysts are presented in table 2 .

Table 2. Dependence on aminoalcohols yield from nature of catalysts

Composin of catalyst	CuI	CuBr	$CuBr_2$	$CuCl_2$	CuCl	$Cu(CH_3COO)_2$	$CuSO_4$
Name of substansces				Yield of reaction , %			
1).6-N-di-ethylamino-3-methylhe- xine-4-ol-2	34,6	47,8	58,4	67,2	80,6	79,2	70,3
2). 6-N-di-butylamino -3-methylhe- xine-4-ol-2	33,8	34,9	40,4	45,3	52,9	63,6	56,4
3). 6-N-pyperidyl-3-methylhexine-4-ol-2	35,7	36,7	51,5	58,7	67	66,8	57,3
4).3-N-di-ethylamno-1-phenyl-propine -1.	46,3	50,8	59,9	64,8	61,1	62,1	63,4

Solts containing in theis composition ions Cu^{+}, Cu^{2+} and Ag^{+} have increased yield of reaction. In presence of salts containing in their composition such ions as Br^{-} and I^{-} yield of products was low, but in presence of such salts as Cu_2Cl_2 and $Cu(CH_3COO)_2$ aminoalcohols have been obtained with high yields.

c) duration of reaction. Yield of aminoalcohols also has depended on duration of reaction. For example, yield of 5-N-dibutylamino-2-methylpentine-3-ol-2 was equaled 30; 41 and 65 % at

time 2; 4 and 8 houres. Data by dependence on yield of some synthesized compounds from duration reaction are presented in table 3 and fig. 2.

Table 3. Dependence products yield on duration of reaction

Name of substance	5-N-dibutylamino-2-methylpentine-3-ol-2 (2)	5-N-diethylamino -2-methylpentin-3-ol-2 (1)	5-N-pyperidyl-2-methylpentine-3-ol-2 (3)
Time, h.	Yield, %		
2	34	30	22
3	40	35	29
4	47	41	33
5	53	44	40
6	60	52	41
7	68	59	52
8	75	65	59
10	70	63	50

1. $(CH_3)_2COHC \equiv CCH_2N(C_2H_5)_2$ (5-N-diethylamino-2-methylpentin-3-ol-2)

2. $(CH_3)_2COHC \equiv CCH_2N(C_4H_9)_2$ (5-N-dibutylamino-2-methylpentin-3-ol-2)

3. $(CH_3)_2COHC \equiv CCH_2NC_5H_{10}$ (5- N-pyperidil -2-methylpentin-3-ol-2)

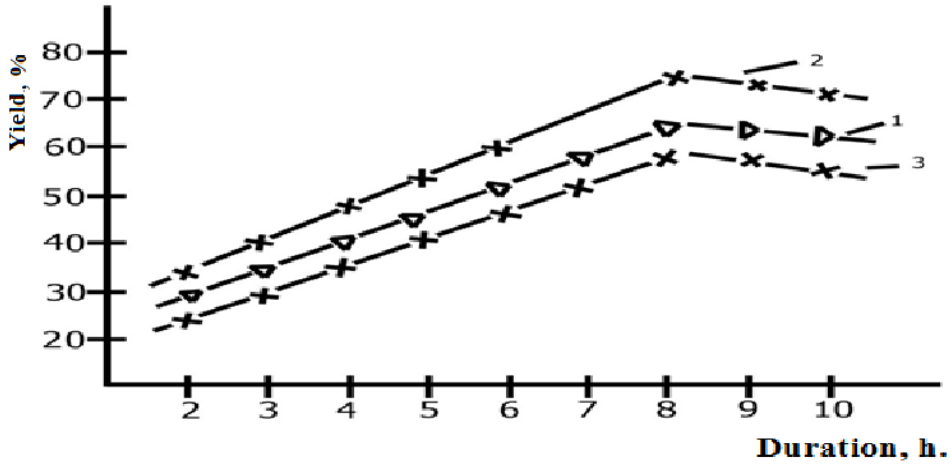


Fig. 2. Dependence on yield of aminoalcohols from reaction time.

g) Nature of solvent. It was shown that yield of aminoalcohols has depended on nature of solvent: in polar solvents such as dioxane (t_b = 101,1) yields of amino-alcohols was hight (83 % and more) and inpolar solvents such as benzole and hexane aminoalcohols were obtained with lower yields. Dependence on aminoal- cohols yields from nature of solvents is presented in table 4.

Table 4. Dependence on the aminoalcohol yield from nature of the solvents.

Name of substance		Solvent ; yield (%)		
№		Hexane	Bensole	Dioxane
1	7-N-diethylaminohexino-5-ol -4	40,6	45,3	49- 52
2	5-N-pyperidil-2-methylhexyl-3-ol-2	48,1	56,4	58-67
3	6-N-dibutylamino-3-methylhexyn-4-ol-3	44,9	47,7	52,9
4	3-N-pyperidil-1-phenylpropyn-1	64,3	72,5	71-83

Mechanism of Mannich reaction didn't determined, but there are two scientifical prepositions about it's mechanism: 1) reaction of aminomethylation of acetyle- nic alcohols and phenylacetylane. This process consists from two stages: a) interaction of acetylenic alcohols and phenyacetylene with formaldehyde:

$$(RR')_2C(OH)C\equiv CH + CH_2O \longleftrightarrow (RR')_2C(OH)C\equiv C\text{-}\ CH_2OH$$

$$C_6H_5C\equiv CH + CH_2O \longleftrightarrow C_6H_5C\equiv C\text{ -}CH_2OH$$

b) Formation of aminoalcohols by condensation of forming intermediates with secondary amines:

$$RR'COHC\equiv CCH_2OH + HNR''R''' \longrightarrow RR'COHC\equiv CCH_2NR''R''' + H_2O$$

$$C_6H_5C\equiv CCH_2OH + HNR''R''' \longrightarrow C_6H_5C\equiv CCH_2NR''R''' + H_2O$$

where : $R = R' = \text{-}\ CH_3$; $R = \text{-}\ CH_3$, $R' = \text{-}\ C_2H_5$; $R = \text{-}\ H$, $R = \text{-}\ C_3H_7$

$R'' = R''' = \text{-}\ CH_3$; $R'' = R''' = \text{-}\ C_2H_5$; $R'' = R''' = \text{-}\ C_4H_9$; $R'' = R''' = \text{-}\ C_5H_{10}$

Second preposition. a) formation of N –(axymethyl) by interaction of secondary amines with formaldehyde :

$$(R''R''')N\text{-}H + CH_2O \longleftrightarrow (R''R''')N\text{-}\ CH_2OH$$

b) condensation throght hydrogen atom at triple bond with intermediate N-(oxymethyl) alcohol:

$$(RR')C(OH)C\equiv CH + HOCH_2N(R''R''') \rightarrow (RR')C(OH)C\equiv CCH_2N(R''R''') + H_2O$$

According to first preposition dimethylethynilcarbinol has reacted with parafor- maldehyde in presence of Cu(I) salt in dioxane as solvent. In this case acetyleni-des didn't reacted with paraphorm and reaction of aminomethylation has based on second hypothesis:

$$(R''R''')N\text{-}H + CH_2O \longrightarrow (R''R''')N\text{-}\ CH_2OH$$

Secondary amines have reacted with formaldehyde with formation of N –(oxy -methyl)-amine :

$$(RR')C(OH)C\equiv CH + HOCH_2N(R''R''') \rightarrow (RR')C(OH)C\equiv CCH_2N(R''R''') + H_2O$$

Table 5. Physico –chemical properties of synthesized acetylenic aminoalcohols

№	Structure formule and name of substance	Yield, %	Temperature of boiling,°C (mm. of Hg st.)	n^{20}_d	d^{20}_n g/sm^3
1	$(CH_3)_2NCH_2C\equiv CCOH(CH_3)_2$ 5-N-dimethylamino-2-methylpentyn-3-ol-2	60	92,7	1,4570	0,9093
2	$(CH_3)_2NCH_2C\equiv CCOH(CH_3)C_2H_5$ 6-N-dimethylamino-3-methylhexyn-4-ol-3	62,0	101/7	1,4590	0,9067

3	$(C_2H_5)_2NCH_2C \equiv CCOH(CH_3)_2$ 5-N-diethylamino-2-methylpeptin-3-ol-2	67,4	92/4	1,4614	0,9011
4	$(C_4H_9)_2NCH_2C \equiv CCOH(CH_3)_2$ 5-N-dibutylamino-2-methylpentyne-3-ol-2	75,0	144-145/17	1,4860	0,9176
5	$C_5H_{10}NCH_2C \equiv CCOH(CH_3)_2$ 5-N-piperidyl-2- methylpentyne-3-ol-2	50-60	112/3	1,4895	-
6	$C_5H_{10}NCH_2C \equiv CCOH(CH_3)C_2H_5$ 6-N-piperidyl-3-methylhexyne-4-ol-3	58-67	124/3	1,4918	-
7	$(CH_3)_2NCH_2C \equiv C-C_6H_5$ 3-N-dimethylamino-1-phenylpropyne-1	61,9	115/8	1,4441	0,9147
8	$(C_2H_5)_2NCH_2C \equiv C-C_6H_5$ 3-N-diethylamino-1-phenylpropyne-1	61,1	140-141/10	1,4321	0,9849
9	$(C_4H_9)_2NCH_2C \equiv C-C_6H_5$ 3-N-dibutylamino-1-phenylpropyne-1	54,5	174/15	1,4040	0,9019
10	$C_5H_{10}NCH_2C \equiv C-C_6H_5$ 3-N-pyperidyl-1-phenyl-propyne-1	71-83	123/3	1,5620	-

IR- spectrums of synlbesized **c**ompounds have been obtained on UR-20 in thin layer of KBr. Valent vibrations of methyl and methylene groupes in IR spectrum of 5-N-diethylamino-2-methylpentyne -3- ol-2 (Fig. 3) have been observed at 2900 -2700 sm $^{-1}$; valent vibrations of CO group at 1800 – 1700 sm^{-1}. Absorption of valent vibrations of – C≡C- group were observed in range 2200 – 2100 sm^{-1}; absorption of deformation vibrations of -C≡C- group were observed at 3315 sm^{-1}.

Wide band in range 3450-3000 sm^{-1} is attributed to valent vibrations of OH- group: deformation vibrations of methylene group were observed at 1400 sm $^{-1}$. It is necessary to note that absorption at 1400 sm^{-1} can be attributed to deformation vibrations – CH_2-N= group.

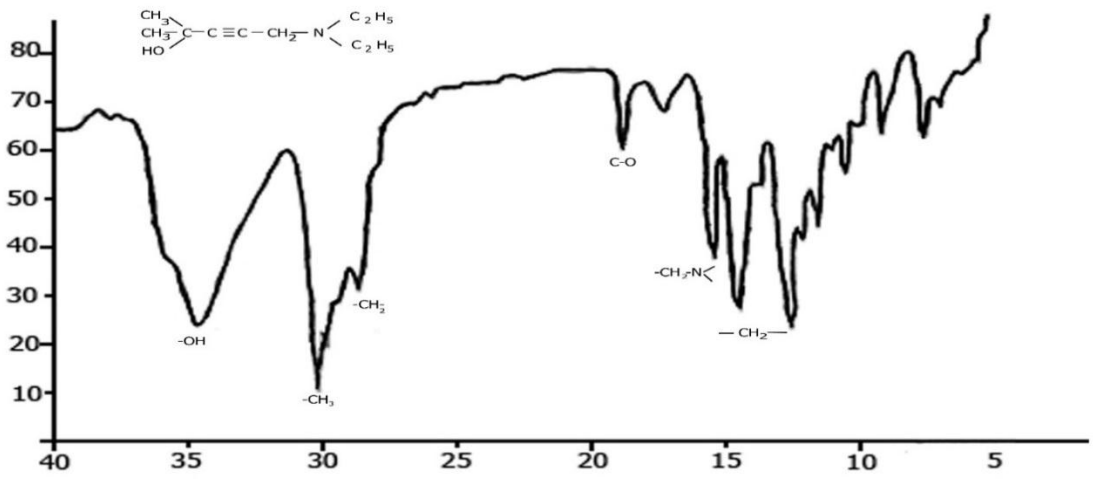


Fig.3. IR – spectrum of 5-N-diethylamino-2- methylpentyne -3-ol-2

Spectrums PMR (^{1}H and ^{13}C) of obtaned compounds were obtained on the Varian -400. PMR spectrums of acetylenic alcohols and phenylacetylene were : in ami-noalcohols there are lines which can be attributed to TMS $(CH_3)_4Si$ NMR of ace- tylenic alcohols and phenylacetylene were obtained in pure type: sectrums of aminoalcohols and aminocompounds were obtained at using $CDCI_3$. In PMR spectrum of 5-N- diethyl-2-methylpentyne -3-ol-2 signals of methyl group were observed at 0,9-1,0 m.d.(9H) ; signal of protone at OH- group was observed at 3,20 m.d. with chemical displacement (1 H); signals of protons of methylene group were observed at 1,5-1,7 m.d. (2 H).

Conclusions.

1. In reactions of synthesise of aminoalcohols on the base of acetylenic alcohols and phenylacetylene yield of products has depended on nature of solvents, catalysts, temperature and duration of reaction.
2. Yield of aminocompounds obtained from phenylacetylene by Mannich reaction was higher in comparision with aminoalcohols, obtained from acetylenic alcohols.
3. Acetylenic aminoalcohols and phenylamines are yellow transparent liquides soluble in water.

Literature

1. Neiland O.Ya. Organic chemistry, -M., Higher school, 1990, - 750 p.
2. Semenov T.A., and Leites I.L. Purification of process gases, -M., 1977.- P. 488
3. Ogorodnikova S.K. Handbook of petrochemist, Vol. 2 -L.,1978 .--592 -P. 4.
4. Herbicidal activity of derivatives of acetylenic alcohols Sirlibaev T.S., Kurbanov A.I., Turgunov E., Kultaev K.K., Koblov R.K., Khikmatov A. Agrochemistry. 1985. - No.11, - P. 105-107
5. Biological activity of some acetylenic aminoalcohols and halogen-containing products based on them Kurbanov A.K., Sirlibaev T.S., Turgunov E., Kultaev K.K., Kovlov R.K, Tarikov S. Agrochemistry, 1986 , - No. 4 -P. 86 -89.
6. Sirlibaev T.S., Kultaev K.K., Kurbanov A.I. Investigation of the antimicrobel activity of some acetylenic compounds and products obtained on their base. Dep. in Uz NIINTI. - 1989. - № 957 - Uz 89. - 8 p.
7. Kurbanov A.I. Syntheses based on secondary, tertiary acetylenic alcohols and pyridylacetylenes, possible fields of application of the obtained compounds: dis ... doc. Chem. Sciences. –T., 1998. -FROM. 270 -275.
8. Kultaev K.K., Turgunov E. An obtaine of singleatomic uncertain alcohols on the base of acethylene and phenyl acethylene and their bromination. Actual problems of modern science, education and training, Urgenhc, 2020, -No. 4.- P. 280-290.
9. Weigand-Khilgetag. Experimental methods in organic chemistry, -M. Chemistry. 1968. - 944 p.
10. Method of obtaining 4- (dimethylamino) -1-alkyl -1-methyl-2-butyn-1-ols . RF Patent No. 2378249. 2010, Blue. No. 1. / S Dzhemilev U.M., Shaibakova M.G., Titova I.G., Makhmudiyarov G.A., Ramazanov I.R., Ibragimov A.G./.