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STUDY OF THE DEVELOPMENT OF METHODS FOR THE SYNTHESIS OF PYRROLE AND ITS DERIVATIVES UNDER NORMAL CONDITIONS ON THE BASIS OF COMMERCIALY AVAILABLE RAW MATERIALS

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Abstract: The aim of this study is to develop methods for the synthesis of a series of pyrrole and its derivatives under normal conditions based on commercially available raw materials in the presence of homogeneous and heterogeneous catalysts. The current level of development of progressive technologies contributes to intensive research in the field of chemistry of heterocyclic compounds, in particular pyrrole and its derivatives.

Keyword: pyrrole, synthesis, chemistry, natural resources, heterocycles, chlorophyll, molecule.

Introduction. With the development of pyrrole chemistry, the issues of obtaining new compounds of the pyrrole series from natural sources and production wastes are becoming increasingly important.

The rational use of local raw materials and natural resources, the development of a waste-free, resource-saving and environmentally friendly technology for the production of practically important products based on local raw materials and industrial waste is one of the urgent tasks of modern chemical technology.

Nitrogen-containing heterocycles, mainly pyrrole and its derivatives, are of great value as a raw material for the production of a number of practically important drugs and the pyrrole core, as the dominant subunit, provides the entire play of colors in both the animal and plant world.

The pyrrole ring is part of the molecules of many natural and biologically active compounds. Derivatives of pyrrole include a number of important plant alkaloids, such as nicotine, atropine, cocaine, etc. The pyrrole ring is contained in

the molecules of the blood dye - hemoglobin and green plant matter - chlorophyll, vitamin B12, bile pigment, a number of antibiotics and others.

In this regard, it is of practical interest to develop effective synthetic methods for producing pyrrole and its homologues based on commercially available compounds, in particular from industrial waste of monoethanolamine and diethanolamine, using homogeneous and polyfunctional low-temperature heterogeneous catalysts based on local raw materials.

Methods. Pyrrole derivatives attract the attention of many researchers due to the diversity and uniqueness of their properties [1].

The pyrrole structure is the basis of such vital compounds as chlorophyll and hemoglobin, which play an important role in basic metabolic processes. Polymeric compounds of the pyrrole series, which have found application in various industries, are of considerable interest.

Many works are devoted to various

aspects of preparative, theoretical and applied chemistry of pyrrole and its derivatives [2-4].

The revival and growth of interest in the chemistry of pyrrole is currently directly related to the production of new compounds of the pyrrole series from natural sources, with a relatively simple structure. In works [5,6] questions of structure, reactivity and synthesis of pyrroles, as well as the possibility of polymerization of the pyrrole nucleus [7,8] are studied.

The discovery of the reaction of ketoximes with acetylene, leading to various types of NH- and N-vinylpyrroles, presented unlimited possibilities in terms of the synthesis and detailed study of polymers of this class [9].

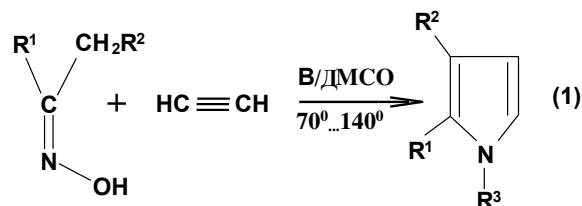
Numerous methods for the synthesis of pyrroles can be roughly divided into three main groups:

1. Synthesis of pyrrole by cyclization of functional aliphatic compounds.
2. Synthesis of pyrrole from amino ketones and ketones.
3. Synthesis of pyrrole from acetylene, ammonia and amines.

The discovery of the reaction of ketoximes with acetylene as a general method for the synthesis of pyrroles has markedly increased interest in the chemistry of pyrrole. This is facilitated by the isolation from natural objects of a large number of relatively simple pyrrole compounds [10,11] - antibiotics, pheromones, toxins. A number of simple pyrroles, such as 2-acetylpyrrole, are found in the volatiles of black tea, Japanese hops, tobacco leaves, valerian, roasted cocoa and coffee.

In 1970 B.A. Trofimov and his co-workers proposed a fundamentally new method for constructing a pyrrole ring-heterocyclization of ketoximes with

acetylene in the system alkali metal hydroxide-dimethyl sulfoxide [12-15]



Where: M- alkali metal; $\text{R}^1, \text{R}^2 =$ alkyl, alkenyl, aryl, aralkyl, hetaryl;

$\text{R}^1, \text{R}^2 = (\text{CH}_2)_n, n = 3+5; \text{R}^3 = \text{H}, \text{CH}_2 = \text{CH}-$.

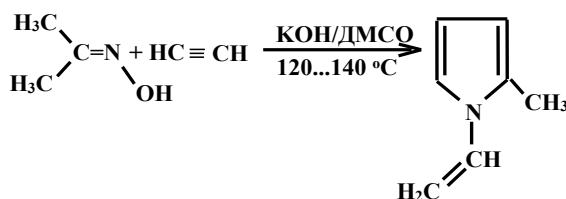
This reaction (Scheme 1) makes it possible to obtain a wide variety of 2-, 2,3-, 2,5- and 2,3,5-alkyl (aryl) pyrroles and their N-vinyl derivatives. The yields strongly depend on the structure of the starting reagents, but in the case of simple ketoximes and unsubstituted acetylene, they are quite stable and under optimal conditions are 70-95% [14,16,17].

Results. The widespread use of pyrrole and its derivatives is delayed due to the lack of cheap and convenient methods for their synthesis. The known production methods, in general, are multi-stage, and the starting compounds are expensive and difficult to obtain.

In this regard, the development of convenient one-stage methods for the synthesis of compounds of the pyrrole series and their derivatives is a very urgent problem.

We have studied the reaction of interaction of acetylene with oximes of symmetric and asymmetric ketones. A method for obtaining pyrroles and their N-vinyl derivatives from acetoxim and acetylene in the liquid phase has been

developed [18].



The reaction was carried out in a flask with a stirrer with a continuous supply of acetylene at atmospheric pressure under the following conditions (temperature 120-140°C, process duration in the range of 2-14 hours, KOH concentration 10-100% relative to the reaction mixture and at the same time took different ratios of ketone oximes with DMSO

Discussions. Currently, there is no unified theory for the selection of catalysts. Although the authors [19] put forward a hypothesis about the selection of catalysts, changes in the nature of their active sites, and also proposed a developed method for studying catalysts with predetermined properties, etc., a large number of catalytic reactions requires a rational selection of catalysts to achieve the desired result.

The developed catalysts should have high catalytic activity, selectivity, mechanical strength, heat resistance, resistance to the action of catalytic poisons, long operating time, easy regenerability, certain hydrodynamic characteristics and low cost [20].

Known catalysts used in industry are selected mainly empirically, which are based on the concept of the mechanism of catalysis for certain types of reactions [21-23].

The most important characteristic of catalysts is their activity, which depends on the following factors:

a) temperatures (or temperature range). For each catalyst, there is an optimal temperature regime at which its maximum

activity is achieved. At lower temperatures, the activity of the catalyst will be low, and at higher temperatures, the occurrence of side reactions is enhanced and the catalyst is deactivated. The more active the catalyst, the lower its optimal temperature regime;

b) pressure, which determines the concentration of the reactants in the reaction volume (with liquid-phase catalysis) or on the catalyst surface (with heterogeneous catalysis);

c) the size of the catalyst particles, which determine the contact surface between the reactants and the catalyst. A decrease in the size of the catalyst particles decreases its diffusion and thermal resistance and, therefore, increases its activity;

d) the content of impurities in the raw material that can cause partial or complete deactivation (poisoning) of the catalyst;

e) a method for preparing a catalyst, its activation, carriers, etc.

The reactions of heterocyclization of amino alcohols and amines is a complex series-parallel process, including the reactions of addition, dehydration, dehydrogenation and dehydrocyclization. Obviously, for such a process, the catalyst must be polyfunctional (have a system of different catalytically active sites) or, with a small choice of components, successfully combine different catalytic properties.

The condensation of amino alcohols and amines with other organic compounds is a complex serial-parallel multistage process, which includes several stages, the main ones of which are:

a) supply of reagents to the catalyst surface;

b) orientation of molecules in the field of the catalyst surface;

c) adsorption, activation of reagents;

d) chemical transformation of activated-adsorbed molecules;

e) desorption and removal of reaction products from the surface into the working volume.

Oxides Cr_2O_3 and ZnO are widely used in the reactions of dehydration, dehydrogenation, and dehydrocyclization. Cadmium compounds catalyze addition and dehydrocyclization processes. Zinc oxide catalyzes the processes of dehydrogenation, dehydration.

Known catalysts (Al_2O_3 , ZnO , CdO , Cr_2O_3) exhibit catalytic activity in dehydrogenation and dehydration reactions [24]. This combination of properties probably explains the fact that almost all hitherto known contacts that are active in the synthesis of nitrogen-containing heterocycles contain the above compounds [25] in various ratios.

The enhancement of the catalytic properties of aluminum oxide during its treatment with acetic acid may be associated with the appearance of stronger aprotic centers such as $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})\text{F}_2$, capable of activating amino alcohols and amines.

Zinc oxide catalyzes the processes of dehydration, dehydrogenation and addition. However, its catalytic activity is manifested only at elevated temperatures, i.e. under conditions of active dehydrogenation of intermediates. To use zinc oxide in the synthesis of pyrrole bases, it is necessary to increase its activity in the addition of ammonia, vinylation of intermediate vinyl amines and other nitrogen-containing compounds, and to decrease its activity in the dehydrogenation reaction.

Thus, based on the foregoing, it can be concluded that for the heterocyclization of amines and amino alcohols, it is necessary to use polyfunctional catalysts containing

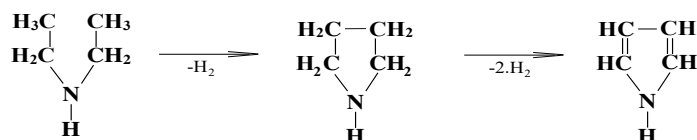
compounds of cadmium, zinc, chromium, and aluminum in various combinations.

Conclusions. We have studied the reaction of conversion of diethylamine (DEA) at $320\text{--}400^\circ\text{C}$ in the presence of zinc-chromium-aluminum catalysts. It was found that as a result of the catalytic transformations of DEA, a complex mixture of nitrogen-containing compounds is formed.

Pyrrolidine, pyrrole, and other heterocyclic compounds were identified from the reaction products by GLC. Gaseous products are composed of ethylene, hydrogen and ammonia.

Detachment of hydrogen from CH or N-H bonds can occur simultaneously, since the energy of CH or N-H bonds has almost the same value (85.56 and 83 kcal/mol, respectively).

Pyrrolidine and pyrrole are formed as a result of DEA dehydrogenation according to the scheme:



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