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NEW HETEROAROMATIC COMPOUNDS

PART XXXI: THE 12,11-BORAZAROPHENALENIUM CATION[1]

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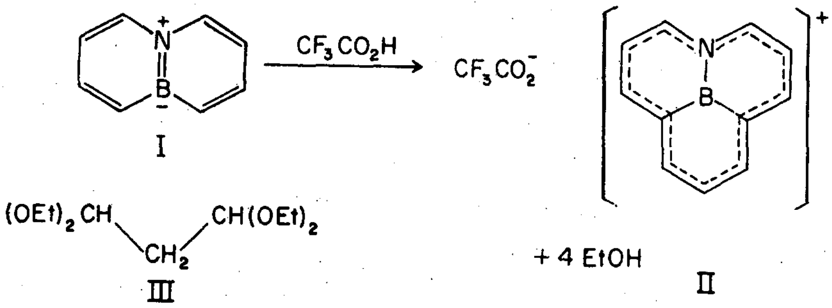
Previous papers in this series[3,4] have described a new series of compounds formed by replacement of two adjacent carbon atoms in an aromatic system by boron and nitrogen.

The most recent member of the series to be described, 10,9-borazaronaphthalene (I), was found to undergo facile substitution in the 4(5) position by the electrophilic reagents D^+ and bromine.[5] It therefore occurred to us that I might react with malondialdehyde in presence of acid to form the tricyclic 12,11-borazarophenalenium cation (II). The cation II would be isoelectronic with the phenalenium cation which has been isolated as the perchlorate.[6]

In an attempt to prepare the trifluoroacetate of II, I (20 mg) was dissolved in trifluoroacetic acid (0.5 ml). Addition of malonaldehyde bis-diethylacetal (III; 34 mg) produced an immediate intense violet colouration (514 mn), and there is strong evidence that this was due to the formation of II by the following reaction:



Firstly, the mass spectrum of the reaction mixture contained a small peak at m/e 166, corresponding to $(C_{11}H_9NB)^+$. Secondly, neither I nor III separately gave a colour with trifluoroacetic acid. Bearing in mind the substitution pattern for I, it is difficult to find an alternative structure for the coloured product. Thirdly, the nmr spectrum of the reaction mixture showed absorption characteristic of ethanol together with a complex multiplet (ratio of ethanolic to aromatic protons 20:9) in the aromatic region (δ6.6 to 7.4), quite different from the pattern given by I. Absence of further absorption shows clearly that the three carbon atoms in III have become incorporated into the aromatic system. Complete analysis of the multiplet was not possible, but its presence in the aromatic region is good evidence for II, by analogy with the nmr spectrum of the trimethylphenalenium cation.[7] Bonthrone and Reid were unable to obtain a satisfactory spectrum of the phenalenium cation itself because of paramagnetic interference due to radical formation.[7]

The coloured product decomposed slowly in solution at room temperature, even under an inert atmosphere, but appeared to be stable indefinitely at -78°. Consequently all physical measurements were made immediately after mixing the reactants.

Attemtpts to isolate a solid perchlorate, pentafluorostannate, hexafluoroantimonate and tetrafluoroborate were not successful. In each case, however, the same intense violet colour was observed and the solutions showed the characteristic absorption at 514 nm.

REFERENCES

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