APPLICATION OF SUPER-BASIC MEDIA IN ACETYLENE CHEMISTRY

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Abstract: *The role of the highly basic KOH-DMSO system in the vinylation of amines is shown. The catalytic vinylation of anabazine with acetylene at atmospheric pressure has been studied. It has been found that anabazine vinyl derivatives are synthesized by analogy.*

Key Words: *Acetylene, amines, anabazine, vinylation, superbasic environment, catalyst, solvent.*

Vinylation is the process of joining acetylene to compounds containing a reactive hydrogen atom: carboxylic acids, alcohols, RSH-type compounds, amines and amides with a hydrogen atom at nitrogen, etc., and in this process compounds with a double bond are formed, i.e., substances containing a vinyl group [1]. Vinyl compounds are synthesized by various methods are widely used in many industries. Among them, vinylation of the corresponding compounds by action on them with acetylene is the most relevant in terms of industrial importance. The vinylation reaction in a general form can be represented by the following scheme:

$$\mathrm{CH \equiv CH + RXH \rightarrow R - X - CH = CH_2}$$

where: x-oxygen, sulfur or nitrogen

Introduction of a vinyl group into the molecules of nitrogen-containing compounds is achieved by indirect and direct methods [2-3]. The direct method is used in the interaction of nitrogen-containing compounds with acetylene.

In recent years, interest in media with ultrahigh basicity and their use in organic synthesis has increased significantly [4].

A superbase is a complex base formed from strong ionic and Lewis bases, capable of complex binding of an alkali metal ion or an onium cation in a medium weakly solvating anions tertiary potassium butylate-dimethyl sulfoxide, butyllithium-tertiary potassium butylate-tetrahydrofuran, KOH-dimethyl sulfoxide, amides of alkali metals in liquid ammonia and the like). The essence of the phenomenon of superbinding consists in the combination of two or more bases, in the increase in the activity of the anion of the base due to the transformation of the cation into a bulk complex cation with delocalized charge.

Ligands - complex formers for cations - ion pair separators are usually other typical bases, including electron-donating dipolar aprotonic solvents sulfoxides, sulfones, amides, phosphine oxides, amines, ammonia, polyesters and polysulfides especially macrocyclic ones), as well as open and cyclic oligomers containing combinations of heteroatoms with unshared electron pairs and multiple bonds.

The most universal of superbase media and at the same time one of the most accessible, stable, and convenient to use is the KOH-DMSO system. To date, a great number of examples of nucleophilic addition reactions to acetylene in the KOH-DMSO system and its analogs have been accumulated [5,6].

The use of superbasic alkali-dipolar aprotonic solvents in acetylene chemistry has made it possible over the past 15 years to optimize the conditions for the preparation of previously inaccessible vinyl and divinyl chalcogenides, their substituted nitrogen-containing heterocycles, and N-vinyl derivatives. Nevertheless, insufficient study of even the most frequently used alkali-DMSO system does not allow us to explain exhaustively the difference in the catalytic activity of alkali and the influence of various factors in vinylation reactions.

Strongly basic super-basic) media are defined as media capable of ionizing weak acids to a greater extent than 0.1 M alkali solution in water. Such are, for example, solutions of dimsils, alkoxides and hydroxides of alkali metals in DMSO.

Several pathways of acetylene activation are known to be realized in super-basic media:

1. Formation of various complexes of acetylene with base

$$HC \equiv CH + KOH \leftrightarrow \begin{bmatrix} K \\ HC = CH \end{bmatrix}^{+} OH^{1}$$

$$[HC \equiv C - H \cdots {}^{-}OH]K^{+}$$

and with the ligand:

$$HC \equiv C - H + {}^{-}O \leftarrow {}^{+}SMe_2 \leftrightarrow HC \equiv C - H \cdots {}^{-}O \leftarrow SMe_2$$

$$\begin{array}{cc} HC \equiv CH & HC \equiv C - H \\ \downarrow & \downarrow \\ Me_2S^{+} \rightarrow O^{-} & Me_2S^{+} \rightarrow O^{-} \end{array}$$

2. Introduction of acetylene into the inner solvate sphere of the cation:

$$Me_2S^{+} \rightarrow O^{-} \rightarrow O^{-} \cdots K^{+} \cdots \begin{array}{c} CH \\ ||| \\ CH \end{array}$$

3. Formation of acetylenides and their ionization:

$$nKOH + HC \equiv CH \xrightarrow{Me_2SO} KC \equiv CH + H_2O(n-1)KOH\ Me_2SO$$

$$KC \equiv CH \leftrightarrow K^{+} + {}^{-}C \equiv CH$$

Complexes of acetylene with alkali metal hydroxides have been isolated and studied. H-bonds of acetylenes with various electron-donor molecules are widely known [7]

Aromatic amines such as aniline, ethylaniline, toluidine, etc. under pressure also react with acetylene in the presence of alkaline catalysts to form mainly resinous substances.

On the other hand, vinylation of some aromatic secondary amines that are weak bases, such as diphenylamine or phenyl-α - and phenyl-β -naphthylamine, leads to the corresponding N-vinylated compounds, which can be isolated under the action of air oxygen despite their easy polymerizability.

Vinylamines having greater stability are obtained by vinylation of cyclic amino compounds containing pyrrole cycle, as in pyrrole itself, indole, carbazole and some other heterocyclic compounds; imidazoles and others. Vinylation of amines is conveniently carried out by periodic acetylation under pressure and with the subsequent application of alkali, zinc oxides, cadmium oxides and their salts with organic acids and their mixtures as a catalyst [8].

The reaction of vinylation of anabasin in the presence of alkali and KOH) using the superoxy systems KOH-DMSO, KOH-DMFA, in solutions of dioxane, benzene, and, for comparison, in the absence of solvent was studied.

The general scheme of the reaction and can be visualized:

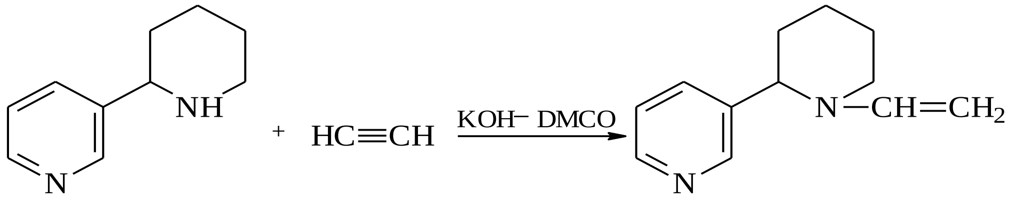

Table 1 summarizes the experimental results obtained during the vinylation reaction both in the presence and absence of different and solvents.

From the obtained enn x data x it is evident that in the absence of solvent and in solutions of benzene and DMFA in the presence of catalyst KOH) N-vinylanabazine is not formed, in solutions of dioxane in the presence of catalyst 10 % ile product is formed with the rate of 5.4 %.

№ n/a	Nature of nt	Quantity of catalyst - KOH, % (from mass of anabasin)	In product flow,
1	-	10	-
2	DMFA	-	-
3	Benzene	10	-
4	Dioxane	10	5,4
5	Dioxane	15	6,3
6	DMSO	10	18,4

7	DMSO	15	18,2
8	DMSO	20	15,1

Increase of catalyst content up to 15 % increases the yield of the formed product. In this case, in DMSO solution, when the catalyst quantity is 10% of wt. of anabasin in the yield of the product is 18.4 %. Increase of the catalyst amount more than 15 % of the mass of the applied amine under similar n conditions leads to insignificant decrease in the course of N-vinylanabasin [9].

Table a 1

Influence of natural solvent and amount of catalyst on the reaction of vinylation of anabazine

reaction duration – 4hour, temperature - 70^{o} C)

The study of influence of the nature of the solvents used showed that DMSO is the most active m in vinylation of anabasin.

The influence of temperature and process time on the reaction of vinylation of anabazine in the presence of KOH-DMSO systems was investigated with the aim of increasing the progress of N-vinylanabasin. The obtained results are given in Table 2.

Table a 2

Influence of temperatures and reaction times iy to vinylate anabasin

(catalyst - KOH - 10%, solvent - DMSO)

№ n/a	Temperature,^{o} C	Duration of the reaction ia, ase	In product flow, %
1	55	4	-
2	70	4	18,4
3	100	4	19,0
4	130	4	21,2
5	150	4	14,3
6	130	2	5,6
7	130	3	13,4
8	130	6	20,0
9	130	8	16,2

From the table it follows, that the increase of temperature in the range 55-130^{o} C at the duration of reaction and 4 asa promotes the formation of the product and at the temperature of 130^{o} C its course reaches a maximum of 21,2 %.

The structure of N-vinylanabasin was proved by^{1} H-NMR and IR spectroscopic methods, and istate was established by TLC and GC.

In the IR spectrum of N-vinylanabasin characteristic bands are observed: in the region of 1500-1510 cm^{-1} valence vibrations of C=C vinyl group and pyridine nucleus. The 3100 cm^{-1} band refers to the valence vibrations of the aromatic CH group of the pyridine core. It was found that 810 cm^{-1} are non-planar strain vibrations of three adjacent aromatic CH groups of the pyridine core (C , C , C$_{456}$), and 880 cm^{-1} are strain vibrations of aromatic CH groups (C).$_{2}$

In^1 H-NMR spectrum of N-vinylanabasin, the following signals are observed in the region of aromatic protons: a singlet in the region of 8.7 m.d. H_2 , the doublet in the region of m8.3 .d. belongs to the proton H_6 , the doublet in the region of 8.0 m.d. - to proton H_4 , the multiplet in the 7.0-7.5 m.d. region relates to proton H_5 , a doublet-doublet signal in the 5.0-5.8 m.d. region is observed that relates to the vinyl group protons. The signal in the region of 3.0-3.2 m.d. refers to the proton of the CH group, the signal in the region of 3.0 m.d. to the protons of CH_2 - relative toα -position of nitrogen, the remaining protons of the piperidine core form a complex signal in the region of 1-2.5 m.d.

OUTCOMES

The role of the highly basic KOH-DMSO system in the vinylation of amines is shown. Catalytic vinylation of anabazine with methylene at atmospheric pressure was studied. It was found that vinyl derivatives of anabazine are synthesized in the same way. e of anabazine.

The influence of temperature, catalyst amount, reaction duration, and natural solvents on vinylation of anabasin was studied. It was found that in all studied systems the optimal solvent is DMSO. The conditions of their vinylation were optimized.

A methodology for homogeneous-catalytic vinylation of anabasine with acetylene at atmospheric pressure in the presence of a highly basic KOH-DMSO system has been developed.

The structure of vinylanabasin was proved by 1H-NMR and IR spectroscopy, the composition by elemental analysis, and the purity by TLC and GC methods.

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