

Study of the Synthesis of Pyrrole and its Derivatives

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ABSTRACT

It is of practical interest to develop effective synthetic methods for obtaining pyrrole and its homologues based on commercially available compounds.

KEYWORDS: medicine, pyrrole, method, ammonia, aromatic, chloride

Not only poor knowledge, but also the significance, as well as the most diverse possibilities of application in technology, medicine, agriculture, etc. many pyrroles and their derivatives are highly bioactive. Among this class of compounds, promising drugs have been found as the dominant subunit providing the entire play of colors, both in the animal and plant world.

Pyrrole rings are part of the molecules of many natural and biologically active compounds. Pyrrole derivatives include a number of important plant alkaloids, such as nicotine atropine and many others. Pyrrole rings are contained in the molecules of the blood dye, hemoglobin, and the green matter of plants - chlorophyll, vitamin B12, alkali pigment, a number of antibiotics, etc.

The widespread use of pyrrole and its derivatives is delayed due to the lack of cheap and convenient methods for their preparation. The various known methods for the synthesis of the pyrrole ring under normal conditions with a moderate yield of the target product are multistage, the starting

materials are in many cases difficult to obtain. The service life of the catalysts and components used is limited, and there are certain difficulties in separating the resulting complex mixture.

In this regard, it is of practical interest to develop effective synthetic methods for obtaining pyrrole and its homologues based on commercially available compounds, in particular, acetylene and its homologues.

Substituted pyrroles are obtained in good yields from butadiene by reacting with ammonia, primary aliphatic, aromatic, heterocyclic amines in the presence of catalysts, with heating [1], as well as the cyclization reaction of diacetylene with primary amines [2-4].

A compound of this type is of interest, since it is known that pyrrole and its derivatives are used in various areas of the national economy [5-7].

In this work, we studied the process of obtaining pyrrole derivatives (Table1) by cyclization of diacetylene with ammonia in the presence of Cu_2Cl_2 , for 1.5 hours, and as a dioxane solvent.

During the synthesis, the influence of various factors was revealed: catalysts, solvents, reaction time and temperature on the yield of the target product.

Table 1 Physicochemical parameters of pyrrole derivatives

Pyrrole derivatives	Exit, %	Temperature, °C	R_f	Gross formulas	Element analysis, N, %	
					вычисл.	найд.
1- derivative	59,7		0,61	$\text{C}_4\text{H}_5\text{N}$	20,89	20,58
2- derivative	68,3	71-72	0,76	$\text{C}_{16}\text{H}_{13}\text{N}$	6,39	6,11
3- derivative	66,2	89-90	0,69	$\text{C}_{16}\text{H}_4\text{Br}_2\text{N}$	3,71	3,48
4- derivative	70,1	113-114	0,73	$\text{C}_{16}\text{H}_4\text{N}_3\text{O}_4$	13,59	13,28

It has been found that dioxane is the most convenient solvent. The highest yields were obtained when using hemichloride copper as a catalyst. The reaction time is 1-2 hours, at wide temperature ranges - 90-230-2 C.

Thus, as a result of the study, the optimal conditions for the occurrence of the cyclization reaction have been found.

The composition and structure of the synthesized compounds were confirmed by the data of elemental analysis and IR spectroscopy. The IR spectra show absorption bands in the range of 1320-1300 cm^{-1} , 1650-1630 cm^{-1} and 3440-3410 cm^{-1} .

At present, further work is being carried out to identify new properties of the obtained compounds.

Information about the catalytic mechanism of the formation of pyrrole and its derivatives from diacetylene mixed with primary aliphatic amines and ammonia was studied in the works. Only a few authors explain the role and amount of the catalyst used in the cyclization of primary analysis with substituted diacetylene [4-6]. It has been proven that copper catalysts form dative bonds with a triple bond and contribute to the formation of P-complexes. Assuming that the salt is in the form with diarylhexadiene [7-9], it can form a complex compound.

We have identified it individually. The study of the EPR spectrum of the starting compounds, the complex of final products and their comparison with the EPR spectra of typical copper derivatives of tolylacetylene and copper phenylacetylenide showed that the molecules of the copper complex 1- (π -methylphilin) 4 (π -chlorophyll) butadiene -

1,3 are an asymmetric line from copper with a width of $H = 165$ Oe and with a q -factor of spectral splitting ($q_{\text{eff}} = 2.107$). The number of unpaired electrons is $2 \cdot 10^{18}$ spin / g. The calculations were carried out according to the method proposed by Blumenfeld et al. [10].

In all cases, when electron paramagnetic resonance influenced the formation of a π -complex of copper with long, changes were observed in the IR spectra in comparison with the spectra of the initial diarylbutadienes.

In the IR spectra of the copper complex 1- (π -methylphenyl)-4- (π -chlorophenyl)-butadiene-1,3, the absorption band in the region of 2148 cm^{-1} , characteristic of the $\text{-C}\equiv\text{C}$ - bond, disappears and new absorption bands appear in the area of $3100\text{-}3165$ (wide) and $3440\text{-}3468 \text{ cm}^{-1}$.

In addition to analytical methods, the amount of copper in the complex was also determined using the ^{64}Cu -labeled activation method. It is likely that with an increase in the temperature of the reaction medium, the stability of the π -complex decreases, and a favorable transition state is created for the attack of a nucleophile (R-NH_2 , NH_3) along one of the triple bonds.

Subsequently, the catalyst is detached from the diacetylene molecule with the simultaneous nucleophilic addition of the second primary amine molecule to the triple bond with the formation of an unstable diaminodiene compound, which under the influence of temperature and catalyst undergoes cyclodeamination with the formation of pyrrole derivatives.

Consequently, the formation of the pyrrole ring proceeds through the formation of the diarylbutadiene copper complex. The transition to the active state of the diene molecule occurs through the decomposition of the π -complex under the reaction conditions. Separately taken copper complexes of diarylbutadiene (without the addition of primary amine) are almost completely distributed with increasing temperature of the reaction medium. Diarylbutadiene-1, 3 completely goes into organic solvent, and the catalyst precipitates.

Thus, as a result of studying the cycloaddition reaction of primary amines to dialcylenes, the influence of the nature and number of substituents of the phenyl radical of the phenyl group, temperature, solvents, duration of the process, as well as the amount and nature of the copper catalyst on

the cyclization process was established and a probable mechanism of this reaction was proposed.

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