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RESEARCH OF THE INFLUENCE OF VARIOUS FACTORS ON THE PROCESS OF SYNTHESIS OF ACETYLENE AMINO ALCOHOLS

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Abstract

This paper considers the influence of various factors on the yield of the main product in the synthesis of acetylenic amino alcohols. The influence of such factors as the structure and nature of acetylenic amino alcohols, the composition and nature of amino compounds, temperature, catalyst, and reaction time on the yield of acetylenic amino alcohols has been studied.

Keywords: secondary acetylenic alcohol, tertiary acetylenic alcohol, acetylenamino alcohol, Mannix reaction, 2-methylbutyn-3-ol-2, hexin-1-ol-3, formaldehyde, monoethanolamine, diethanolamine, phenylamine, benzylamine.

Introduction

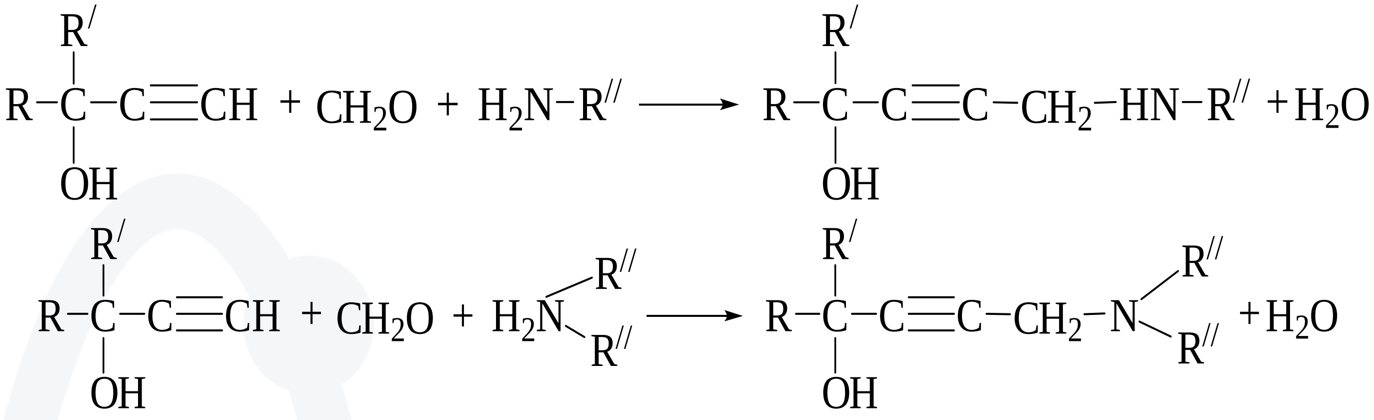
Currently, polyfunctional acetylene derivatives are widely used as biologically active substances in the chemical and oil and gas industries, medicine and pharmaceuticals, and agriculture. The synthesis of acetylenic alcohols, diols, amino alcohols, acetylenic acids and hydroxy acids based on acetylene, their widespread use as medicines in medicine and chemical reagents in agriculture and other fields is one of the most urgent problems.

A number of scientific studies have been carried out on the synthesis of acetylene amino alcohols based on acetylene compounds. However, studies on the production of such substances based on acetylene compounds and aromatic amines, mono- and diethanolamines have been little studied [1-5]. In this regard, in this work, we studied the possibility of synthesizing some acetylenic amino alcohols, which are not listed in the literature, based on secondary and tertiary acetylenic alcohols and the above amino compounds.

Discussion of Results

As indicated in the literature, to obtain acetylenic amino alcohols from acetylenic alcohols, aminomethylation of acetylenic alcohol is carried out with primary or secondary amines with the participation of paraformaldehyde.

In this work, the synthesis of the corresponding amino alcohols was carried out according to the following scheme by aminomethylation of acetylenic alcohols. The reactions of aminomethylation of secondary and tertiary acetylenic alcohols with amino compounds of various nature in the presence of formaldehyde were carried out. Phenylamine, benzylamine, monoethanolamine, diethanolamines were used as amines [6–8].



$$R-\underset{OH}{\overset{R'}{C}}-C\equiv CH + CH_2O + H_2N-R'' \longrightarrow R-\underset{OH}{\overset{R'}{C}}-C\equiv C-CH_2-HN-R'' + H_2O$$

$$R-\underset{OH}{\overset{R'}{C}}-C\equiv CH + CH_2O + H_2N\begin{smallmatrix}R''\\R''\end{smallmatrix} \longrightarrow R-\underset{OH}{\overset{R'}{C}}-C\equiv C-CH_2-N\begin{smallmatrix}R''\\R''\end{smallmatrix} + H_2O$$

$$R = -CH_3\,,\ -C_2H_5\,,\ -C_3H_7\,;\ \ R' = -H\,,\ -CH_3\,;$$
$$R'' = -C_2H_4OH\,,\ -C_6H_5\,,\ -CH_2C_6H_5$$

Initially, the effect of temperature and reaction time on the yield of acetylenic amino alcohols was studied to determine the optimal conditions for aminomethylation of tertiary acetylenic alcohols with amino compounds in the presence of formaldehyde. The synthesis of acetylenic amino alcohols was carried out in a medium of 1,4-dioxane under a copper (I) chloride catalyst, the reaction time was 1-7 hours, at a temperature of 80-100°C. Depending on the nature of the starting components and the catalyst, the product yield ranged from 8.1 to 60.0%.

Table 1 Effect of temperature and reaction time on the synthesis of 5-(2-hydroxyethyl) amino-2-methylpent-3-yn-2-ol in the presence of copper (I) - chloride based on 2-methylbut-3-yn-2-ol

Temperature, °C	Reaction time, h.	Product yield, %	Average reaction rate, %/h
80	1	8,1	8,1
	3	23,0	7,7
	5	31,9	6,4
	7	36,2	5,2
90	1	13,1	13,1
	3	30,0	10,0
	5	40,3	8,6
	7	47,0	6,7
95	1	17,2	17,2
	3	40,0	13,3
	5	56,1	11,2
	7	60,0	8,6
100	1	17,8	17,8
	3	40,5	13,5
	5	56,4	11,3
	7	59,8	8,5

The structural structure of the synthesized 5-(2-hydroxyethylamine)-2-methylpentyn-3-ol-2 was confirmed by IR- and ^{1}N-NMR, ^{13}C-NMR spectra.

Analysis of the IR- spectrum of acetylenamino alcohol - 5-(2-hydroxyethylamino)-2-methylpent-3-yn-2-ol shows that the stretching vibrations of methyl groups in the molecule are in the region of 2935.46 cm^{-1}., bending vibrations are in the region of 1463.21 cm^{-1}, tertiary stretching vibrations of the C–O bond, characteristic of alcohols in the region of 1170.72 cm^{-1}, stretching vibrations of the -OH group in the region of 3287.65 cm^{-1}, bending vibrations were observed in the regions of 1362.47 and 1378.05 cm^{-1}, stretching vibrations of the NH group in the region of 3358.75 cm^{-1} and deformation vibrations in the region of 1595.34^{-1}.

A comparative study of aminomethylation reactions of secondary acetylenic alcohol - hexin-1-ol-3 and tertiary acetylenic alcohol - 2-methylbutyn-3-ol-2 in the presence of ethanolamine and diethanolamines was studied.

For the theoretical interpretation of the synthesis processes performed, the charge distribution in the molecule of the initial substances (2-methylbut-3-yn-2-ol, hex-1-in-3-ol, ethanolamine, diethanolamine) was determined using the program Chem3D Ultra 10.0. The spatial structure of the molecules of the source material and the charge distribution in them are shown in Figures 1-4.

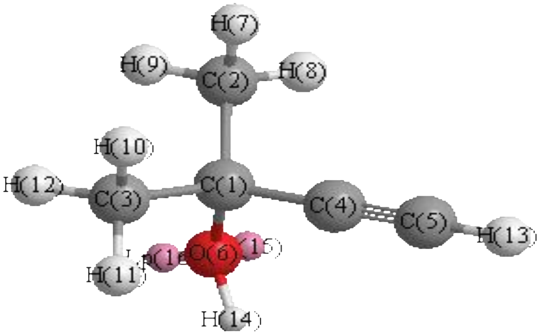


Fig.1. Structure and charge distribution of the 2-methylbutyn-3-ol-2 (A) molecule (ChemOffice, ChemDraw Ultra 10.0).

Here: 0,298 [C(1)]; -0,123 эВ [C(2)]; -0,130[C(3)]; 0,085 [C(4)]; **-0,235 [C(5)];** -0,381 [O(6)]; 0,041 [H(7)]; 0,038 [H(8)]; 0,039 [H(9)]; 0,041 [H(10)]; 0,038 [H(11)]; 0,039 [H(12)]; 0,052 [H(13)]; 0,198 [H(14)].

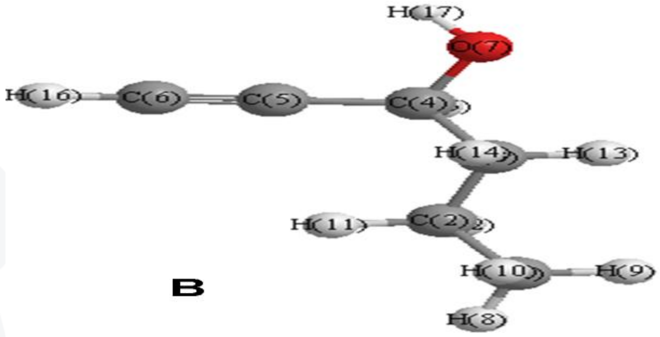
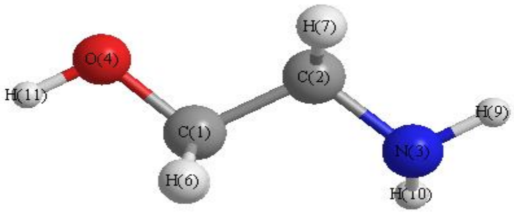


Fig.2. Structure and charge distribution of the hex-1-in-3-ol (B) molecule (ChemOffice, ChemDraw Ultra 10.0).

Here: -0,129 [C(1)]; -0,048 [C(2)]; -0,048[C(3)]; 0,220 [C(4)]; 0,078 [C(5)]; -0,220 [C(6)]; -0,371 [O(7)]; 0,039 [H(8)]; 0,039 [H(9)]; 0,039 [H(10)]; 0,031 [H(11)]; 0,030 [H(12)]; 0,030 [H(13)]; 0,029 [H(14)]; 0,030 [H(15)]; 0,052 [H(16)]; 0,197 [H(17)].



C

Fig.3. Structure and charge distribution of the ethanolamine (C) molecule (ChemOffice, ChemDraw Ultra 10.0).

Here: 0,151 [C(1)]; 0,031 [C(2)]; **-0,283 [N(3)]**; -0,375 [O(4)]; 0,012 [H(5)]; 0,013 [H(6)]; 0,025 [H(7)]; 0,007 [H(8)]; 0,110 [H(9)]; 0,110 [H(10)]; 0,199 [H(11)]; 0,029 [H(14)]; 0,030 [H(15)]; 0,052 [H(16)];

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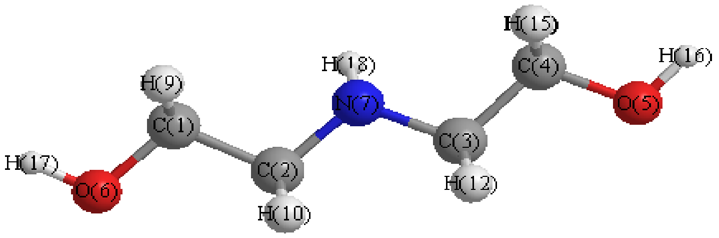


D

Fig. 4. Structure and charge distribution of the diethanolamine (D) molecule (ChemOffice, ChemDraw Ultra 10.0).

Here: 0,151 [C(1)]; 0,022 [C(2)]; 0,022 [C(3)]; 0,151 [C(4)]; -0,375 [O(5)]; -0,375 [O(6)]; **-0,198 [N(7)]**; 0,011 [H(8)]; 0,012 [H(9)]; 0,024 [H(10)]; 0,004 [H(11)]; 0,024 [H(12)]; 0,004 [H(13)]; 0,011 [H(14)]; 0,012 [H(15)]; 0,198 [H(16)]; 0,198 [H(17)]; 0,102 [H(18)].

Theoretical calculations show that the reactivity of monoethanolamine is high because the charge of the nitrogen atom N (3) in monoethanolamine (C) is -0.283 eV, and the charge of the nitrogen atom N (7) in diethanolamine (D) is -0.198 eV. However, since the ethanolamine based amino alcohol molecule contains a second hydrogen atom attached to the nitrogen atom, this amino alcohol again undergoes an aminomethylation reaction. Therefore, the yield of the main product, 5-(2-hydroxyethylamine)-2-methylpent-3-yn-2-ol, is low.

The yields and some physico-chemical constants of synthesized acetylene aminoalcohols are given in Table. 2 and 3.

Table. 2 Some physico-chemical constants of acetylene aminoalcohols

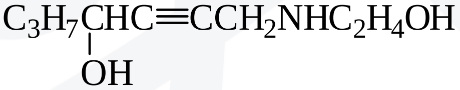
№	Chemical compounds	Yield, %	Temperature of boiling or melting (°C) / mm of merc.	d_4^{20}	n_D^{20}
I	 $(CH_3)_2\underset{OH}{\underset{\vert}{C}}C\equiv CCH_2NHC_2H_4OH$	60,0	142-145/46	0,9630	1,4658
II	 $(CH_3)_2\underset{OH}{\underset{\vert}{C}}C\equiv CCH_2N(C_2H_4OH)_2$	67,1	165-166/46	0,9740	1,4670
III	 $(CH_3)_2\underset{OH}{\underset{\vert}{C}}C\equiv CCH_2N(C_6H_5)_2$	55,8	72 / 760	–	–
IV	 $(CH_3)_2\underset{OH}{\underset{\vert}{C}}C\equiv CCH_2N(CH_2C_6H_5)_2$	63,0	64 /760	–	–
V	 $C_3H_7\underset{OH}{\underset{\vert}{C}}HC\equiv CCH_2NHC_2H_4OH$	54,4	140-141/76	0,9720	1,4783
VI	 $C_3H_7\underset{OH}{\underset{\vert}{C}}HC\equiv CCH_2N(C_2H_4OH)_2$	62,7	158-160/76	0,9910	1,4800

Table. 3 Elementary composition of acetylene aminoalcohols

№ Compounds	Brutto formulas	Elementary composition (%)					
		Calculated			Found		
		C	H	N	C	H	N
I	$C_8H_{15}NO_2$	61,15	9,55	8,92	61,20	9,61	8,78
II	$C_{10}H_{19}NO_3$	59,70	9,45	6,96	59,56	9,42	7,11
III	$C_{18}H_{19}NO$	81,51	7,17	5,28	81,57	7,10	5,35
IV	$C_{20}H_{23}NO$	81,91	7,85	4,78	81,83	7,92	4,81
V	$C_9H_{17}NO_2$	63,15	9,94	8,20	63,25	10,00	8,05
VI	$C_{11}H_{21}NO_3$	61,39	9,76	6,53	61,20	9,85	6,40

According to the results of the table, the yield of amino alcohols based on tertiary acetylene alcohols was higher than the yield of amino alcohols based on secondary acetylene alcohols. Also, the yield of amino alcohols obtained on the basis of secondary amines was higher than the yield of amino alcohols obtained on the basis of primary amines [9, 10, 11].

Conclusions

When studying the synthesis processes of acetylene amino alcohols, it was found that the yield of acetylene amino alcohols theoretically and practically depends largely on the nature and structure of acetylene alcohols and amino compounds [9-13].

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