SYNTHESIS OF PYRYLIUM SALTS NOT SUBSTITUTED IN THE α-POSITION

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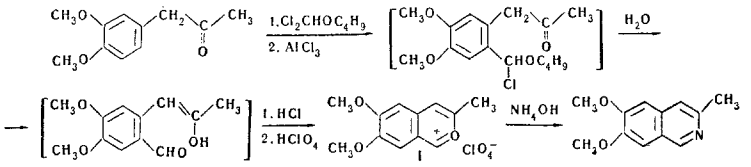
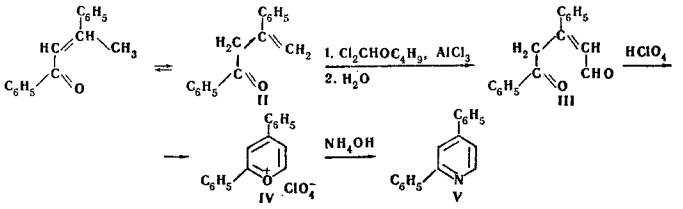
Continuing investigations in the field of the synthesis of pyrylium and 2-benzopyrylium salts containing no substituents in the α-position [1,2], we have studied the formylation of 3,4-dimethoxyphenylacetone and dypnone with butyl dichloromethyl ether in the presence of anhydrous aluminum chloride. This gave pyrylium chloroaluminates which were converted by subsequent treatment with 70% perchloric acid into the corresponding stable perchlorates.

The formylation of 3,4-dimethoxyphenylacetone gave a good yield (60%) of 6,7-dimethoxy-3-methyl-2-benzopyrylium perchlorate (I), mp 238–240° C (from acetic acid). IR spectrum, cm^{-1}: 1642, 1608, 1584, 1249, 1098. Found, %: C 47.58; H 4.45; Cl 11.34. Calculated for $C_{12}H_{13}O_7Cl$, %: C 47.27; H 4.30; Cl 11.65.



The formylation of dypnone, reacting in the isomeric form of a β,γ-unsaturated ketone (II), took place at the active double bond with the formation of the unsaturated keto aldehyde (III) which cyclized to the previously unknown 2,4-diphenylpyrylium salt IV:



Compound IV was obtained in the form of light green crystals with mp 218° C (from acetic acid). IR spectrum, cm^{-1}: 1632, 1594, 1091. Found, C 60.95; H 4.10; Cl 10.64. Calculated for $C_{17}H_{13}O_5Cl$, %: C 61.33; H 3.93; Cl 10.67.

When the salts obtained were treated with concentrated aqueous ammonia, the corresponding nitrogen bases were obtained: **6,7-dimethoxy-3-methylisoquinoline** with mp 129.5° C (from ethanol). Yield 75%. Found, %: C 70.92; H 6.24. Calculated for $C_{12}H_{13}O_2N$, %: C 70.90; H 6.42. **Picrate**, mp 258° C (decomp., from acetic acid); and **2,4-diphenylpyridine** (V) (83%), mp 70° C, after chromatography on a column of alumina [benzene–chloroform (2:3)]. **Picrate**, mp 189° C (from ethanol), according to the literature [3], mp 69° C, picrate 187° C.

The compounds synthesized, like other pyrylium salts with free α- or γ-positions, should be highly reactive in nucleophilic addition [4] and other reactions.

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