

# Synthesis Monoamine and Diamines Based on Acetylene.

Kultaev Kuzibay Kazakbayevich,

Tashkent state pedagogical  
university named after Nizami,  
faculty of natural Sciences,  
department of Chemistry and Methods  
of its Teaching, Associate professor,  
+ 93 536 50 94 E-mail :  
[Kultayev60@bk.ru](mailto:Kultayev60@bk.ru).

**Annotation:** in this work, we studied the synthesis of monoamines based on acetylene amine alcohols and diamines in the presence of acetylene, paraform and secondary amines by the Mannich reaction. The structure, physicochemical constants and conditions for the formation of synthesized monoamines and diamines in high yield have been determined. The structure of the synthesized products was confirmed by IR and PMR spectra. Their physicochemical constants and yields have been determined. A dependence of the product yield on the nature of the catalyst was found.

**Keywords:** 3-N-dimethylaminopropine -1, 3-N-diethylaminopropyne-1, 1,4-di (N,N-dimethylamino) butyne -2, 1,4-di (N,N-diethylamino) butyne-2, Mannich reactions.

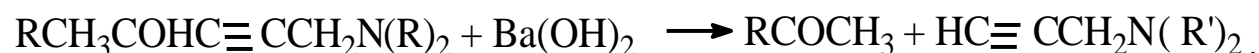
## INTRODUCTION.

Monoamines and diamines containing acetylenic group are used in polymer industry as valuable monomers for organic synthesis and also in medicine as biologically active compounds [1-4]. Propargylamine and its derivatives are used as medicines against oncological diseases [5,6]; as means for decreasing of arterial blood pressure [7] and also for treatment of Parkinson diseases [8]. In molecules monoamines electronic clouds are distributed irregularly as they are displaced to amino-group at triple bond, what is caused by hybridization of carbon atom. In row  $sp^3$ ,  $sp^2$  and  $sp$ - hybridization electronegativity of carbon atom has increased. In ethynyl radical carbon atom is in  $sp$ -hybridization but nitrogen atom in amino-group has  $sp^3$ - hybridization. In acetylenes having monosubstituted radical owing to its positive induction effect (+I) electronic cloud is displaced to carbon atom which hasn't radical which correspondingly has charged negatively. Such displacement of electrons has lightened reaction of exchange of hydrogen atom at triple bond and electrophilic addition for monoamines. Atom of nitrogen in mono- and diamines has ability to form quaternary salts owing to its divided electronic pair.

## LITERATURE VIEW

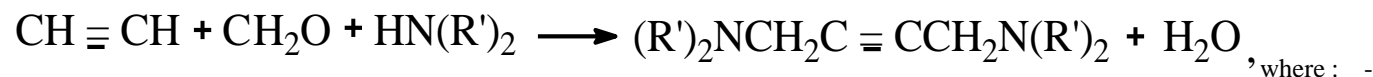
Monoamines impossible to synthesize on the base of Mannich reaction because they during reaction have transferred in diamines with high yield. By this reason at first aminoalcohols were obtained which then were undergone to decomposition

with formation of monoamines.  $Ba(OH)_2$ , KOH and NaOH were used as splitting agents in powdery air. It was investigated influence of catalysts nature on yield of monoamines. Reaction of synthesis of monoamines by catalytical decomposition of synthesized acetylenic aminoalcohols can be presented by following scheme:



where: R = -  $CH_3$ ; -  $C_2H_5$ ; -  $N(R')_2$  = -dimethylamino; -diethylamino; - piperidino; - morpholino groups.

Acetylenic diamines were obtained by Mannich reaction and their formation can be presented by following scheme:



where:  $N(R')_2$  = - dimethylamino; - diethylamino; - piperidino; - morpholino groups.

The main aim of this investigation- synthesis of monoamines by catalytical decomposition of aminoalcohols and their physico-chemical properties and also synthesis of diamines from acetylene on the base of Mannich reaction and obtain of their halogen derivatives and quaternary salts.

Synthesis of 1-(N-dimethylamino) propyne-2. Mixture of 2,82g (0.02 mole) N-dimethylamino-2-methylpropyne-3-ol-2 and 0.08g dried powdery  $Ba(OH)_2$  at temperature 50-60°C has been heated during 2-3 hours. The obtained mixture was extracted by diethyl ether by volume 50 ml and was dried by  $K_2CO_3$ . For obtain of monoamine ether extract has been distilled and obtained monoamine was distilled in deflagmatoral flask. In result 1,079 g (yield 65-70% from theoretical) of 1-N-dimethylaminopropyne-2 were obtained.

Synthesis of 1,4-di-(N,N-diethylamino) butyne-2. In flask by volume 500ml (provided by mechanical stirrer) in 100 ml of dioxane 0,73g (0,01 mole) of hydrochloride diethylamino and 0,03g (0,01mole) paraformaldehyde have been dissolved. The mixture was heated on electric stove before 60-70° and at mixing during 3-4h reaction was carried out at strong stream of gaseous acetylene. To mixture 5-6 drops of solution HCl were added for obtain paraphorm from polyformaldehyde. Obtained black

mixture of liquids was distilled in diflegmatoral flask. After distillation of dioxane remain mixture has been distilled under vacuum. In result of carrying out reaction 1,36g of 1,4- di-(N, N-diethylamino) butine-2 were obtained with yield 69,7%.

### DISCUSSIONS.

Chemical structure of obtained mono- and diamines was proved by methods IR, NMR  $^{13}\text{C}$  and PMR  $^1\text{H}$ . In IR- spectrum of 1-N-diethylaminopropine-2 band of absorption in range  $2975\text{-}2221\text{ cm}^{-1}$  is attributed to valent vibrations of methyl and methylene groups; band of absorption in range  $2325\text{-}2100\text{ cm}^{-1}$  is attributed to  $\text{-C}\equiv\text{C-}$  group; band absorption at  $3300\text{ cm}^{-1}$  is attributed to valent vibrations  $\text{-C}\equiv\text{C-H}$  group. Also there are deformation vibrations of  $\text{-CH}_2\text{-}$  group in range  $1400\text{ cm}^{-1}$ .

In IR- spectrum of 1-morpholinopropine-2 (fig. 1 ) there is intensive band of vibrations at  $3250\text{ cm}^{-1}$ , attributed to valent vibrations of hydrogen atom at  $\text{-C}\equiv\text{C-H}$  group; valent vibrations at  $2250\text{ cm}^{-1}$  are attributed to  $\text{-C}\equiv\text{C-}$  group.

In NMR  $^{13}\text{C}$  spectrum of 1-N- piperidinopropine-2 (fig.2) there are chemical displacements in range 73,2- 80 m.d. atoms of carbons in  $\text{-C}\equiv\text{C-}$  group; in range 24,3-26,2 m.d and 52,7 m.d. - nucleous of carbon atoms in piperidine ring.

In IR- spectrum of diamines for example 1,4-di-(N,N- piperidine)butine-2 there are bands of absorption in range  $2950\text{-}2600\text{ cm}^{-1}$  attributed to  $\text{-CH}_2\text{-}$  groups; band of deformation vibrations of  $\text{-CH}_2\text{-}$  groups was absorbed at  $1450\text{ cm}^{-1}$ . Absence of absorption typical for valent vibrations  $\text{-C}\equiv\text{C-}$  group in range  $2200\text{-}2100\text{ cm}^{-1}$  has indicated on the symmetry of diamines molecules.

In PMR spectrum of diamine 1,4-di-(pyperidino) butine-2  $\text{-CH}_2\text{-}$  groups of two pyperidinic rings have given signals with  $\delta$  1,41-1,51 m.d .(12 H) and 4  $\text{CH}_2\text{-}$  groups disposed in  $\alpha\text{-}$  position to nitrogen atom have given signals with  $\delta$  2,30-2,36 m.d; pyperiding ring (8 H) and also signals of protons of  $\text{-CH}_2\text{-}$  groups are observed in range  $\delta$  3,13 m.d (4 H).

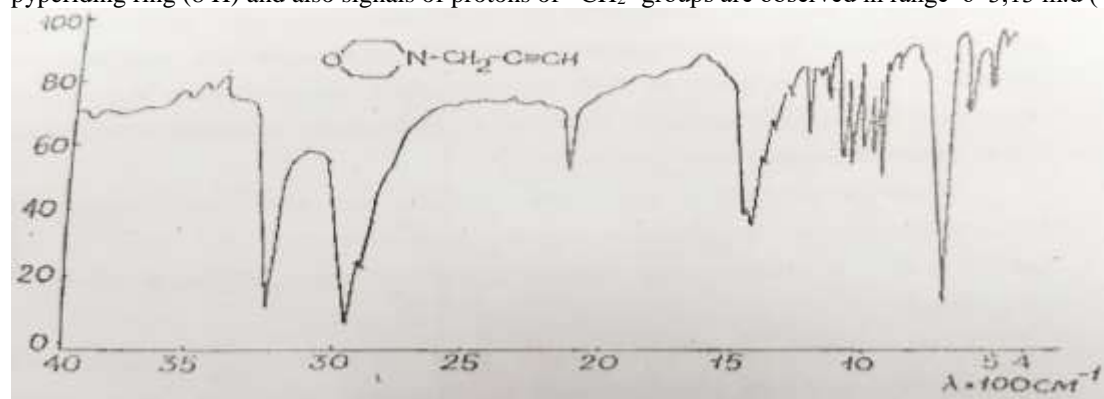


Fig. 1. IR spectrum of 1-N-morpholinopropine -2.

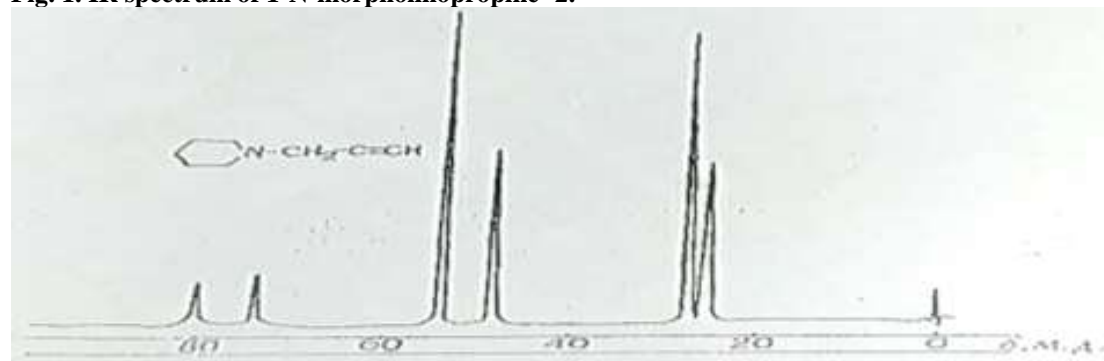


Fig. 2.  $^{13}\text{C}$  NMR spectrum of 1-N-piperidinopropine-2

Table 1

Physico -chemical constants of synthesized monoamines

|   | Name and formula of monoamines   | Brutto formula                       | Yield, % | Boiling temperature $^{\circ}\text{C}$ \ mm. Hg st. | $n_{\text{D}}^{20}$ | $d_4^{20}$ |
|---|--|--------------------------------------|----------|---|---------------------|------------|
| 1 | 1-N-dimethylamino propine-2<br>$\text{HC}\equiv\text{CCH}_2\text{N}(\text{CH}_3)_2$          | $\text{C}_5\text{H}_9\text{N}$       | 65-70    | 79- 80  | 1,4175              | 0,7792     |
| 2 | 1-N-diethylamino -propine-2<br>$\text{HC}\equiv\text{CCH}_2\text{N}(\text{C}_2\text{H}_5)_2$ | $\text{C}_7\text{H}_{13}\text{N}$    | 71,5     | 119-120   | 1,4296              | 0,8042     |
| 3 | 1-N-dibutylamino -propine-2<br>$\text{HC}\equiv\text{CCH}_2\text{N}(\text{C}_4\text{H}_9)_2$ | $\text{C}_{11}\text{H}_{21}\text{N}$ | 52,1     | 87-89/19  | 1.4600              | 0,8116     |

|   |  |                                    |       |       |        |   |
|---|--|------------------------------------|-------|-------|--------|---|
| 4 | 1-N- piperidino-propine-2<br>$\text{HC} \equiv \text{CCH}_2\text{C}_5\text{H}_{10}$      | $\text{C}_8\text{H}_{13}\text{N}$  | 70-78 | 72/35 | 1,4718 | - |
| 5 | 1-N-morpholino -propine-2<br>$\text{HC} \equiv \text{CCH}_2\text{C}_4\text{H}_8\text{O}$ | $\text{C}_7\text{H}_{11}\text{NO}$ | 63-65 | 68/10 | -      | - |

Table 2  
Physico - chemical properties of synthesized diamines

| № | Name and formula of diamines   | Yield, % | Boiling temperature<br>°C/mm. Hg<br>st | $n_D^{20}$ | $d_4^{20}$ |
|---|--|----------|--|------------|------------|
| 1 | 1,4-di(N,N- dimethylamino) -butine-2<br>$(\text{CH}_3)_2\text{NCH}_2\text{C} \equiv \text{CCH}_2\text{N}(\text{CH}_3)_2$                 | 51,3     | 178-179                                | 1,4533     | 0,8660     |
| 2 | 1,4-di(N,N- diethylamino)- butine-2<br>$(\text{C}_2\text{H}_5)_2\text{CH}_2\text{C} \equiv \text{CCH}_2\text{N}(\text{C}_2\text{H}_5)_2$ | 69,7     | 220-221                                | 1,4582     | 0,8013     |
| 3 | 1,4-di(N,N-dibutylamino)- butine-2<br>$(\text{C}_4\text{H}_9)_2\text{NCH}_2\text{C} \equiv \text{CCH}_2\text{N}(\text{C}_4\text{H}_9)_2$ | 74,4     | 180-181/15                             | 1,4563     | 0,862      |
| 4 | 1,4-di(N,N-piperidino) butine-2<br>$\text{C}_5\text{H}_{10}\text{NCH}_2\text{C} \equiv \text{CCH}_2\text{NC}_5\text{H}_{10}$             | 70-80    | 149/3                                  | 1,4954     | -          |
| 5 | 1,4-di(N,N-morpholino) butine-2<br>$\text{OC}_4\text{H}_8\text{NCH}_2\text{C} \equiv \text{CCH}_2\text{NC}_4\text{H}_8\text{O}$          | 73-82    | 150/3                                  | 1,4931     | -          |

**Conclusion:** Yield of monoamines has depended on molecular mass of acetylenic amino alcohols: with it's increasing they have decomposed lightly. For example, 5-N-dimethylamino-2-methylpentine-3-ol-2 has decomposed hardly in comparison with aminoalcohol 6-N-dimethylamino-3-methylhexino-4-ol-3. Thermal decomposition of aminoalcohols also has depended on nature of catalyst. At using of  $\text{Ba}(\text{OH})_2$  (160°C) reactions were carried with high yields in comparison with using KOH (160°C) at the same experimental conditions. Decomposition of aminoalcohols in the presence  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  is characterized by lowering yields.

#### USED LITERATURE

1. Азербайев И.Н., Сарбаев Т.Т. Химия регулирует рост растений . Алма –Ата : Наука, 1966. – С. 8.
2. Атавин А.Т., Дмитриева З.Т., Трофимов Б.А. Биологически активные соединения, - Л.: Наука. 1968. - С. 113
3. Гербицидная активность производных ацетиленовых спиртов Т.С. Сирлибаев, А.И. Курбанов, Э.Тургунов, К.К. Култаев, Р.К.Коблов, А.Хикматов Агрохимия . 1985, № 11. - С.105 -107.
4. Биологическая активность некоторых ацетиленовых аминоспиртов и гало-генсодержащих продуктов на их основе А.И.Курбанов, Т.С.Сирлибаев, Э.Тургунов, К.К.Култаев, Р.К.Ковлов, С. Тариков Агрохимия, 1986, №4. -С. 86 -89
5. Fudzuki Sun. J. Chem. Soc. Jap., Pure Chem. Sec. Синтез ацетиленовых аминов . РЖХим., 1967, 2Ж146.
6. J.H. Biel. N- alkylpiperidyl alkynyl amines . РЖХим., 1960, 93528П.
7. Котляревский И.Л., Андриевская Э.К. Моно и диамины, производные р-диэтинилбензола . Изв. АН СССР. Сер. хим. 1966. №3. - С. 546-549.
8. Лискер И.С. Физические методы исследования в агрономитинге. Физические методы и средства получения информации в агрономитинге. - Л.1987.- С. 3-21.