PYRYLATION OF HALO SUBSTITUTED PYRYLIUM SALTS

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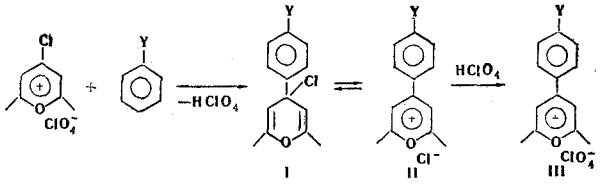
The reaction of γ-unsubstituted pyrylium salts with nucleophilic reagents does not stop at the electrophilic substitution stage. A hydride ion is subsequently lost from the resulting pyran, giving a new pyrylium cation [1]. We have found that the presence of a halogen atom in the 4-position of the starting pyrylium salt does not hinder the electrophilic substitution reaction, but that it does modify the rest of the process. The halogen atom in the pyran I apparently becomes the anion in the pyrylium cation (II), and the presence of a Lewis acid (for example, perchloric acid when pyrylium perchlorate is used) leads to replacement of the halogen anion by the anion of the acid which is present.



The reaction proceeds readily on boiling an equimolecular mixture of the halo-substituted pyrylium salt with the nucleophile (dialkylaniline, N-alkylindoline, N-alkyltetrahydroquinoline, N-alkylindole, dialkylresorcinol) in a polar organic solvent (dimethylformamide, acetonitrile).

The structures of the pyrylium salts obtained were confirmed by IR spectroscopy, independent synthesis, and elementary analyses.

The final products (III) obtained by this method were often obtained in a purer state than those obtained by the pyrylation reaction [1], as shown by their higher mp's.

Further examination of this reaction will determine the limits of its applicability, and the mechanism of the process.

LITERATURE CITED

1. S. V. Krivun, DAN, 180, 615, 1968.

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