



Synthesis of Pyridines from Acetylene and Ammonia

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ABSTRACT

Highly efficient, stable catalysts and technology for 2- and 4-methylpyridines from acetylene and ammonia have been developed. Polyfunctional catalysts containing oxides and fluorides of zinc, iron, cadmium, aluminum and other metals are used as contacts.

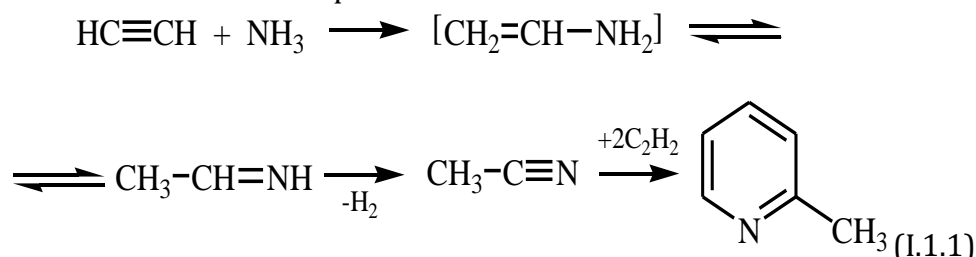
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Pyridine and its derivatives are of great value as raw materials for the production of pharmaceuticals, dyes, pesticides, extractants for the extraction of rare and trace metal ions, ion exchange resins, etc. [1].

Currently, they are used as the main raw material for the synthesis of vinylpyridines, valuable monomers in the production of rubbers with special properties, the production and consumption of which in the world is growing from year to year.

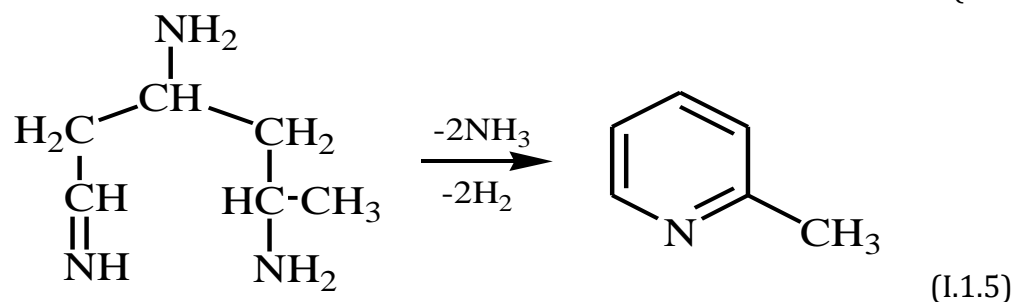
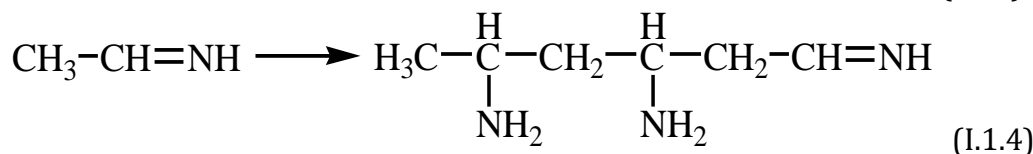
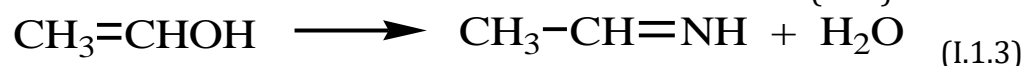
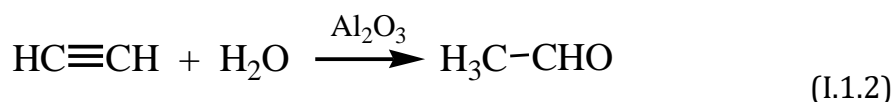
The catalytic heterocyclization of acetylene with ammonia in the presence of



Among the works on the synthesis of pyridine bases from acetylene and ammonia, only a few [1-2] touch on the probable mechanism of the process. According to Chichibabin, the synthesis of pyridine bases from acetylene and ammonia on aluminum oxide proceeds through the intermediate

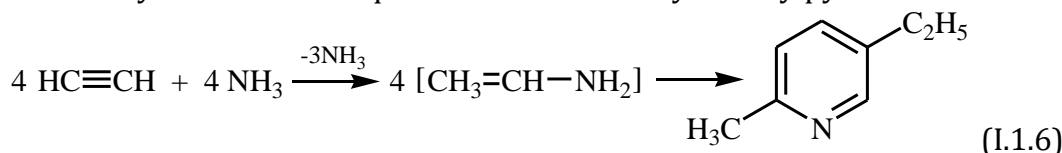
cadmium pyrophosphate [1] supported on alumina was studied. The influence of various factors on the yield of final products was studied and it was shown that at a temperature of 400 °C, the ratio of acetylene:ammonia = 2:1 and a total space velocity of 80 h⁻¹, the yield of 2-methylpyridine reaches 15%, 4-methylpyridine - 10% in terms of acetylene. A mechanism has been proposed for the formation of 2-methylpyridine through an intermediate product, acetonitrile, followed by its condensation with acetylene:

formation of acetaldehyde. The water present in aluminum oxide combines with acetylene to form acetaldehyde, which then forms aldimine with ammonia. Trimerization of the latter by the type of aldol condensation followed by dehydrocyclization leads to 2- and 4-methylpyridines:



It is known that pyridine bases are formed from acetylene and ammonia without a catalyst [1]. This proves that the formation of pyridine bases from acetylene and ammonia does not necessarily follow the sequence of

acetaldehyde. Reppe [2] believes that unstable vinylamine is first obtained from acetylene and ammonia, and then, as a result of its condensation with elimination of ammonia, 2-methyl-5-ethylpyridine is obtained:

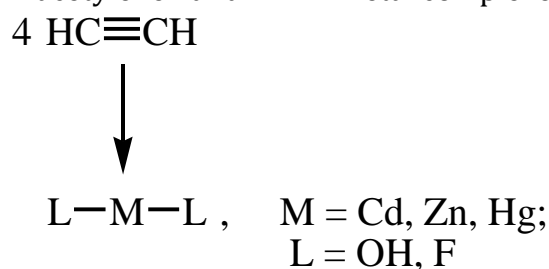


Repe's suggestion was made on the basis of the results of liquid-phase condensation of acetylene with ammonia as the main product, where 2-methyl-5-ethylpyridine is formed.

It is assumed [1-2] that the formation of the structure of nitrogen-containing compounds from acetylene and

ammonia (and also with the participation of methanol) consists of the following stages:

1. Formation of π -complexes and metal amides. When acetylene interacts with catalyst components containing metals of IB, IIB, and VIIB groups of the Periodic Table, π -metal complexes are formed:

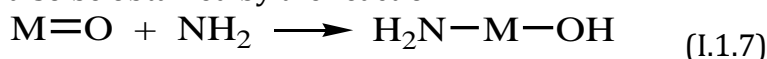


Ammonia and amines are well sorbed on metal-containing centers that exhibit the properties of Lewis acids, including hydroxyfluorides of cadmium, zinc, iron,

aluminum, etc. The presence of hydroxyfluorides in the composition of catalysts facilitates the formation of metal amides:



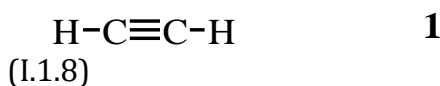
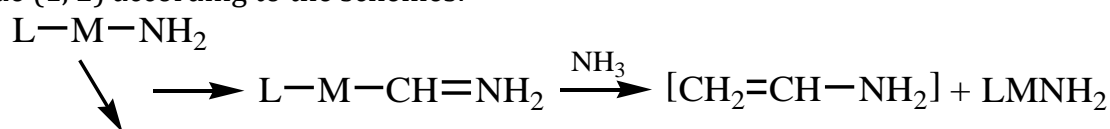
Metal amides can also be obtained by the reaction:



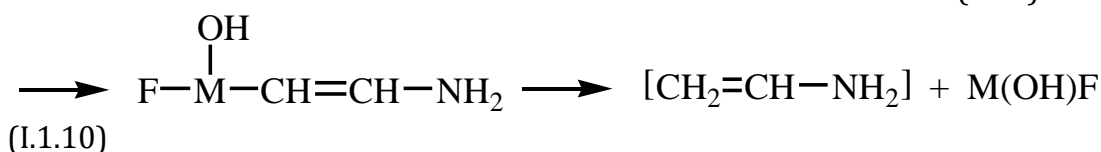
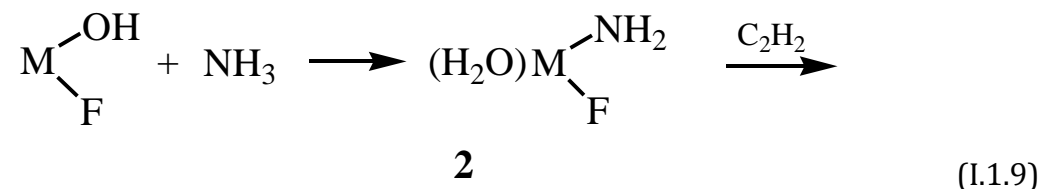
The amide group, apparently, is also formed in the center associated with acetylene.

2. Formation of unstable vinylamine or ethylideneimine. Vinylamine and its

ethylideneimine are formed as a result of the interaction of the π -complex of acetylene with metal amide (1, 2) according to the schemes:

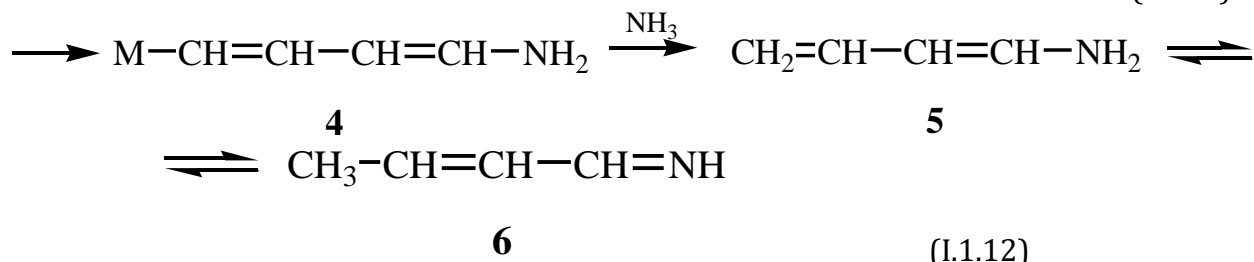
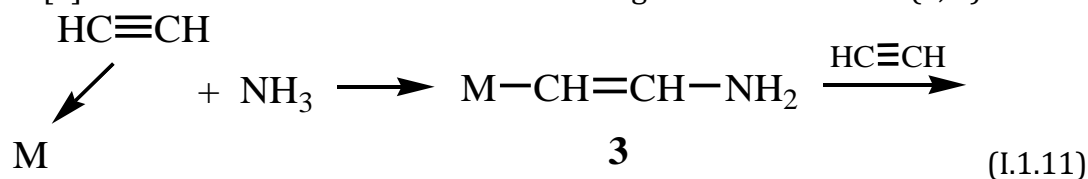


or

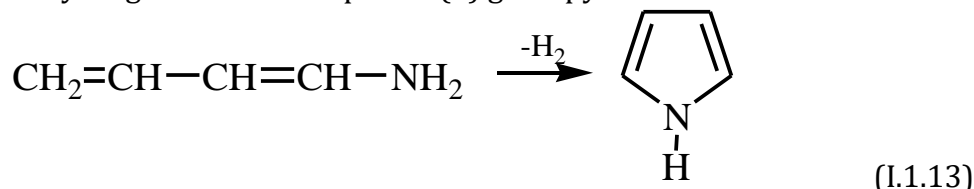


In the presence of strong dehydrogenating catalysts such as zinc, bismuth, and chromium oxides, vinylamine is dehydrogenated via ethylideneimine to acetonitrile. The formation of pyridine bases is not observed [2].

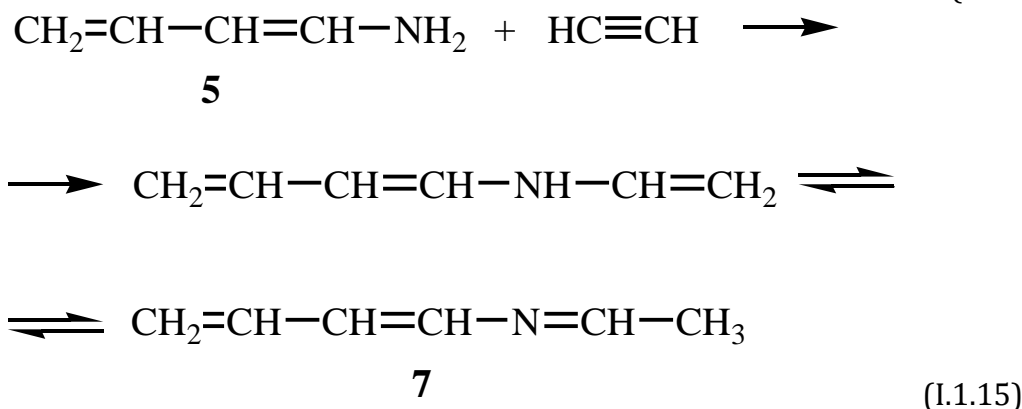
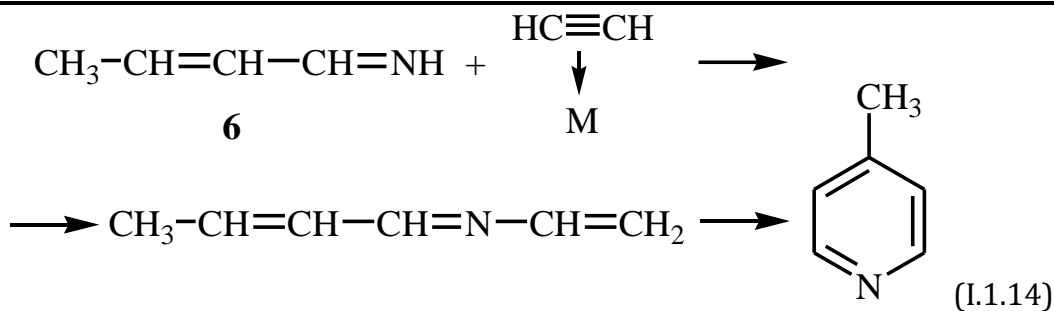
The stage of dehydrocyclization is the formation of heterocycles. The formation of heterocycles can be represented as a result of the formation of linear C_4 -nitrogen-containing molecules (5) through intermediate metal-organic intermediates (3, 4):



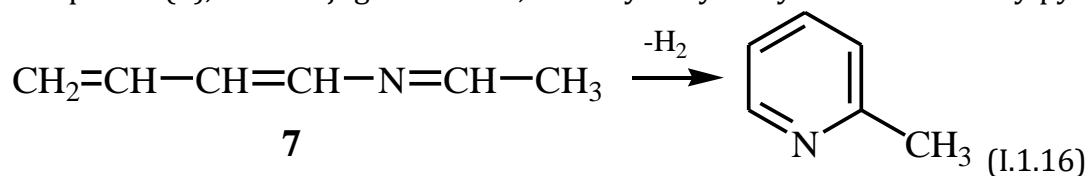
Dehydrogenation of compound (5) gives pyrrole:



2- and 4-Methylpyridines are obtained by vinylation of compounds (5) and (6) according to the reaction:



Compound (7), as a conjugated triene, is easily dehydrocyclized to 2-methylpyridine:



It has been established that the formation of heterocyclic compounds from acetylene and ammonia occurs predominantly in the presence of 3-5% zinc oxide, 3-4% chromium (III) oxide, and 5-12% zinc or cadmium hydroxyfluorides in the composition of the catalysts.

By choosing the composition of catalysts, it is possible to direct the reaction towards the formation of either pyridine and 3-methylpyridine, or 2- and 4-methyl-pyridines.

References:

1. Tangyarikov N.S., Musulmanov N.Kh., Turobzhonov S.M., Ikramov A., Prokofiev V.Yu. Catalytic hydration of acetylene and its derivatives. - Moscow, Lenand, 2014. P. 150.
2. Turobzhonov S.M., Chemistry and technology of pyridines and their derivatives, Moscow, 2019.