

The Selective N-Alkylation of Monoethanolamine in PTC Condition

Abstract

In this paper the special attention is given to selective alkylation of very widespread organic molecule - ethanolamine. The direct mono-N alkylation of monoethanolamine (MEA) with alkyl bromide as electrophilic reagent was performed in PTC system. It was presented the mechanism of process, which includes the formation of corresponding complexes ethanolamine with ammonium ions.

Keywords: Monoethanolamine; Alkylation; Regioselectivity; Allylbromide; Alkylbromide; PTC; TBAB; Allylethanolamine; Alkylethanolamine

Mini-Review

Volume 2 Issue 1 - 2018

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Received: October 26, 2017 | Published: January 31, 2018

Introduction

Low molecular weight biogenic amine monoethanolamine (colamine, MEA) has of great practical interest. MEA is a component of certain phosphatides. MEA belongs to the number of compounds that stimulate growth and the general level of metabolism of plants and animals [1].

Alkyl derivatives of MEA are used in the production of surfactants, dyes, in the manufacture of drugs as a buffer substance and for the stabilization of emulsions, in the manufacture of herbicides, cosmetics, antihistamines, are also of practical interest [1]. It is widely known also as useful "acid" gases (H_2S , CO_2 , SO_2 , etc.) as absorbents in the process of cleaning process for gases in oil refineries, chemical industries [1]. Here are presented the examples of selective N-alkylation of MEA.

Results and Discussion

It was previously established that the alkylation of MEA with alkyl halides leads to the formation of mono- N and di-N, N alkylation products, the yield of which depends on the ratio of monoethanolamine and alkyl halide [2].

N, N-dialkylation of MEA by alkylhalides was carried out in the presence of solid potassium hydroxide also. With a 2-fold excess of the alkyl halide, N, N-dialkylated aminoethanol is formed with a yield of 60-65%. The same authors have shown that in the water-snap environment, the derivative of piperazine is formed when MEA is reacted with dibromoethane [3].

In the known literature, the alkylation of aminoethanol has been studied for obtain the corresponding alkyl analogs for technical purposes [1]. We have proposed a systematic study of the selective alkylation of this important compound, in order to obtain products exclusively of nitrogen and oxygen-alkylation. In this paper has been shown, a possibility for easily and economically selectively synthesize an N- mono alkylated product. It had been known an effective and reactant efficient method to perform the challenging direct mono-N-alkylation of primary and secondary amines with small alkyl groups (C1-C3) by virtue of flow micro reactor features [4].

Previously was studied the regioselective alkylation of ambident nucleophile phenol anion. Is has been established, that phenol alkylation by allyl bromide in PTC "liquid - liquid" system results at the formation of a number products with predominance of allyl phenyl ether. The exclusive formation last almost from 90% by the yield takes place in a system "solid phase-liquid" with usage of powdered, dehydrated potassium hydroxide [5,6].

The selectivity of mono-N-alkylation of ethanolamine depends both on a stochiometry of reactants and from a type used alkyl halide [1]. The exclusive formation of a product N-allyl-ethanolamine- 66 % is reached in PTC "liquid-liquid" system (catalyst tetrabutylammonium bromide-TBAB) at a ratio of reactants: ethanolamine: allyl bromide- 5:1 at 60°C for 3 hours. The exclusive formation of mono-allylated products takes place at a ratio of reactants 1:1 in presence TBAB at 85-90°C for 3 hours with an output about 70% - with alkyl halides as amyl bromide, nonyl bromide and decyl bromide. The offered method for selective N-alkylation of MEA in PTC system (entries 5-8) in comparison with the traditional methods has advantages for high selectivity of process.

The occurrence of several competitive products of alkylation of MEA type of organic molecules (several center for electrophilic interaction in MEA- till quaternization of nitrogen & oxygen alkylation) is a phenomenon frequently met in organic synthesis. Direct mono-N-alkylation with alkylhalides often fails due to competitive consecutive over alkylation processes, even if a single equivalent of electrophile is used (entries 1-4). With bulky and less active electrophiles (entries 8-9) monoalkylation had a placed with high yield, but with light and higher electrophilic allyl group remains extremely difficulties (Table 1, Figure 1).

It's generally known that alkylation of amines takes place as a result of the electrophilic attack of an alkyl electrophile on the nitrogen atom [2]. It's known also that, according to the more common PTC mechanism, alkylation takes place at the interface between the phases - organic and aqueous [5]. The resulting amine complex with Quat (Δ) promotes an increase in the acidity

of the hydrogen atoms in nitrogen, thereby facilitating the rapid cleavage of the proton and the formation of N-monoalkylamine derivative (C). The reaction of the alkyl halide takes place with

formation of nitrogen anion (B) of the aminoethanol whose nucleophilicity is higher than that of hydroxyl group,

Table 1: N-alkylation of MEA in PTC system (TBAB 10mol%, T°C 60-65, 3 h).

| E | R | Ratio, % MEA: RBr | PTC System | Ratio (%) | |
|----|--------|----------------------|----------------------|---------------------------------------|---|
| | | | | HOCH ₂ CH ₂ NHR | HOCH ₂ CH ₂ NR ₂ |
| 1 | Allyl | 1:01 | liq/liq ^a | - | 29,6 |
| 2 | “- | “- | liq/liq | - | 29,8 ^b |
| 3 | “- | “- | solid/liq | - | 36,2 |
| 4 | “- | “- | liq/liq ^c | - | 30,0 |
| 5 | “- | 5:1 | liq/liq ^a | 40,9 | 8,3 |
| 6 | “- | “- | liq/liq | 66,0 | - |
| 7 | Amyld | 1:01 | liq/liq ^a | 7,3 | - |
| 8 | Amyld | “- | liq/liq | 70,2 | - |
| 9 | Nonyld | “- | liq/liq | 70,0 | - |
| 10 | Decyld | “- | liq/liq | 68,2 | - |

- Without catalyst,
- Also N,N,O-MEA - 4,4%
- With Catamin AB
- ToC 85-90, 3 h

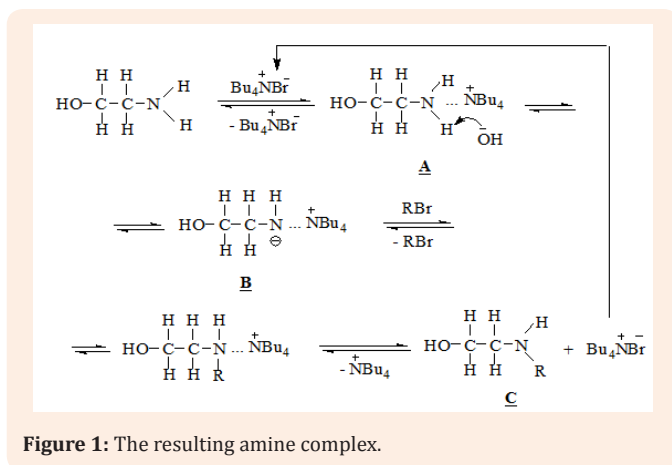


Figure 1: The resulting amine complex.

The formation of a di-N, N-alkylated product in the case of alkyl electrophiles does not take place because of the sterical difficulties in nitrogen. In the case of the allyl group, the formation of the N,N-diallyl product is suppressed by a large amount of monoethanolamine in the reaction medium. This is of all, there are devoted to technological problems of the synthesis of mentioned important organic compounds in PTC system.

Experimental Part

Reaction products were analyzed by chromatograph. For gaze-liquid chromatography (GLCh) method here are used with

the heat conductivity detector; columns from stainless steel in the size 2m x 3mm; the additional-7%, silicon elastomer E-301 on chemosorbe AW-HMDS (0,26-0,36 mm), 15 % Carbox 20M on Chromatone N-AW-HMDS (0,126-0,160 mm) and 5 % E-30 on chromatone DMCS (0,400-0,630 mm); gas-carrier-helium (speed of 30-60 ml/mines) temperature of columns 40-240°. The products are identified using TLC method as well. Silufol UV-254 plates are used. The eluente for TLC was C₆H₆: EtOH (2:1 volume ratio) mixture. The spots are developed by iodine vapors. The isolated products are identified by IRS (specord IR-75) and NMR (Varian "mercury-300" RS) methods. The chemical shifts are expressed by ppm with respect to Si(CH₃)₄, solvent was CDCl₃.

The General Procedure for N-allylethanolamine Synthesis

The mixture of reactants

Ethanolamine: Allyl bromide: aqueous solution of 40% KOH 5:1:1 and TBAB 10mol%, T°C 60-65, 3 h) introduced to a reaction flask with biunique bulb supplied by a reflux condenser, dropping funnel, intensively hashed drop wise adding allyl bromide. During an adding of allyl bromide the temperature of reaction mixture has mounted up to 60°C. This temperature supported during 3h. Then a reaction mixture chilled till 10-15°C and triply abstracted by a diethyl ether (or chloroform). The obtained extract is dried above MgSO₄. The yield of alkylation products is updated outgoing from the data GLCh, with the method of internal normalization, in matching with known samples.

N-allylethanolamine: b.p. 96-98°C/25mm, n_{20}^D 1, 4637, d_4^{20} 0,8964, IR spectrum: 980, 1630, 3020 (CH=CH₂), 3200-3400 (OH, NH), NMR: 2,65 (2H, NCH₂CH₂); 3,62m (2H, CH₂CH₂OH); 3,18m (2H, CH₂CH=CH₂); 3,50c (1H, OH); 4,95-6,25m (3H, CH=CH₂). The analysis - is founded %: C 59, 29; H 10, 75; N 13, 97. C₅H₁₁NO. Is computed of %: C 59, 41; H 10, 89. N 13, 86.

N,N-diallylethanolamine: b.p. 76-78°C/10mm, n_{20}^D 1,4653, d_4^{20} 0,9030, IR spectrum: 920, 990, 1635, 3020, 3085 (CH=CH₂), 3400-3500 (OH, NH), NMR: 2,52 (2H, NCH₂CH₂); 3,53m (2H, CH₂CH₂OH); 3,68m (4H, CH₂CH=CH₂); 3,87c (1H, OH); 4,94-5,37 (4H, 2CH=CH₂) 5,57-6,23m (2H, CH=CH₂). The analysis - is founded %: C 67,98; H 10,72; N 9,87. C₈H₁₅NO. Is computed of %: C 68, 09; H 10,64. N 9,93.

N-almylethanolamine: b.p. 140-142°C/10mm, n_{20}^D 1, 4465, d_4^{20} 0, 8531; 0,95m (3H, CH₃), 1,35m (6H, 3(CH₂)), 2,56m (4H, 2NCH₂); 3,40c ((2H, CH₂O)); The analysis - is founded %: C 64,21; H 12,89; N 10,76. C₇H₁₇NO. Is computed of %: C 64, 12; H 12,98; N 10,69.

N-nonylethanolamine: b.p. 200-203°C/5mm, n_{20}^D 1,4599, d_4^{20} 0,8687; 0,92m (3H, CH₃), 1,25m (14H, 7(CH₂)), 2,41m (4H, 2NCH₂); 3,33m (2H, CH₂O);

N-decylethanolamine: b.p. 223-225°C/5mm, n_{20}^D 1, 4578, d_4^{20} 0, 8706; 0, 95m (3H, CH₃), 1,25m (16H, 8(CH₂)), 2,43m (4H, 2NCH₂); 3,35m (2H, CH₂O).

Conclusion

The regioselective N-mono alkylation of ethanolamine takes

place in conditions of a phase transfer catalysis that depends on a stoichiometry of reagents and from a type electopfile.

Acknowledgement

None.

Conflict of Interest

There is no conflict of interest.

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