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MONOAMINES AND DIAMINES CONTAINING ACETYLENE GROUPS AND THEIR REACTIONS WITH HALOGENS.

Kultaev Kuzibay Kazakbayevich,
Tashkent state pedagogical university
named after Nizami, faculty of Natural Sciences,
department of Chemistry and Methods
of its Teaching, Associate professor,
E-mail : Kultayev60@.bk.ru

Резюме: Ушбу мақолада ацетилен аминспиртлари асосида моноаминлар ва Манних реакцияси бўйича ацетилен, параформ ва иккиламчи аминлар ишти - рокида диаминлар синтези ўрганилди. Синтезланган моноамин ва диамин - ларнинг тузилиши, физик -кимёвий доимийлиги ва юқори унумда ҳосил бўлиш шароити аниқланди. Моноамин ва диаминлар молекуласида кимё- вий актив марказлар : $C \equiv C$, $-N=$ атоми ва $-C \equiv C -H$ мавжуд. Уч боғнинг галогенланиш реакцияси ва азот атомининг галоген тутган кислоталар таъ- сирида тўртламчи туз ҳосил этиши ўрганилди. Синтезланган ҳосилаларнинг тузилиши ИК - ва ПМР – спектрлар билан тасдиқланди. Уларнинг физик кимёвий доимийликлари ва унуми аниқланди. Катализатор табиатига махсулот унуми боғлиқлиги топилди.

Калит сўзлар : 3- N-диметиламинопропин -1; 3-N- диэтиламинопропин- 1; 1,4- ди(N,N-диметиламино)бутин -2; 1,4-ди (N,N-диэтиламино)бутин -2, Манних реакцияси, тўртламчи туз, цис- ва транс изомер, инфрақизил спектр, парамагнит резонанс, валент тўлқин тебраниши, деформацион тўлқин функция, конденсатланиш реакцияси.

Аннотация: В данной работе изучен синтез моноаминов на основе ацетиленовых аминспиртов и диаминов в присутствии ацетилена, параформа и вторичных аминов по реакции Манниха. Определены структура, физико-химические константы и условия образования синтезированных моноаминов и диаминов с высоким выходом. В молекулах моноаминов и диаминов имеются хими -чески активные центры такие как $-C \equiv C-$, $-N=$ и $-C \equiv C -H$. Изучены реакции галогенирования тройной связью моно – и диаминов и образование их четвертичных солей с галогенсодержащими кислотами . Строение синтезированных продуктов подтверждено ИК- и ПМР-спектрами. Определены их физи -кохимические константы и выходы. Обнаружена зависимость выхода продуктов от природы катализатора.

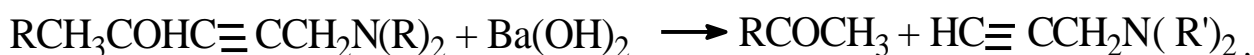
Ключевые слова : 3-N-диметиламинопропин -1; 3-N-диэтиламинопропин-1; 1,4-ди(N,N-диметиламино)бутин-2; 1,4-ди(N,N-диэтиламино) бутин -2, реакция Манниха, четвертичная соль, цис- и транс-изомеры, инфракрасный спектр, парамагнитный резонанс, колебание валентной волны, волновая функция деформации, реакция конденсации.

Abstract: In this work the synthesis of monoamines on the base of acetylene aminoalcohols and diamines in the presence of acetylene, paraform and secondary amines by the Mannich reaction was investigated. The structure, physico-chemical constants and conditions of formation of synthesized monoamines and diamines with high yields have been determined. In the molecules of monoamines and diamines there are chemically active centers: $-C \equiv C-$, atom $-N=$ and $-C \equiv C - H$. The reactions halogenation of triple bond by halogenated acids and the formation of a quaternary salts have been studied. The structure of the synthesized products was confirmed by IR and PMR spectrums. Their physico-chemical constants and yields have been determined. Dependence of the products yield on the nature of the used catalysts was determined.

Key words: 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 reaction, quaternary salt, cis- and trans- isomers, infrared spectrum, paramagnetic resonance, valent vibrations, deformation vibrations, condensation reaction.

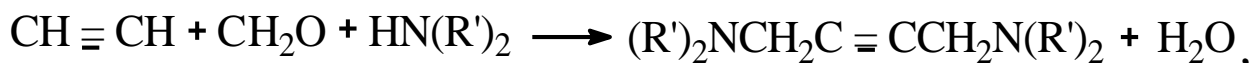
Introduction. Monoamines and diamines containing acetylenic group are used in polymer industry as valuable monomers for organic synthesis and also in medicine as biologically active compounds [1-4]. Propargylamine and its derivatives are used as medicines against oncological diseases [5.6]; as means for decreasing of arterial of blood pressure [7] and also for treatment of Parkinson disease [8]. In molecules monoamines electronic clouds are distributed unevenly 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 not divided electronic pair.

Base part. 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 [9] 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 catalytic 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 : - $\text{N}(\text{R}')_2$ = - dimethylamino; - diethylamino; - piperidino; - morpholino groups.

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

Synthesise of 1-(N-dimethylamino) propine-2. Mixture of 2,82g (0.02 mole) N-dimethylamino-2- methylpentine-3-ol-2 and 0.08g dried powdery $\text{Ba}(\text{OH})_2$ 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- dimethyl -aminopropine-2 were obtained.

Synthesis of 1,4-di-(N, N-diethylamino) butine-2. In lask 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 obtaine paraphorm from polyformaldehyde. Obtained black mixture of liquids was distilled in diflegmatoral flask. After distillation of dioxane remain mixture has been distillated 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%.

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

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

In NMR ^{13}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 (fig. 3) there are bands of absorption in range 2950-2600 sm^{-1} attributed to $-\text{CH}_2-$ groups; band of defornation vibrations of $-\text{CH}_2-$ groups was absorbed at 1450 sm^{-1} . Absence of absorption typical for valent vibrations $-\text{C} \equiv \text{C}-$ group in range 2200-2100 sm^{-1} has indicated on the symmetry of diamines molecules.

In PMR spectrum of diamine 1,4-di-(piperidino) butine-2 (Fig. 4) $-\text{CH}_2-$ groups of two piperidinic rings have given signals with δ 1,41-1,51 m.d .(12 H) and 4 CH_2- groups disposed in α - position to nitrogen atom have given signals with δ 2,30-2,36

m.d; piperiding ring (8 H) and also signals of protons of $-\text{CH}_2-$ groups are observed in range δ 3,13 m.d (4 H).

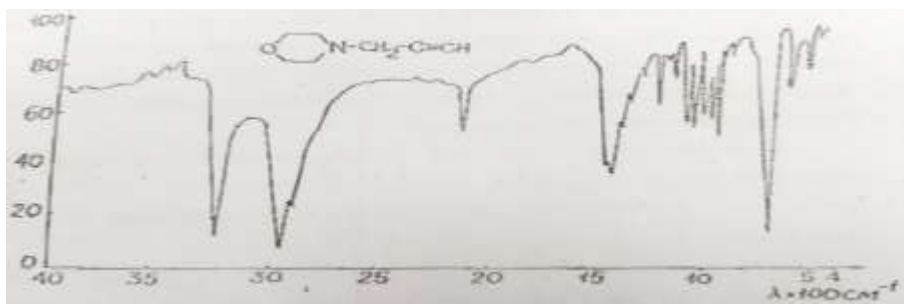


Fig. 1. IR- spectrum of 1-N-morpholinopropine-2

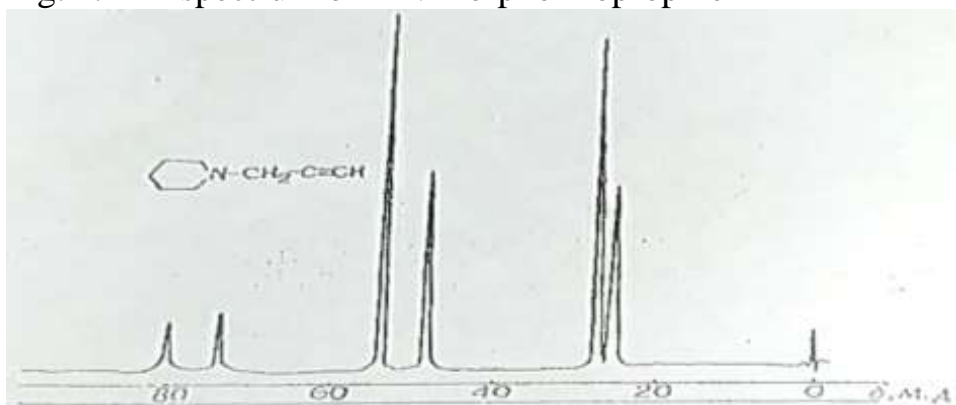


Fig.2. NMR ^{13}C spectrum of 1-N- piperidinopropine-2

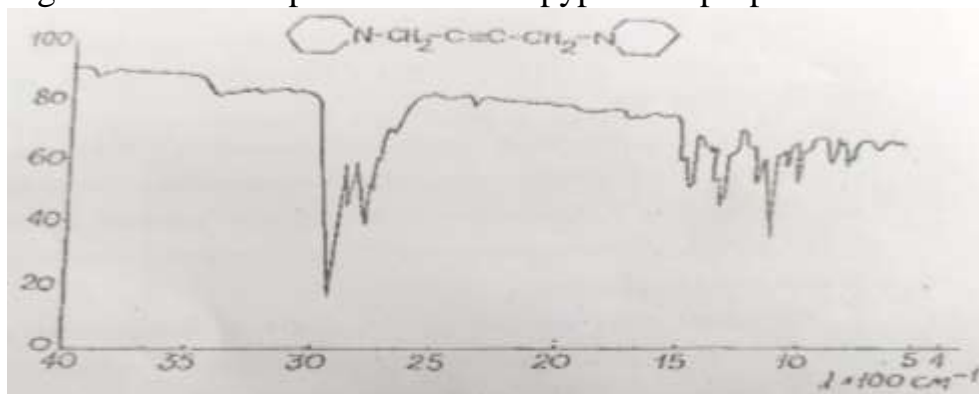


Fig. 3. IR- spectrum of 1,4-di(N,N- piperidine) butine-2

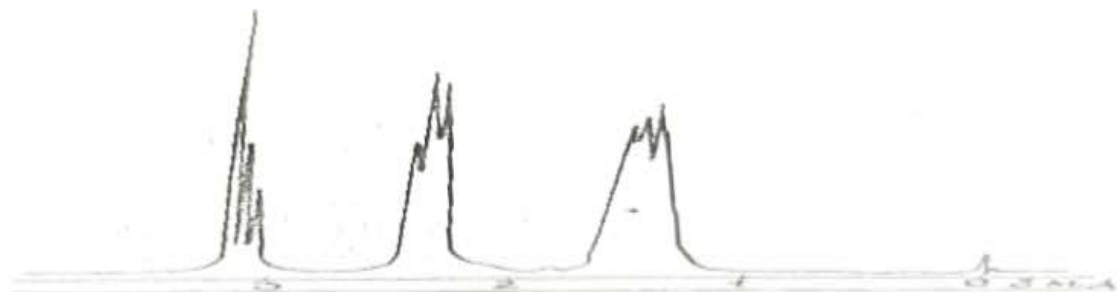


Fig. 4. PMR spectrum of 1,4-di(N,N- piperidino) butine-2

In tables 1 and 2 yields and physico-chemical constants of some synthesized compounds are presented.

Table 1
Physico -chemical constants of synthesized monoamines



	Name and formula of monoamines	Brutto formula	Yield, %	Boiling temperature °C \ mm. Hg st.	n_D^{20}	d_4^{20}
1	1-N-dimethylamino propine-2 $HC \equiv CCH_2N(CH_3)_2$	C_5H_9N	65-70	79- 80	1,4175	0,7792
2	1-N-diethylamino propine-2 $HC \equiv CCH_2N(C_2H_5)_2$	$C_7H_{13}N$	71,5	119-120	1,4296	0,8042
3	1-N-dibutylamino propine-2 $HC \equiv CCH_2N(C_4H_9)_2$	$C_{11}H_{21}N$	52,1	87-89/19	1.4600	0,8116
4	1-N-piperidino-propine-2 $HC \equiv CCH_2C_5H_{10}$	$C_8H_{13}N$	70-78	72/35	1,4718	-
5	1-N-morpholino propine-2 $HC \equiv CCH_2C_4H_8O$	$C_7H_{11}NO$	63-65	68/10	-	-

Table 2
Physico - chemical properties of synsized diamines

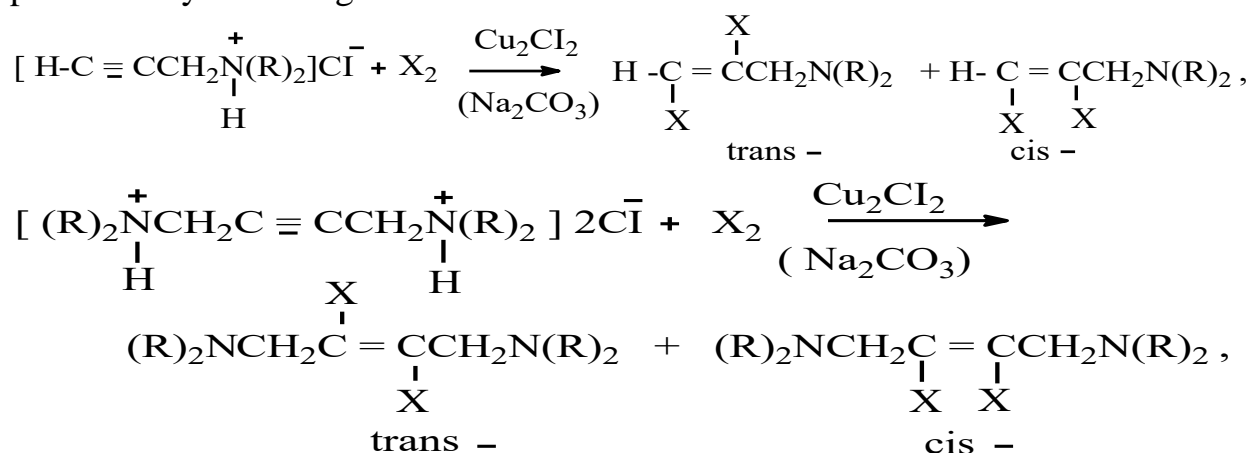
№	Name and formular of diamines	Yield, %	Boiling temperature °C \ mm. Hg st	n_D^{20}	d_4^{20}
1	1,4-di(N,N- dimethylamino) -butine-2 $(CH_3)_2NCH_2C \equiv CCH_2N(CH_3)_2$	51,3	178-179	1,4533	0,8660
2	1,4-di(N,N- diethylamino) butine-2 $(C_2H_5)_2CH_2C \equiv CCH_2N(C_2H_5)_2$	69,7	220-221	1,4582	0,8013
3	1,4-di(N,N-dibutylamino) butine-2 $(C_4H_9)_2NCH_2C \equiv CCH_2N(C_4H_9)_2$	74,4	180-181/15	1,4563	0,862
4	1,4-di(N,N-pyperidino) butine-2 $C_5H_{10}NCH_2C \equiv CCH_2NC_5H_{10}$	70-80	149/3	1,4954	-
5	1,4-di(N,N-morpholino) butine-2 $OC_4H_8NCH_2C \equiv CCH_2NC_4H_8O$	73-82	150/3	1,4931	-

Halogenation of mono- and diamines.

Halogenation of mono- and diamines has been carried at by mechanism of electrophylic addition and at this nitrogen atoms have formed with halogen atoms – salts, which are thermostable, water- soluble but didn't soluble in organic solvents such as acetone, benzole and in CCl_4 [10]. At bromination and chlorination of mono- and diamines their hydrohaloginated salts were obtained. Reactions were carried out in

polar solvent CCl_4 in the presence Cu_2Cl_2 as catalyst during 4-5 h at mixing at 25-30°C.

By results of gaseous-chromatographical analysis it was determine that mixture of products has been consisted from cis- and trans- halogen containing compounds, yield of which has co changen from nature of solvent, concentration of initial compounds and temperature. At relatively high temperatures (higher 30°C) trans-halogencontaining isomers have been formed and at low temperatures (-5-0°) cis-isomers were formed. Reactions of halogenation of mono- and diamines can be presented by following scheme:



where : - $\text{N}(\text{R}')_2$ – dimethylamino; – diethylamino; - piperidino; - morpholino groups, X = - atoms of Cl and Br .

Synthesis of hydrochloride salts. Through solution of 8,3g.(0,1 mole) 1-N-dimethylaminopropine-2 in 100 ml of acetone at cooling by ice water gaseous HCl has been passed. Obtained white crystalline salts have been filtrated throught paper filter and were dried at room temperature.

Synthesise of trans-1,2-dibrom-3-N-diethylaminopropen-1. In 50 ml CHCl_3 by mixing 14,75 g (0,1 mole) hydrochloride 1-N-diethylamino-propine-2 and 0,1 g Cu_2Cl_2 were added and obtained mixture was heated to 35°C, then to this mixture 16,6 g (0,2 mole) of bromine was added by drops during 1-2 hours and at this decolouration was observed. Reaction mixture has been washed by water solution of thiosulfate soliumn (1,0%) and has been dried by mixture of CHCl_3 and MgSO_4 . After of solvent distillation remained mass was dissolved in hexane and was remain on night. Solution of products in hexane has been distilled in diflegmatoral flask (high-1m; diametr-2,0 sm) and of this trans- and cis- brominated derivatives were extracted. In result of reaction 10,4 g (yield 54%) trans-1,2-dibromine-3-N-diethylaminopropen1 and 8,8g (yield 46%) cis-1,2-dibromine-3-N-diethylaminopropen1 have been obtained.

Reaction of halogenation of acetylen diamines was carried out anologically to monoamines.

Some physico-chemical properties of obtained products and their yields are presented in table 3,4

Table 3

Physico-chemicals characteristics of unsaturated dihalogenated products synthesized on the base of monoamines



№	Name and structural formula of substance	Yield,%	Boiling temperature °C/ mm.Hg st.	n_D^{20}	D_n^{20}
1	Cis-1,2-dibromine-3-N-diethylaminopropen-1 $(C_2H_5)_2NCH_2C \begin{array}{l} = CH \\ \quad \\ Br \quad Br \end{array}$	46,0	92-93 /2	1,5052	1,5167
2	Trance -1,2--dibromine-3-N-diethylamino-propen-1 $(C_2H_5)_2NCH_2C \begin{array}{l} = CH \\ \quad \\ \quad Br \\ Br \end{array}$	54,0	81/2	1,5102	1,5294
3	Cis-1,2-dichloro-3-N-diethylaminopropen-1 $(C_2H_5)_2NCH_2C \begin{array}{l} = CH \\ \quad \\ Cl \quad Cl \end{array}$	48,1	86,2	1,4625	1,0603
4	Trance-1,2-dichloro-3-N-diethylaminopropen-1 $(C_2H_5)_2NCH_2C \begin{array}{l} = CH \\ \quad \\ \quad Cl \\ Cl \end{array}$	59,1	74/2	1,4684	1,0719

Table 4

Physico-chemical characteristics of unsaturated dihalogenated and quarternary salts obtained on the base of diamines

№	Name and structural formula of compound	Brutto formula	Yield,%	Boiling temperature, °C
1	Trance- 2,3-dibromine-1,4 –di (N,N-dimethylamino) buten-2 $(CH_3)_2NCH_2C \begin{array}{l} = CCH_2N(CH_3)_2 \\ \quad \\ Br \quad Br \end{array}$	$C_8H_{16}N_2Br_2$	46,7	57- 58
2	Trance -2,3-dibromine-1,4 –di(N,N-diethylamino) buten-2 $(C_2H_5)_2NCH_2C \begin{array}{l} = CCH_2N(C_2H_5)_2 \\ \quad \\ Br \quad Br \end{array}$	$C_{12}H_{24}N_2Br_2$	38,6	69,0
3	Trance- 2,3-dichlore-1,4- di(N,N-dimethylamino) buten-2 $(CH_3)_2NCH_2C \begin{array}{l} = CCH_2N(CH_3)_2 \\ \quad \\ Cl \quad Cl \end{array}$	$C_8H_{16}N_2Cl_2$	52,6	60,5

4	Trance -2,3-dichlore-1,4- di(N,N- diethylamino) buten-2 $\begin{array}{c} \text{Cl} \\ \\ (\text{C}_2\text{H}_5)_2\text{NCH}_2\text{C} = \text{CCH}_2\text{N}(\text{C}_2\text{H}_5)_2 \\ \\ \text{Cl} \end{array}$	$\text{C}_{12}\text{H}_{24}\text{Cl}_2\text{N}_2$	48,5	64 - 65
5	Hydrochloride-1-N- dimethylamino propine-2 $\begin{array}{c} + \\ \\ [(\text{CH}_3)_2\text{NCH}_2\text{C} \equiv \text{CH}] \text{Cl}^- \\ \\ \text{H} \end{array}$	$\text{C}_5\text{H}_{10}\text{NCl}$	78,4	174- 175
6	Hydrochloride-1-N- diethylamino propine-2 $\begin{array}{c} + \\ \\ [(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{C} \equiv \text{CH}] \text{Cl}^- \\ \\ \text{H} \end{array}$	$\text{C}_7\text{H}_{14}\text{NCl}$	80,1	176-177
7	Hydrochloride 1,4-di(N,N- dimethylamino) butin-2 $\begin{array}{c} + \qquad \qquad \qquad + \\ \qquad \qquad \qquad \\ [(\text{CH}_3)_2\text{NCH}_2\text{C} \equiv \text{CCH}_2\text{N}(\text{CH}_3)_2] 2\text{Cl}^- \\ \qquad \qquad \qquad \\ \text{H} \qquad \qquad \qquad \text{H} \end{array}$	$\text{C}_8\text{H}_{18}\text{N}_2\text{Cl}_2$	75,9	186-188
8	Hydrochloride 1,4-di(N,N- diethylamino) butin-2 $\begin{array}{c} + \qquad \qquad \qquad + \\ \qquad \qquad \qquad \\ [(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{C} \equiv \text{CCH}_2\text{N}(\text{C}_2\text{H}_5)_2] 2\text{Cl}^- \\ \qquad \qquad \qquad \\ \text{H} \qquad \qquad \qquad \text{H} \end{array}$	$\text{C}_{12}\text{H}_{26}\text{N}_2\text{Cl}_2$	77,3	188-189

Chemical structure of obtained compounds has been proved by IR- and NMR-¹³C spectroscopically. In IR- spectrum of trance -2,3-dibromine-1,4-di(N,N- dimethylamino)buten-2 (Fig. 5) new band of absorption of - C=C- band in range 1690 cm^{-1} was observed which was absent in initial diamine. Bands of absorption in range 2900-2700 cm^{-1} were attributed to - CH₂- groups. Wide band of deformation vibrations of group - CH₂-N= has been observed in range 1440 cm^{-1} . And also in ranges 1296 and 620 cm^{-1} deformation vibrations of -C=C- bond have been observed.

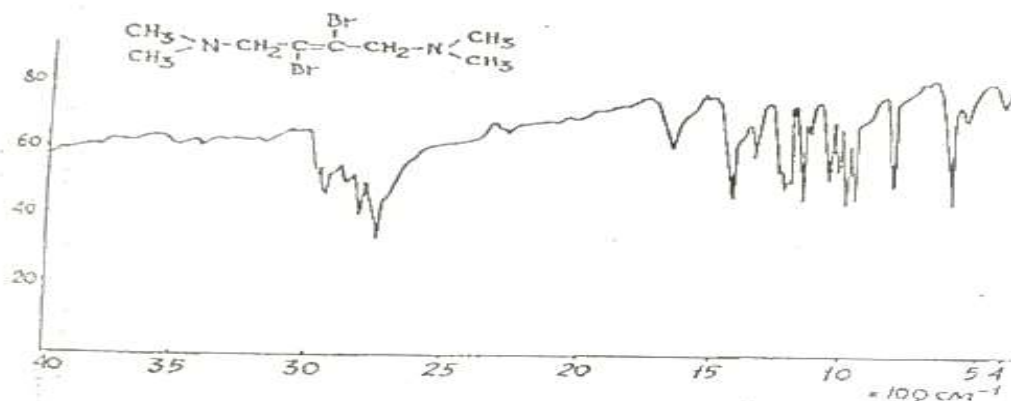


Fig. 5 IR- spectrum of trance -2,3-dibromine-1,4-di(N,N- dimethylamino)-buten-2

In NMR ^{13}C spectrum of trans -2,3-dibromine-1,4-di(N,N- dimethyl - amino)buten-2 (Fig .6) there are signals of carbon atoms $\text{C}_{3,6}$ (- $\text{CH}_2\text{-N=}$) at 65,4 m.d; $\text{C}_{1,2,7,8}$ (- CH_3) at 34 m.d and $\text{C}_{4,5}$ (- C=C-) at 124,3 m.d.

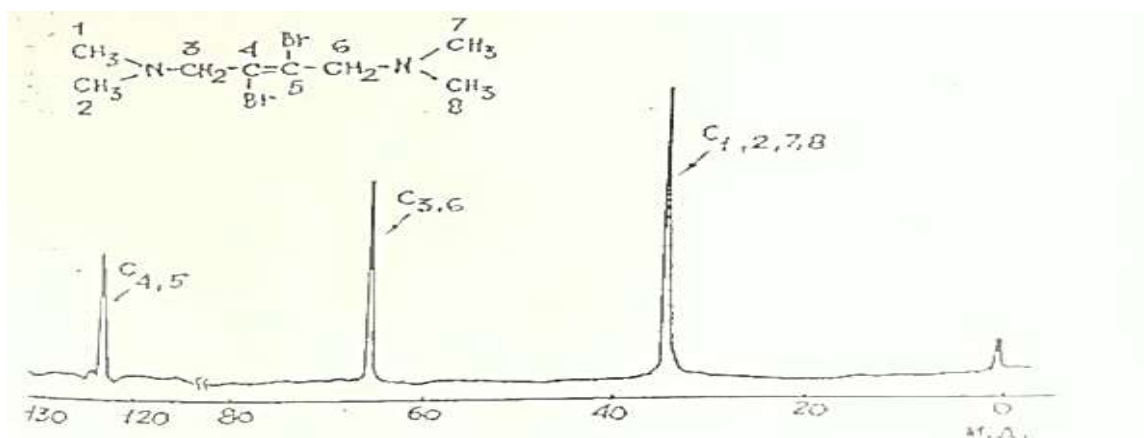


Fig.6 . NMR ^{13}C spectrum of trans -2,3-dibromine-1,4-di(N,N-dimethyl amino)buten-2

Conclusions : 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-methylpentene-3-ol-2 has decomposed hardly in comparison with aminoalcohol 6-N-dimethylamino-3-methylhexene-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 Na_2CO_3 and K_2CO_3 is characterized by lowering yields.

Halogen derivatives of mono and diamines are formed as cis- and trans isomers. At using CHCl_3 and CCl_4 as solvents yields of trans-dihalogen containing compounds were higher in comparison with cis- isomers (temperature 30°C)

Recommendation : 1. Acetylenic diamines are light to synthesize with high yields by Mannich reaction. Presence of two nitrogen atoms in molecules diamines facilitated formation of quaternary salts with organic halogenalkyls such as methylidene, methylbromide and ethylbromide. Their quaternary salts were obtained and also their biological activity was investigated.

2. In molecules of monoamines there is mobile hydrogen atom at triple bond what has allowed to synthesis amino acids by reaction of carboxylation using CO_2 .

3. Defence of chemically active metals from corrosion is very important task in industry and by this reason it is necessary to investigate inhibitional properties of obtained mono and diamines in process of chemical corrosion of metals with aim of their using as inhibitors.

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