SYNTHESIS OF 4-(4-PYRAZOLYL)-SUBSTITUTED PYRYLIUM SALTS AND PYRIDINES

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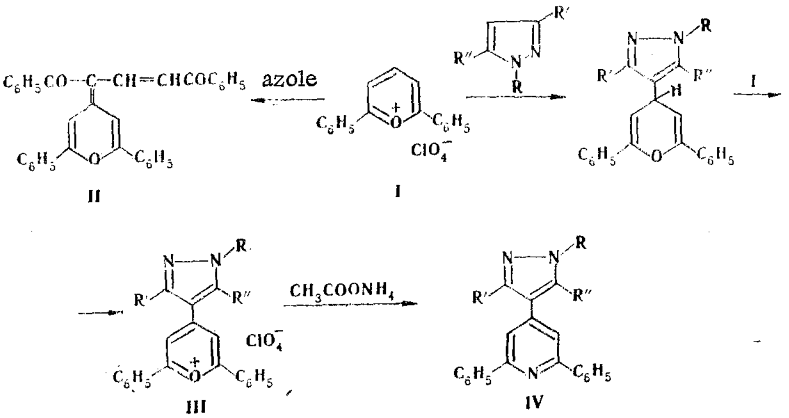
The reaction of pyrylium salts that contain an unsubstituted electrophilic carbon atom in the ring with pyrrole, indole, piperazine, tetrahydroquinoline, and N-substituted anilines, which leads to the synthesis of hetaryl(or aryl)pyrylium salts, has been investigated in detail [1]. However, their reactions with azoles have not been studied. Moreover, it is known that pyridine causes hydrolysis of 2,6-diphenylpyrylium perchlorate (I) to give 1,5,2',6'-tetraphenylpyranylidene-pentene-1,5-dione (II) [2]. It seemed of interest to establish which of the two processes — hetarylation of salt I or its hydrolysis under the influence of a nitrogen atom of the pyridine type — will be realized in the reaction of perchlorate I with azoles.

We have found that most of the investigated azoles promote the hydrolysis of salt I. However, the increased electron density on the C_4 atom in methylpyrazoles makes it possible to partially realize the C hetarylation of salt I to give 2,6-diphenyl-4-(4-pyrazolyl)pyrylium perchlorates (III). The reaction was carried out for 1 h in refluxing dimethylformamide (DMF) at a salt I:azole ratio of 1:1.3. Compounds IIIa-c were obtained in 10, 40, and 36% yields, respectively, and had mp 271, 292-293, and 299-300°C (from ethanol—acetonitrile), respectively. Refluxing salts III with ammonium acetate in acetic acid gave pyrazolylpyridines IVa-c with mp 177, 226-227, and 130°C (from ethanol), respectively.



Azole = imidazole, 3-5-diphenylisoxazole, pyrazole, 3,5-diphenylpyrazole, benzimidazole, indazole, benzothiazole;

IIIa, IVa $R=R''=H$; $R'=CH_3$; b $R=H$, $R'=R''=CH_3$; c $R=R'=R''=CH_3$

The structures of perchlorates III and pyridines IV were confirmed by data from IR and PMR spectroscopy. The results of elementary analysis of the compounds obtained were in agreement with the calculated values.

LITERATURE CITED

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