REACTION OF 4-ETHOXYCHROMYLIUM SALTS WITH SOME AMINES

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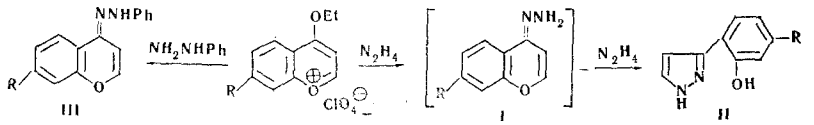
The reactions of 4-ethoxychromylium salts with some amines were studied. It was shown that o-hydroxyarylpyrazoles and chromone phenylhydrazones, respectively, are formed by the reaction of these salts with hydrazine and phenylhydrazine. The action of primary aromatic amines leads to replacement of the 4-ethoxy group by a 4-arylamino group, while the reaction of the 4-ethoxychromylium salts with N,N-diethylaniline gives 4-ethoxy-4'-diethylaminoflavylium salts.

In a previous paper [1] we reported a new method for the synthesis of 4-ethoxychromylium salts from o-hydroxyaryl alkyl ketones, ethyl orthoformate, and perchloric acid. Salts of this type have considerable activity with respect to nucleophilic reagents [2, 3].

To ascertain the reactivities of the 4-ethoxychromylium salts, we studied the reaction of these salts with several amines. It was shown that products with different structures are formed in the reaction of 4-ethoxychromylium salts with hydrazine and phenylhydrazine. o-Hydroxyaryl-substituted pyrazoles (II) are obtained from hydrazine, while the reaction with phenylhydrazine leads to chromone phenylhydrazones (III):



The reaction was carried out by refluxing the chromylium salt with the appropriate amine in glacial acetic acid. The structure of 3-(o-hydroxyphenyl)pyrazole was proved by the presence of a hydroxy group (IR spectrum and qualitative reaction with $FeCl_3$), which completely excludes the structure of the isomeric chromone hydrazone. In addition, the physical constants of this compound are in agreement with the data for the previously described 3-(o-hydroxyphenyl)pyrazole obtained by the reaction of chromone with hydrazine hydrate [4]. The absence of a hydroxyl group in III (when R = H), which is confirmed by qualitative reactions, makes it possible to choose structure III for these compounds.

It is fully possible that the intermediate chromone hydrazone (I), which, under the influence of the strongly basic hydrazine, undergoes ring opening with subsequent cyclization to a pyrazole, precedes the formation of pyrazoles in the reaction of 4-ethoxychromylium perchlorates with hydrazine.

When hydrazine is replaced by phenylhydrazine, the basicity of the secondary nitrogen atom is probably insufficient for opening of the pyran ring under the conditions of this reaction. The results obtained in a study of the reaction of a 4-methylthioflavylium salt with amines [5] are in agreement with this. Thus the reaction of 4-methylthioflavylium iodide with hydrazine results in the formation of flavone hydrazone, which, on refluxing in alkaline solution, is recyclized to the corresponding pyrazole. Phenylhydrazine

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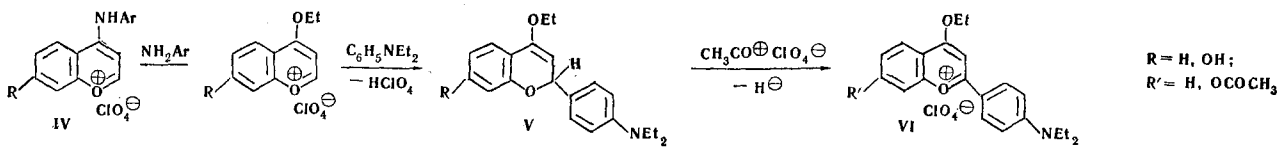
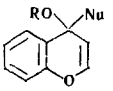
gives flavone phenylhydrazone, which cannot be converted to a pyrazole even when it is refluxed with alkali.

Depending on their structures, aromatic amines form different types of products. Primary amines replace the ethoxy group by an arylamino group. The IR spectra of IV contain a band at 1625-1631 cm^{-1}, which is characteristic for the pyrylium cation.



Tertiary aromatic amines behave differently. Thus the reaction of 4-ethoxychromylium salts with N,N-diethylaniline in acetic anhydride leads to p-diethylamino-substituted flavylium salts (VI). A free hydroxyl group (R = OH) is acylated by acetic anhydride under the reaction conditions. The results obtained are in good agreement with the data in [3], where it is shown that nucleophilic attack is directed to the α position of the pyrylium ring during the reaction of a 4-methoxychromylium salt with dimethyl- and diethylanilines.

By correlating our results with the literature data, we can conclude that the activity of the γ position is greater than that of the α position of the pyrylium ring in 4-alkoxychromylium salts. This fact is fully explainable if one takes into account the considerably greater ease of stabilization of the intermediate 4-substituted chroman structures



that are obtained as a result of the addition of a nucleophile as compared with the stability of 2H-chroman structures (V). In fact, detachment of an alkoxy group is required to obtain a stable product from the 4-substituted derivative, while detachment of a hydride ion which involves a greater expenditure of energy, is necessary in the case of 2H-chroman.

EXPERIMENTAL

3-(2-Hydroxyphenyl)pyrazole. A mixture of 2.7 g (0.01 mole) of 4-ethoxychromylium perchlorate and 0.64 g (0.02 mole) of hydrazine was refluxed in 5 ml of acetic acid for 40-50 min. The solution was cooled and diluted with water, and the product was extracted with ether. The ether extract was dried with sodium carbonate and evaporated to give 1.3 g (81%) of a product with mp 95° (from petroleum ether) [4].

3-(2,4-Dihydroxyphenyl)pyrazole. This was similarly obtained in 95% yield from the 7-hydroxy-4-ethoxychromylium salt and hydrazine and had mp 215° (from aqueous alcohol). Found: C 61.7; H 5.0; N 15.6%. $C_9H_8N_2O_2$. Calculated: C 61.35; H 4.52; N 15.73%.

Chromone Phenylhydrazone. A mixture of 2.7 g (0.01 mole) of 4-ethoxychromylium perchlorate and 1.76 ml (0.016 mole) of phenylhydrazine was refluxed in acetic acid for 40 min. The reaction mixture was diluted with water and filtered to give 1.6 g (70%) of a product with mp 112° (from methanol). Found: C 76.5; H 5.3; N 11.2%. $C_{15}H_{12}N_2O$. Calculated: C 76.25; H 5.12; N 11.43%.

7-Hydroxychromone Phenylhydrazone. This was similarly obtained in 40% yield from 4-ethoxy-7-hydroxychromylium perchlorate and had mp 125° (from aqueous methanol). Found: C 71.2; H 4.9; N 10.9%. $C_{15}H_{12}N_2O_2$. Calculated: C 71.41; H 4.79; N 11.10%.

4-Phenylaminochromylium Perchlorate. A mixture of 0.68 g (0.0025 mole) of 4-ethoxychromylium perchlorate and 0.23 ml (0.01 mole) of aniline in acetic acid was refluxed for 15 min and cooled to precipitate 0.67 g (81%) of colorless crystals with mp 182° (from acetic acid). Found: C 56.3; H 3.7; Cl 11.2%. $C_{15}H_{12}ClNO_5$. Calculated: C 56.00; H 3.72; Cl 11.02%.

4-(4-Methoxyphenylamino)chromylium Perchlorate. This was similarly obtained in 80% yield from 4-ethoxychromylium perchlorate and p-anisidine. The yellow needles melted at 251° (from acetic acid).

Found: C 54.4; H 4.2; Cl 10.2%. $C_{16}H_{14}ClNO_6$. Calculated: C 54.54; H 4.00; Cl 10.07%.

4-(4-Methoxyphenylamino)-7-hydroxychromylium Perchlorate. This was obtained in 95% yield from 4-ethoxy-7-hydroxychromylium perchlorate and p-anisidine as brown needles with mp 227° (from acetic acid). Found: C 52.0; H 3.8; Cl 9.3%. $C_{16}H_{14}ClNO_7$. Calculated: C 52.17; H 3.80; Cl 9.26%.

4-Ethoxy-4'-diethylaminoflavylium Perchlorate. A mixture of 0.68 g (0.0025 mole) of 4-ethoxychromylium perchlorate and 0.8 ml (0.005 mole) of N,N-diethylaniline in 5 ml of acetic anhydride was heated at 95° for 40-50 min and cooled. Treatment of the mixture with ether precipitated 0.7 g (70%) of a product with mp 212° (from alcohol). Found: C 59.4; H 5.5; Cl 8.1%. $C_{21}H_{24}ClNO_6$. Calculated: C 59.78; H 5.73; Cl 8.40%.

4-Ethoxy-4'-diethylamino-7-acetoxyflavylium Perchlorate. This was similarly obtained in 50% yield from 7-hydroxy-4-ethoxychromylium perchlorate and N,N-diethylaniline as red crystals with mp 219°. Found: C 57.3; H 5.5; Cl 7.2%. $C_{23}H_{26}ClNO_8$. Calculated: C 57.56; H 5.46; Cl 7.39%.

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