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CHEMISTRY

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1957

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Abstract

Full Text

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MECHANISM OF THE CLEAVAGE REACTION OF PYRIDINE BASES

(Presented by Academician I. L. Knunyants on 9 II 1957)

Despite the considerable number of works devoted to cleavage of the pyridine ring, the mechanism of this reaction has not yet been clarified. It is known that the reaction of cleavage of pyridine chlorodinitrophenylate and bromocyanide by primary and secondary aromatic amines proceeds at a very high rate and leads to the formation of salts of dianils of glutaconic aldehyde (I) (1).

$$\mathrm{ArRN{—}CH = CH{—}CH = CH{—}CH = \overset{+}{N}RAr\overset{-}{X}}$$

$$\mathrm{R = H\ or\ Alk;\ \ X = Cl,\ \ Br}$$

In the interaction of pyridine chlorodinitrophenylate with fatty amines (primary and secondary), products are formed from rupture of only one nitrogen–carbon bond in the pyridine ring (II) (2).

$$\mathrm{(NO_2)_2C_6H_3NH{—}CH = CH{—}CH = CH{—}CH = \overset{+}{N}RAlk\overset{-}{Cl}}$$

$$\mathrm{R = H\ or\ Alk}$$

Analogous compounds (III) were isolated by I. L. Knunyants and T. Ya. Kefeli upon the action of 6-amino- and 6-methoxy-8-aminoquinoline on pyridine chlorodinitrophenylate (3).

$$\mathrm{R{—}NH{—}CH = CH{—}CH = CH{—}CH = NC_6H_3(NO_2)_2}$$

III

R : [[quinoline residue structure]] , [[methoxy-substituted quinoline residue structure]]

Ebert found that upon the action on β-picoline and β-ethylpyridine of bromocyanide and aromatic or heterocyclic amines, cyan-imines of substituted glutaconic aldehydes are formed (V; R = α-CH_3, C_2H_5) (4). None of the authors mentioned, however, carried out the conversion of the compounds they obtained into symmetrical derivatives of glutaconic aldehyde with two amine residues.

Thus, it remained unclear whether the cleavage reaction of pyridine proceeds (in particular, in the case where the second reacting component is an aromatic amine) through the stage of an intermediate compound (IV), or whether elimination of the nitrogen atom from the pyridine ring occurs in one step, as the result of the simultaneous interaction of the cation of the pyridinium salt with two molecules of amine.

$$\mathrm{RNH{—}CH = CH{—}CH = CH{—}CH = NAr} \qquad \mathrm{R = C_6H_3(NO_2)_2,\ CN.}$$

IV

In order to investigate the mechanism of opening of the pyridine ring, we carried out the cleavage reaction of various pyridine bases with cyanogen bromide and tetrahydroquinoline (in acetone or ether solution). From the reaction mixture, along with the bromides of ditetrahydroquinolides (VI), it was possible to isolate halogen-free compounds, which proved to be the corresponding cyanimines (V):

$$\text{[pyridinium cyanide bromide]} + \mathrm{C_9H_{10}NH} \longrightarrow \mathrm{C_9H_{10}N{-}CH{=}CH{-}C{=}C{-}CH{=}NCN} + \mathrm{C_9H_{10}N{-}CH{=}CH{-}C{=}C{-}CH{=}NC_9H_{10}Br}$$

$$R = \beta\text{-}OCH_3,\ OC_2H_5,\ OC_6H_5;\ \alpha\text{-}NHCOCH_3,\ CON(C_2H_5)_2$$

In all cases, the cyanimines were obtained predominantly. Such a course of the cleavage reaction of substituted pyridines indicates its generality for various pyridine bases.

The simultaneous formation in the reaction mixture of cyaniminic derivatives and ditetrahydroquinolides gave grounds to suppose that the cyanimines are intermediate compounds in this reaction.

It remained unclear, however, why the final cleavage products were not formed predominantly, but rather the intermediate compounds. To prove that the cyanimines are intermediate products of the opening, we attempted to convert them into symmetrical ditetrahydroquinolides. For this purpose, the cyanimin was treated with the salt of a second molecule of the amine (tetrahydroquinoline hydrobromide). Under these conditions, under mild conditions (in alcoholic solution, with slight heating or at room temperature), it was possible to accomplish the transition from cyanimines to symmetrical ditetrahydroquinolides. This reaction proceeds comparatively slowly according to the equation:

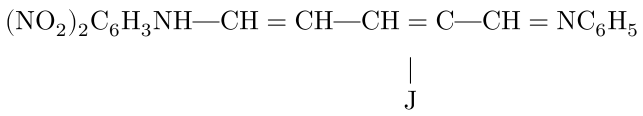
$$\mathrm{C_9H_{10}N{-}CH{=}CH{-}C{=}C{-}CH{=}NCN + C_9H_{10}NH \cdot HBr = NH_2CN +}$$
$$\mathrm{C_9H_{10}N{-}CH{=}CH{-}C{=}C{-}CH{=}NC_9H_{10}Br}$$

$$R = \beta\text{-}OCH_3,\ OC_2H_5,\ OC_6H_5;\ \alpha\text{-}CON(C_2H_5)_2$$

In the cleavage of some pyridine bases, the transition of the cyanimine into the ditetrahydroquinolide is especially clearly noticeable. Thus, for example, when γ-methoxypyridine interacts with cyanogen bromide and tetrahydroquinoline, bright-yellow crystals of the cyanimine crystallize out very rapidly. Then the yellow color of the solution gradually changes to orange, and the crystalline mass assumes a heterogeneous appearance—a mixture of yellow crystals of the cyanimine and orange crystals of the ditetrahydroquinolide.

Thus, the cyaniminic derivatives are indeed intermediate products of the opening of pyridine bases. The predominant formation of cyanimines in the cleavage of substituted pyridines may be explained by the high rate of rupture of the C_α—N bond in the pyridine ring, exceeding the rate of rupture of the C—N bond in the cyanimine molecule. If, in addition, one takes into account the low solubility of the cyaniminic derivatives substituted in the chain in acetone or ether, it becomes clear why the cleavage reaction is directed mainly toward the formation of cyanimines.

It follows from this that if the solubility of the cyanimine derivative is in some way increased (for example, by replacing one solvent with another), then the ratio of the substances formed in the reaction mixture may shift toward the tetrahydroquinolide. Indeed, in the cleavage of γ-phenoxypyridine by cyanogen bromide and tetrahydroquinoline, not in ether (in which the corresponding cyanimine is poorly soluble), but in ethyl alcohol, it was possible to obtain only one bromide of the tetrahydroquinolide of β-phenoxyglutaconic aldehyde. It was further found that, when β-iodopyridine reacts with chlorodinitrobenzene in an ethyl-alcohol medium, only the monoanil of α-iodo-$\delta(2',4'$-dinitrophenyl)amino-\$ \$2,4-pentadienal (VII) is formed in good yield:



$$\mathrm{(NO_2)_2C_6H_3NH{—}CH = CH{—}CH = \underset{\displaystyle J}{\underset{|}{C}}{—}CH = NC_6H_5}$$

VII

$$\mathrm{C_6H_5NH{—}CH = CH{—}CH = C{—}CH = NC_6H_5 \cdot HBr}$$

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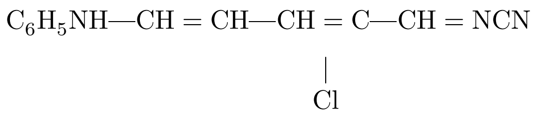
$$\underset{\mathrm{J}}{|}$$

VIII

In methanol (in which monoanil VII is more readily soluble), along with the monoanil, the hydrobromide of the dianil of α-iodoglutaconic aldehyde (VIII) is also obtained. The circumstance that, in the cleavage of pyridine itself by cyanogen bromide and amines, the corresponding cyaniminines cannot be isolated is apparently explained not so much by the good solubility of the cyaniminines as by the high rate of rupture of the C—N bond in the cyanimine.

From the standpoint of the ideas developed here, the observations made by Dieckmann in the cleavage of β-chloropyridine by cyanogen bromide and aniline in ether solution can readily be explained (^{4}).

The intensely orange precipitate obtained as a result of this reaction contained only small amounts of the hydrobromide of the dianil of α-chloroglutaconic aldehyde, while in significant part it consisted of aniline hydrobromide. When alcohol and aniline hydrochloride were added to the reaction mixture, the yield of the dianil hydrobromide increased sharply. The accelerating effect of the addition of aniline hydrochloride on the cleavage reaction seemed quite incomprehensible, since aniline hydrochloride itself is incapable of cleaving pyridine bromocyanide or chlorodinitrophenylate. Evidently, in the cleavage of β-chloropyridine, the cyanimine (IX), poorly soluble in ether, is first formed:

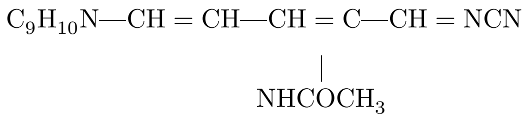


$$\mathrm{C_6H_5NH{—}CH=CH{—}CH=\underset{\underset{\displaystyle Cl}{|}}{C}{—}CH=NCN}$$

IX

The latter, upon addition of alcohol and aniline hydrochloride to the reaction mixture, partially passes into solution and reacts with aniline hydrochloride to form the hydrochloride of the dianil of α-chloroglutaconic aldehyde.

In obtaining cyaniminines from β-substituted pyridines, the formation of two isomers should have been expected. For example, in the cleavage of β-acetaminopyridine, cyaniminines X and XI could have been formed. However, up to the present, in all cases only one isomer has been isolated. Apparently, in the cleavage of β-substituted pyridines, predominantly only one of the Cα—N bonds is broken.



$$\mathrm{C_9H_{10}N{—}CH=CH{—}CH=\underset{\underset{\displaystyle NHCOCH_3}{|}}{C}{—}CH=NCN}$$

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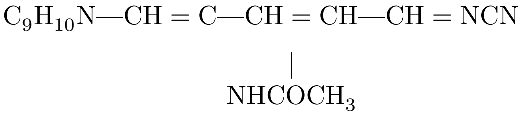
X



$$\mathrm{C_9H_{10}N{-}CH=\underset{\substack{|\\ NHCOCH_3}}{C}{-}CH=CH{-}CH=NCN}$$

XI

The position of the substituents in these derivatives has not yet been established. It may nevertheless be assumed that they are in the α-position to the group CH=NCN.

The cyanimine of β-methoxyglutaconic aldehyde was isolated in the form of two differently colored forms—bright yellow and bright red. Both forms have one and the same composition and practically the same melting point. An analogous phenomenon was also observed in the case of the cyanimine of β-ethoxyglutaconic aldehyde.

It is known that the salts of dianils of glutaconic aldehydes can exist in the form of two differently colored forms. Zincke explains the difference in the coloration of these modifications by dimorphism (5). The same phenomenon may perhaps also occur in the cyanimines studied. It should be borne in mind, however, that the possibility of cis–trans isomerism in cyanimines exists. This question requires special investigation.

L. V. Ivanova took part in the experimental portion of the work.

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Received
28 I 1957

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