DUAL REACTIVITY OF 1,2-DISUBSTITUTED DIHYDRO-N-HETEROAROMATIC SYSTEMS.

9.* ALKALINE HYDROLYSIS AND AROMATIZATION OF N-ACYL PARTIALLY HYDROGENATED DERIVATIVES OF PYRAZINE AND QUINOXALINE

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The aromatization with splitting of the N-acyl groups of 2,3-disubstituted N-acyl- and N,N'-diacyl-1,2-dihydro-, and 1,2,3,4-tetrahydropyrazines and quinoxalines under the effect of alcohol alkali was studied. A new reaction of recyclization of 1,4-diacyl-1,2,3,4-tetrahydroquinoxaline was discovered.

Aromatization of N-substituted 1,2-dihydrobenzopyridines is essentially dependent on the nature of the substituent on the ring nitrogen atom: the greater the electron-acceptor properties it has, the more difficult the reaction is [2]. N-acyl derivatives of dihydro-N-heteroaromatic compounds are most difficult to aromatize [2], especially the mono- and diacyl derivatives of dihydro- and tetrahydro-1,4-diazines [1]. It could be hypothesized that

![Chemical structures](image)

Ind=3-indolyl  I—III a R=CH₃, b R=C₆H₅, c R=C₆H₅—Cl_-, d R=C₆H₅—NO₂_-, e R=C₆H₅—CH₃_-, f R=C₆H₄—CH₃; g R=C₆H₄—CH₃


when the N-acyl groups are removed, aromatization of dihydroheteroaromatic compounds will be significantly facilitated. In this respect, we conducted hydrolysis and subsequent aromatization of a series of N-acyl derivatives of 1,2-di- and 1,2,3,4-tetrahydropyrazines and quinoxalines I-V with an alcohol alkali (see previous page).

It was found that the N-acyl derivatives of 1,2-dihydroquinoxaline II are hydrolyzed most easily, as should be expected based on the mechanism of alkaline hydrolysis of the amide bond, where the benzoyl residues with electron-acceptor substituents (IIId) are most easily split, those with electron-donor substituents (IIe) are split with more difficulty, and the acetyl residue (IIa) is split with even more difficulty. Oxidation of the intermediately formed unstable dihydro compounds VI is easily realized with the oxygen in the air and is accelerated by blowing pure oxygen through the reaction mixture.

![Diagram of chemical reaction](image)

Dialkylaminophenyl derivatives of 1,4-diacetyl-1,4-dihydroquinoxaline Va, b are hydrolyzed in such soft conditions. However, the dihydroquinoxalines VIII formed in these cases were more stable and were not oxidized by the oxygen in the air, but by chloranil:

![Diagram of chemical reaction](image)

Compounds VIII can be represented by three isomeric structures:

![Structures A, B, and C](image)

Structure A is excluded due to the well-known instability of 1,4-dihydroquinoxaline derivatives with substituents in the pyrazine part of the molecule [3]. Of the two possible structures B and C, the mass spectra and PMR data confirm structure B. A molecular ion peak (M⁺) of 251⁺ of which corresponds to its molecular weight, is recorded in the mass spectrum of compound VIIIa. After M⁺, the peaks of the [M − H]⁺, [M − 2H]⁺, and [M − 3H]⁺ ions are most intense, which is characteristic of compounds of structure B formed as a result of loss of three hydrogen atoms to the polycyclic aromatic system [4]. The absence of peaks for [M − C₆H₄N(CH₃)₂]⁺ (131) and [C₆H₅N(CH₃)₂]⁺ (120) in the mass spectrum of compound VIIIa excludes structure C, since such compounds split the substituent bound with the sp²-carbon atom of the heterocycle under the effect of electron impact [4]. Structure B is also confirmed by the presence of the peak of the [(CH₃)₄N-C₆H₄-CN]⁺ ion (146), which can only be formed from this structure, in the mass spectrum of compound VIIIa. A singlet of methyl groups at 3.03, a broadened singlet of the NH group proton at 3.95, a singlet of two methylene protons at 4.42 ppm, and a multiplet of aromatic protons with the center at 7.12 ppm are observed in the PMR spectrum of compound VIIIa.

Brief boiling of compounds I in a 10% ethanol solution of alkali unexpectedly resulted in isomeric compounds Xa, b of the same composition but with an open tetrahydropyrazine ring instead of the products of hydrolysis:

![Diagram of chemical reaction](image)

The data from elementary analysis, which remained unchanged in going from compounds I to X, also support the structures of X. The changes in the IR spectra of compounds X are

*Here and below, the values of m/z are given for the ion peaks.*