

## N-PYRYLATION OF SECONDARY AMINES

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In an investigation of the reaction of  $\alpha$ - or  $\gamma$ -unsubstituted pyrylium salts with nucleophilic agents (pyrylation) it was found that this sort of interaction is not extended to secondary amines [1] since splitting out of a hydride ion from the dialkylamino-substituted pyran formed does not occur. In this study it was shown that 4-halo-substituted pyrylium salts react with secondary cyclic and alicyclic amines to give 4-dialkylamino-substituted pyrylium salts.

This N-pyrylation proceeds readily at room temperature or with brief heating of a mixture of the components [pyrylium salt-amine (1:2)] in chloroform, methylene chloride, or acetonitrile.

Thus, brief shaking of 2,6-diphenyl-4-chloropyrylium perchlorate with piperidine (1:2) in chloroform leads to the formation of 2,6-diphenyl-4-piperidinopyrylium perchlorate (60%) with mp 288 deg (from nitromethane). Brief refluxing of 2,6-diphenyl-4-chloropyrylium perchlorate with diisobutylamine gives the pyrylated amine in 73% yield with mp 269 deg (from nitromethane). 2,6-Diphenyl-4-chlorothiapyrylium perchlorate forms 2,6-diphenyl-4-piperidinothiapyrylium perchlorate (88%) with mp 292 deg (from nitromethane) by refluxing with piperidine in chloroform. Chlorine-substituted pyrylium salts react similarly with diethylamine, dipropylamine, morpholine, and other secondary amines.

The compounds obtained were identified by means of IR spectra and alternative synthesis of 2,6-diphenyl-4-piperidinopyrylium perchlorate from 2,6-diphenyl-4-methoxypyrylium perchlorate and piperidine via the method described for the 2,6-dimethyl-4-piperidinopyrylium salt [2].

## LITERATURE CITED

1. S. V. Krivun, Dokl. Akad. Nauk SSSR, 180, 615 (1968).
2. R. M. Anker and A. H. Cook, J. Am. Chem. Soc., 69, 117 (1946).

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