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SYNTHESIS OF HAGOGENCONTAINING COMPOUNDS BASED ON MONO- AND DIAMINES

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KEYWORD

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.

ABSTRACT

In this work the synthesis of monoamines on the base of acetylene amino- alcohols and diamines in the presence of acetylene, paraform and secondary ami-nes by the Mannich reaction.was inivestigated. The structure, physico-chemical culconstants 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 ≡ C-, atom –N= and -C ≡ 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.

INTRODUCTION

Monoamines and diamines containg acetylenic group are used in polymer industry as valuble monomers for organic synthesis and also in medicine as biologically active compounds [1-4]. Propargylamine and it's 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 Parkhinson diseas [8]. In molecules monoamines electronic clouds are distributed irreen lars tlochat is they displaced to amino-group at triple bond. what is caused by hybrization of carbon atom. In row sp3, sp2 and sp-hybrization electronegative of carbon atom has increased. In ethynyl radical carbon atom is in sp-hybrization but nitrogen atom in amino-group has sp3- hybrization. In acetylenes having monosubstitut radical owing of it's positive induction effect (+I) electronic cloud is displaced to carbon atom which hasn't radical which correspondenly has charged negatively. Such displacement of electrons has lighten 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 quarternary salts owing to it's didn't divided electronic pair.

Base part. Monoamines impossible to synthesise on the base of Mannich reaction because they during reaction have transfered in diamines with high yield. By this reason at first aminoalcohols were obtained [9] which then were undergone to demcomposition 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:

$$RCH_3COHC\equiv CCH_2N(R)_2 + Ba(OH)_2 \longrightarrow RCOCH_3 + HC\equiv CCH_2N(R')_2,$$

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 :

$$CH\equiv CH + CH_2O + HN(R')_2 \longrightarrow (R')_2NCH_2C\equiv CCH_2N(R')_2 + H_2O,$$

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 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 $Ba(OH_2)$ at temperature 50-60°C has been heated during 2-3 hours. The obtained mixture was extracted by diethylic 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 theorical) 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 polyformaldehyge. 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 ^{1}H. 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 atributed to –C≡C- group; band absorption at 3300sm^{-1} is attributed to valent vibrations - C≡C-H group. Also there are deformation vibrations of -CH_2 - group in range 1400sm^{-1}.

In IR- spectrum of 1-morpholinopropine-2 there is intensive band of vibrati-ons at 3250 sm^{-1}, attributed to valent vibrations of hydrogen atom at - C ≡ C–H group; valent vibrations at 2250sm^{-1} are attributed to -C≡ C - group.

In NMR ^{13}C spectrum of 1-N- pyperidinapropine-2 there are chemical displa- cements in range 73,2- 80 m.d. atoms of carbons in -C≡C- group; in range 24,3-26,2 m.d and 52,7 m.d. - nucleous of carbon atoms in pyperidine ring.

In IR- spectrum of diamines for example 1,4-di-(N,N- pyperdine)butine-2 there are bands of absorption in range 2950-2600 sm^{-1} attributed to - CH_2 - groups; band of defonation vibrations of –CH_2- groups was absorbed at 1450 sm^{-1}. Absence of absorption typical for valent vibrations –C ≡ C- group in range 2200-2100sm^{-1} has indicated on the symmetry of diamines molecules.

In PMR spectrum of diamine 1,4-di-(pyperidino) butine-2 -CH_2- groups of two pyperidinic 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; pyperiding ring (8 H) and also signals of protons of –CH_2- groups are observed in range δ 3,13 m.d (4 H).

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	$C_{11}H_{21}N$	52,1	87-89/19	1.4600	0,8116

	$HC \equiv CCH_2N(C_4H_9)_2$					
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

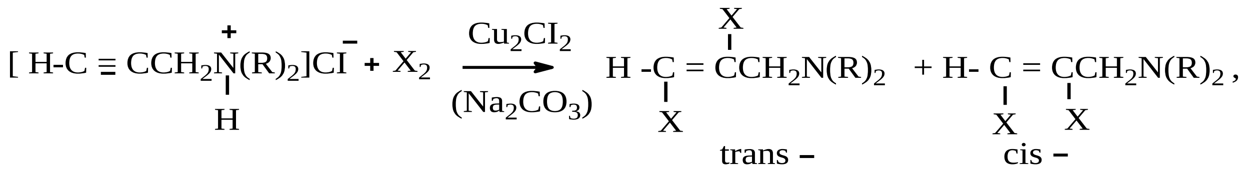
Physico - chemical properties of synsisized diamines

№	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	-

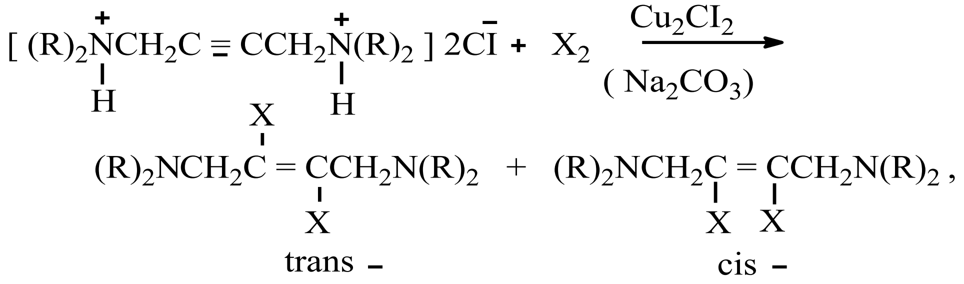
Halogenation of mono- and diamines.

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-chromotogrophical analysis it was determine that mixture of products has been consisted from cis- and tranc- 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) tranc- 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:



$$[\mathrm{H\text{-}C \equiv CCH_2\underset{H}{\overset{+}{N}}(R)_2}]\overset{-}{\mathrm{CI}} + X_2 \xrightarrow[(Na_2CO_3)]{Cu_2CI_2} \underset{\text{trans –}}{\mathrm{H\text{-}\underset{X}{C} = \overset{X}{C}CH_2N(R)_2}} + \underset{\text{cis –}}{\mathrm{H\text{-}\underset{X}{C} = \underset{X}{C}CH_2N(R)_2}},$$



$$[\mathrm{(R)_2\underset{H}{\overset{+}{N}}CH_2C \equiv CCH_2\underset{H}{\overset{+}{N}}(R)_2}]\,2\overset{-}{\mathrm{CI}} + X_2 \xrightarrow[(Na_2CO_3)]{Cu_2CI_2}$$

$$\underset{\text{trans –}}{\mathrm{(R)_2NCH_2\overset{X}{C} = \underset{X}{C}CH_2N(R)_2}} + \underset{\text{cis –}}{\mathrm{(R)_2NCH_2\underset{X}{C} = \underset{X}{C}CH_2N(R)_2}},$$

where : - N(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 crystalic salts have been filtrated throught paper filter and were dried at room temperature.

Synthesise of trance-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 ware 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 remainal on night. Solution of products in hexane has been distilled in diflegmatoral flask (high-1m; diametr-2,0 sm) and of this trance- and cis- brominated derivatives were extracted. In result of reaction 10,4 g (yield 54%) trance-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 dihaloginated products synthesized on the base of monoamines

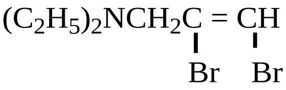
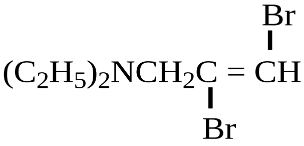
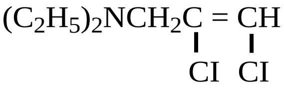
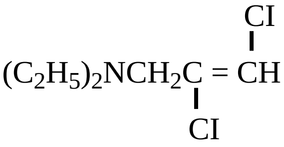
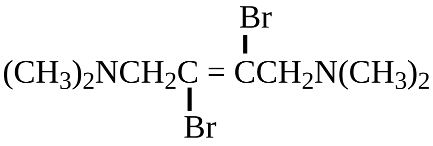
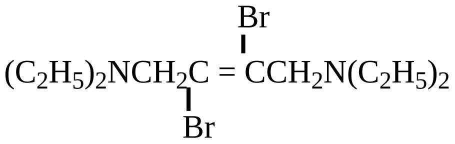
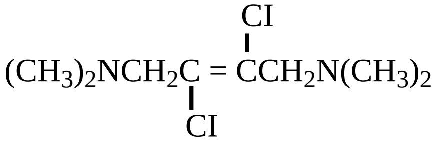
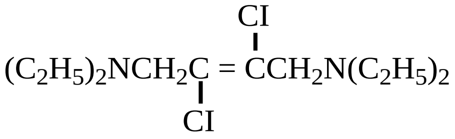
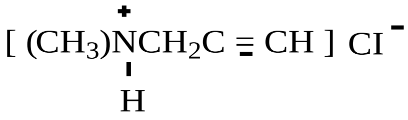
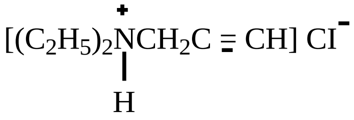
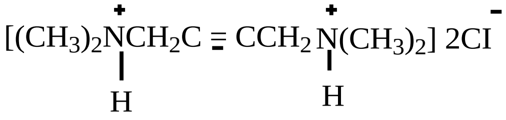
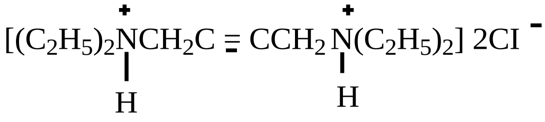
№	Name and structural formula of substance	Yield,%	Boiling temperature °C/ mm.Hg st.	n^{20}_D	D^{20}_n
1	Cis-1,2-dibromine-3-N-diethylaminopropen-1  $(C_2H_5)_2NCH_2\underset{Br}{C} = \underset{Br}{CH}$	46,0	92-93 /2	1,5052	1,5167
2	Trance -1,2--dibromine-3-N-diethylamino-propen-1  $(C_2H_5)_2NCH_2\underset{Br}{C} = \overset{Br}{CH}$	54,0	81/2	1,5102	1,5294
3	Cis-1,2-dichloro-3-N-diethylaminopropen-1  $(C_2H_5)_2NCH_2\underset{CI}{C} = \underset{CI}{CH}$	48,1	86,2	1,4625	1,0603
4	Trance-1,2-dichloro-3-N-diethylaminopropen-1  $(C_2H_5)_2NCH_2\underset{CI}{C} = \overset{CI}{CH}$	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 com-pound	Brutto formula	Yield,%	Boiling temperature, °C
1	Trance- 2,3-dibromine-1,4 –di (N,N-dimethylamino) buten-2  $(CH_3)_2NCH_2\underset{Br}{C} = \overset{Br}{C}CH_2N(CH_3)_2$	$C_8H_{16}N_2Br_2$	46,7	57- 58

2	Trance -2,3-dibromine-1,4 –di(N,N-diethylamino) buten-2  $(C_2H_5)_2NCH_2\underset{Br}{C} = \overset{Br}{C}CH_2N(C_2H_5)_2$	$C_{12}H_{24}N_2Br_2$	38,6	69,0
3	Trance- 2,3-dichlore-1,4- di(N,N-dimethylamino) buten-2  $(CH_3)_2NCH_2\underset{CI}{C} = \overset{CI}{C}CH_2N(CH_3)_2$	$C_8H_{16}N_2CI_2$	52,6	60,5
4	Trance -2,3-dichlore-1,4-di(N,N- die-thylamino) buten-2  $(C_2H_5)_2NCH_2\underset{CI}{C} = \overset{CI}{C}CH_2N(C_2H_5)_2$	$C_{12}H_{24}CI_2N_2$	48,5	64 - 65
5	Hydrochloride-1-N-dimethylamino propine-2  $[\ (CH_3)\underset{H}{\overset{+}{N}}CH_2C \equiv CH\ ]\ CI^-$	$C_5H_{10}NCI$	78,4	174- 175
6	Hydrochloride-1-N-diethylamino propine-2  $[(C_2H_5)_2\underset{H}{\overset{+}{N}}CH_2C \equiv CH]\ CI^-$	$C_7H_{14}NCI$	80,1	176-177
7	Hydrochloride 1,4-di(N,N- dimethyl-lamino) butin-2  $[(CH_3)_2\underset{H}{\overset{+}{N}}CH_2C \equiv CCH_2\underset{H}{\overset{+}{N}}(CH_3)_2]\ 2CI^-$	$C_8H_{18}N_2CI_2$	75,9	186-188
8	Hydrochloride 1,4-di(N,N- diethyla-mino) butin-2  $[(C_2H_5)_2\underset{H}{\overset{+}{N}}CH_2C \equiv CCH_2\underset{H}{\overset{+}{N}}(C_2H_5)_2]\ 2CI^-$	$C_{12}H_{26}N_2CI_2$	77,3	188-189

Chemical structure of obtained compounds has been proved by IR- and NMR-^{13}C spectroschopically. In

IR- spectrum of trance -2,3-dibromine-1,4-di(N,N- dimethyl- amino)buten-2 (Fig.1) new band of absorption of - C=C- band in range 1690 sm^{-1} was observed which was absent in initial diamine. Bands of absorption in range 2900-2700 sm^{-1} were attributed to - CH_2- groups. Wide band of deformation vibrations of group - CH_2-N= has been observed in range 1440 sm^{-1}. And also in ranges 1296 and 620 sm^{-1} deformation vibrations of -C=C- bond have been observed.

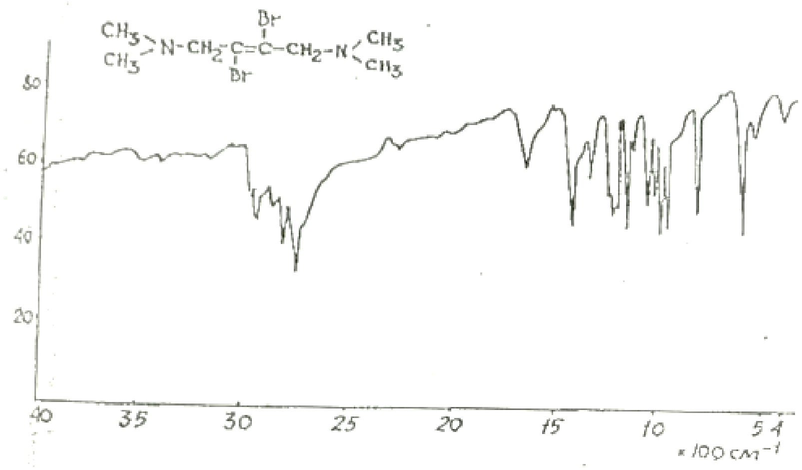


Fig. 1 IR- spectrum of trance -2,3-dibromine-1,4-di(N,N- dimethylamino)- buten-2

In NMR ^{13}C spectrum of trance -2,3-dibromine-1,4-di(N,N- dimethyl -amino)buten-2 (Fig .2) there are signals of carbon atoms $C_{3,6}$(-CH_2-N=) at 65,4 m.d; $C_{1,2,7,8}$(- CH_3) at 34 m.d and $C_{4,5}$(- C=C-) at 124,3 m.d.

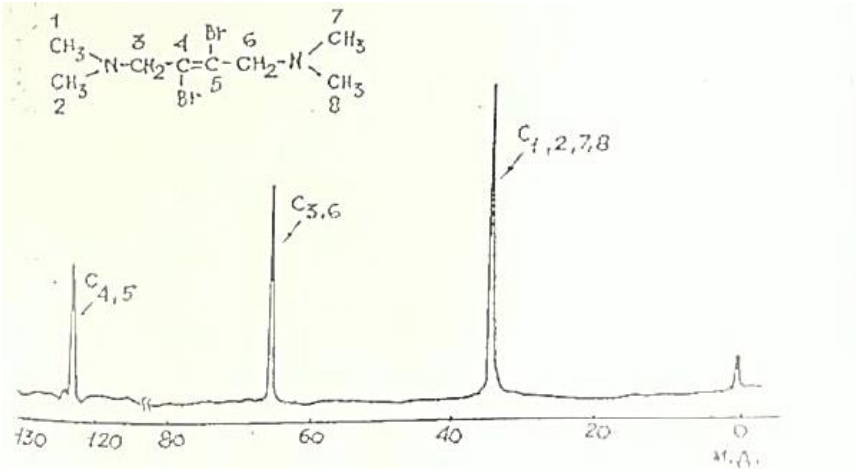


Fig.2. NMR ^{13}C spectrum of trance -2,3-dibromine-1,4-di(N,N-dimethyl amino)buten-2

CONCLUSIONS

Yield of monoamines has depended on molecular mass of acetylene-icamino alcohols: with it's increasing they have decomposed lightly. For example, 5-N-dimethylamino-2-methylpentine-3-ol-2 has decomposed hardly in compa-risision with aminoalchohol 6-N-dimethylamino-3-methylhexino-4-ol-3. Thermal decomposition of aminoalcohols also has depended on nature of catalyst. At using of $Ba(OH)_2$ (160°C) reactions were carried with high yields in comparision 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 trance isomers. At using $CHCl_3$ and CCl_4 as solvents yields of trance-dihalogencon - taining compounds were higher in comparison with cis- isomers (temperature 30°C)

RECOMMENDATION

1. Acethylnic diamines are light to synthesize with high yields by Mannich reaction. Presence of two nitrogen atoms in molecules diamines faci-lated formation of quartenary salts with organic halogenalkyls such as methylidine, methylbromide and ethylbromide. Their quartenary 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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