



SUBSTITUTION REACTIONS OF SOME HETEROCYCLIC COMPOUNDS

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SUMMARY

1-Bromoacridine, 3-bromoacridine, and 4-bromoacridine have been prepared for the first time, by unambiguous syntheses. The infrared spectra of the monobromoacridines, their ultraviolet spectra in ethanol and in 1*N* sulphuric acid, and their pKa values have been measured. Tentative assignments for the infrared bands due to CH deformations have been made on the basis that each ring could be considered individually. The pKa values have been related to the inductive and mesomeric effects of the bromo-substituents.

The Ullmann condensation of 5-bromo-2-chlorobenzoic acid with *o*-bromoaniline was found to give 4-bromodiphenylamine-2-carboxylic acid.

10-Bromophenanthridine has been synthesized for the first time, by an unambiguous route, and 6-bromophenanthridine has also been prepared. The infrared spectra of all the possible monobromophenanthridines were measured and tentative assignments for the bands due to CH deformations have been made. The ultraviolet spectra of the free bases and the protonated forms of all the monobromophenanthridines with the exception of 6-bromophenanthridine have been measured and discussed. The pKa values of the monobromophenanthridines except the 6-isomer have been determined and an attempt has been made to relate them to the mesomeric and inductive effects of the bromo-substituent.

A method, using thin-layer chromatography, for the quantitative separation of mixtures of acridine and the monobromoacridines has been developed.

Brominations of acridine in concentrated sulphuric acid containing silver sulphate, and in acetic acid containing silver acetate, were studied quantitatively. Those in sulphuric acid gave mainly 4-bromoacridine with less of the 2-isomer, while those in acetic acid gave mainly the 2-isomer. Probable reasons for this difference are discussed. The bromination results have been compared with those obtained from nitration by Lehmstedt; and have also been compared with theoretical predictions of the relative reactivity of the positions in acridine to electrophilic attack. Polybromination was always observed in these reactions, even though an excess of acridine was used. The known 2,7-dibromoacridine and also 2,5-dibromoacridine were isolated from bromination reactions. The structure of 2,5-dibromoacridine was deduced from n.m.r. evidence.

The bromination of phenanthridine was carried out in concentrated sulphuric acid containing silver sulphate. The products were qualitatively separated and 10-bromophenanthridine, 4-bromophenanthridine, 2-bromophenanthridine, and two dibromophenanthridines were isolated. These results are somewhat different from those observed in the nitration of phenanthridine. They are briefly discussed in relation to theoretical predictions.