THE PREPARATION AND PROPERTIES OF SOME POLYCYCLIC HETEROCYCLIC SYSTEMS.

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R. Pettit

R. PETTIT.

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INTRODUCTION

In the past fifty years or more the chemistry of polycyclic aromatic hydrocarbons has been of both practical and theoretical interest and has received considerable attention from organic chemists. Perhaps the main reason for this is that many of these compounds occur in coal tar products and, as well as being of some commercial use, have thus been readily available for further investigation. More recently it has been found that several polycyclic aromatic hydrocarbons, when administered to animals, induce malignant tumours and this has promoted further research into this class of compounds. Further, in attempting to explain the unique chemical behaviour of aromatic systems the application of quantum mechanical methods to such systems has been highly successful and has greatly added to the interest shown in this field of organic chemistry.

However, the study of the corresponding polycyclic aromatic heterocyclic nitrogen compounds has received much less attention than their homocyclic analogues. In the latter part of the last century, resulting from Perkin's discovery of mauve, a great fillip was given to the investigation of nitrogen heterocyclic systems; the manufacture of synthetic dyes rapidly became a major industry and the search for new synthetic dyes was greatly intensified. As a result of this many new heterocyclic ring systems were discovered and their properties examined. However it was soon realised that for a compound to have satisfactory dyeing properties it must contain what we now refer to as auxochromic and chromophoric centres. The unsubstituted aromatic azahydrocarbons therefore did not possess satisfactory dyeing properties and in this connection were little further investigated. A number of alkaloids and several compounds having important biological activities are characterised by the presence, within their structures, of a polycyclic heterocyclic system. However, these systems are always almost completely saturated and, in the case of compounds of biological interest especially, are highly substituted and their properties differ considerably from those of the parent aromatic heterocyclic compounds. The latter compounds have therefore been of small interest to workers in these fields and have received little investigation at their hands.

This then, together with the fact that the polycyclic heterocyclic aromatic compounds are not readily available and could only be obtained in many cases by difficult synthesis, largely accounts for the neglect of this branch of chemistry. That the study of such systems has been largely neglected is clearly evident from the fact that of the twelve possible mono-aza-1:2-benzanthracenes only five have been prepared, of the sixty-six possible bi-aza-1:2-benzanthracenes two have been prepared and, as yet, none of the one hundred and twenty possible tri-aza-1:2-benzanthracenes have been prepared. The situation is similar with respect to aza derivatives of other important aromatic hydrocarbons such as chrysene, benzphenanthrene, triphenylene, etc. where again only a very small proportion of the possible number of compounds has been prepared ("Six membered heterocyclic nitrogen compounds with four condensed rings", C.F.H. Allen, Interscience Publishers, 1951).

Nevertheless since the study of the chemistry of the simpler mono-, bi- and tri-cyclic aromatic heterocyclic nitrogen compounds such as pyridine, pyrazine, quinoline, isoquinoline, quinoxaline, acridine, phenazine, etc., and a comparison of these compounds with their analogous hydrocarbon, has revealed many interesting features, it seemed highly desirable to extend this study to the more complex systems containing four or more fused rings.

The purpose of the present work was then to further investigate the chemistry of some polycyclic heterocyclic compounds, especially those containing four or five fused rings and having one or more nitrogen atoms in the ring system. This obviously represents a vast number of compounds and the work has had to be restricted to a few chosen problems. Several rather diverse subjects have been studied and the results are given in this thesis under the following headings.

I. The absorption spectra of polycyclic aromatic azahydrocarbons.

II. Quinonoid structures in polycyclic heterocyclic systems.

III. The chemistry of some complex polycyclic azahydrocarbons.

IV. The Elbs reaction and its application to the synthesis of polycyclic azahydrocarbons.

V. The conjugating ability of the various positions in a polycyclic aromatic ring system.