CONDENSATION OF 2-AMINO-3,4,5,6-TETRAHYDROIMIDAZO[4,5,1-ij]QUINOLINIUM AND 2-AMINO-2-PYRROLINIUM SALTS WITH β-DIKETONES

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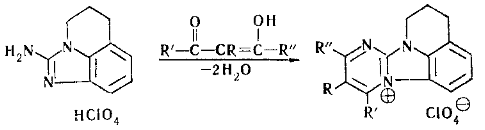
The corresponding 12,1,2,3-tetrahydropyrimido[2',1' : 2,3]imidazo[4,5,1-ij]quinolinium and 7,8-dihydro-6H-pyrrolo[1,2-a]pyrimidinium salts were obtained by the condensation of 2-amino-3,4,5,6-tetrahydroimidazo[4,5,1-ij]quinoline hydrochloride and 2-amino-2-pyrroline hydrochloride with β-diketones. The structures of the products of condensation with unsymmetrical diketones were determined from their PMR spectra.

It has been shown [1] that 1-substituted 2-aminobenzimidazole salts react with β-diketones, β-chlorovinyl ketones, and other similar carbonyl compounds to form pyrimido[1,2-a]benzimidazolium salts. 2-Amino-3,4,5,6-tetrahydroimidazo[4,5,1-ij]quinoline, which can be considered to be a substituted benzimidazole, behaves similarly, and its salt (I) reacts with β-diketones to give 12,1,2,3-tetrahydropyrimido[2',1' : 2,3]imidazo[4,5,1-ij]quinolinium derivatives (II).



I II

The reaction products — quaternary salts — form dyes with, for example, p-dimethylaminobenzaldehyde and ethyl orthoformate, and this serves as a qualitative test for the occurrence of the reaction. The structure of II was confirmed by the PMR spectra: in particular, when $R = H$, this proton in the spectrum of II is situated in the region of the chemical shift of aromatic protons. The reaction of I with benzoylacetone, which is an unsymmetrical β-diketone, might lead to two isomeric products. In fact, a single isomer — II ($R = H$, $R' = CH_3$, $R'' = C_6H_5$) — is formed, as established by means of the PMR spectra. The protons of the methyl groups in the PMR spectrum of II ($R = H$, $R' = R'' = CH_3$) have chemical shifts of 2.48 and 2.85 ppm, where 2.48 corresponds to the γ-methyl group with respect to the quaternary nitrogen atom, while 2.85 corresponds to the α-methyl group. This assignment was made in analogy with the assignments made in a number of pyrimido[1,2-a]benzimidazole salts [1]. A signal from the protons of a single methyl group is observed in the spectrum of the crude product of the condensation with benzoylacetone, and one of the possible isomers is consequently formed; the chemical shift of this signal is 2.80 ppm; i.e., isomer II ($R = H, R' = CH_3$, $R'' = C_6H_5$) is formed. The character of the appearance of the signals of the phenyl protons serves as an additional confirmation of the structure selected; in this case, the signal is split into a group of bands, which is evidence for a phenyl group in the α position relative to the tertiary nitrogen atom [2].

1,1,3,3-Tetraethoxypropane reacts with salt I as the acetal of a β-dialdehyde to form pyrimidine-unsubstituted II ($R = R' = R'' = H$).

2-Amino-2-pyrroline (III) was used as a simpler cyclic amidine in the reaction with β-diketones. Its reaction with β-keto esters, α-ethylene ketones, and malonic esters to form dihydropyrrolopyrimidinones

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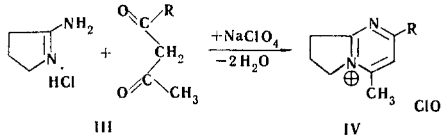
and tetrahydropyrrolopyrimidine derivatives was recently accomplished [2]. The reaction with β-diketones leads to 7,8-dihydro-6H-pyrrolo[1,2-a]pyrimidinium derivatives (IV).



Like II, salts IV form polymethine dyes. The formation of a pyrimidinium ring is confirmed by the presence of the signal of an aromatic proton in the PMR spectrum of IV. The signals of the protons of the methyl groups in IV ($R=CH_3$) coincide, and it is therefore impossible to determine the structure of the product of the condensation with benzoylacetone from the chemical shifts of the methyl group. The structure of this product was determined from the character of the appearance of the phenyl protons, which give two groups of peaks at weak and strong fields with an intensity ratio of 2: 3. As already noted, this corresponds to a phenyl group in the α position with respect to the tertiary nitrogen atom; thus the product of the reaction with benzoylacetone has the IV ($R=C_6H_5$) structure.

EXPERIMENTAL

The PMR spectra of trifluoroacetic acid solutions were determined with a Varian A-60-A spectrometer. The chemical shifts are presented on the δ scale with respect to tetramethylsilane.

8,10-Dimethyl-12,1,2,3-tetrahydropyrimido[2',1':[2,3]imidazo[4,5,1-ij]quinolinium Perchlorate. A mixture of 1.35 g (5 mmole) of I [3] and 2 ml (20 mmole) of acetylacetone was heated at 180-190° for 2 h. The mixture was cooled, and the precipitated crystals of II ($R=H$, $R'=R''=CH_3$) were isolated to give 0.8 g (42%) of a product with mp 215° (from water). PMR spectrum: 2.48 ppm, protons of the methyl group in the 10 position; 2.85 ppm, protons of the methyl group in the 8 position; 2.05, 2.8, and 4.22 ppm, triplets of the methylene groups; 6.92 ppm, pyrimidinium protons; 7.10-7.80 ppm, benzene ring protons. Found: N 12.60; Cl 10.32%. $C_{15}H_{16}ClN_3O_4$. Calculated: N 12.44; N 10.49%.

8-Methyl-10-phenyl-12,1,2,3-tetrahydropyrimido[2',1': 2,3]imidazo[4,5,1-ij]quinolinium Perchlorate. This compound was similarly obtained in 59% yield from I and benzoylacetone and had mp 315-318° (from nitromethane). PMR spectrum: 2.80 ppm, protons of the methyl group in the 8 position; 2.07, 2.80, and 4.22 ppm, methylene protons; 6.78-8.05 ppm, aromatic protons. Found: N 10.68; Cl 8.82%. $C_{20}H_{18}ClN_3O_4$. Calculated: N 10.50; Cl 8.81%.

8,9,10-Trimethyl-12,1,2,3-tetrahydropyrimido[2',1': 2,3]imidazo[4,5,1-ij]quinolinium Perchlorate. This compound was similarly obtained in 23% yield from I and 3-methylpentane-2,4-dione and had mp 233-235° (from water). Found: N 12.10; Cl 10.19%. $C_{16}H_{18}ClN_3O_4$. Calculated: N 11.93; Cl 10.09%.

8,10-Dimethyl-9-ethyl-12,1,2,3-tetrahydropyrimido[2'1': 2,3]imidazo[4,5,1-ij]quinolinium Perchlorate. This compound was similarly obtained in 19% yield from I and 3-ethylpentane-2,4-dione and had mp 204-206° (from water). Found: N 11.41; Cl 9.94%. $C_{17}H_{20}ClN_3O_4$. Calculated: N 11.35; Cl 9.70%.

12,1,2,3-Tetrahydropyrimido[2',1': 2,3]imidazo[4,5,1-ij]quinolinium Perchlorate. A mixture of 3 mmole of I and 6 mmole of 1,1,3,3-tetraethoxypropane was heated for 3 h in 5 ml of alcohol to give 18% of a product with mp 263-265° (from methanol). Found: N 13.51; Cl 11.20%. $C_{13}H_{12}ClN_3O_4$. Calculated: N 13.57; Cl 11.45%.

2,4-Dimethyl-7,8-dihydro-6H-pyrrolo[1,2-a]pyrimidinium Perchlorate. A mixture of 2 g (16 mmole) of 2-amino-1-pyrroline hydrochloride [4, 5] and 2 ml (20 mmole) of acetylacetone was heated at 155-165° for 3 h. The reaction mixture was washed repeatedly with ether and dissolved in the minimum amount of alcohol. The product was precipitated as the perchlorate to give 1.1 g (27%) of a product with mp 175-176° (from ethanol). PMR spectrum: 2.47 ppm (six protons), two equivalent methyl groups; 2.30, 3.37, and 4.45 ppm, complex triplets of the methylene groups in the 7, 8, and 6 positions; 7.30 ppm, pyrimidinium proton. Found: N 11.49; Cl 14.20%. $C_9H_{13}ClN_2O_4$. Calculated: N 11.25; Cl 14.26%.

4-Methyl-2-phenyl-7,8-dihydro-6H-pyrrolo[1,2-a]pyrimidinium Perchlorate. This compound [2.58 g (20%)] was similarly obtained from III and benzoylacetone and had mp 215° (from ethanol). PMR spectrum: 2.47 ppm, protons of the methyl group in the 4 position; 2.28, 3.33, and 4.40 ppm, methylene groups in the 7, 8, and 6 positions; 7.10-7.40 ppm, three phenyl protons; 7.60-7.95 ppm, two phenyl protons and a pyrimidinium proton. Found: N 9.34; Cl 11.33%. $C_{14}H_{15}ClN_2O_4$. Calculated: N 9.00; Cl 11.41%.

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