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NEW ROUTES TO CONDENSED POLYNUCLEAR COMPOUNDS . PART I
A CONVENIENT SYNTHESIS OF PHENANTHRIDINE

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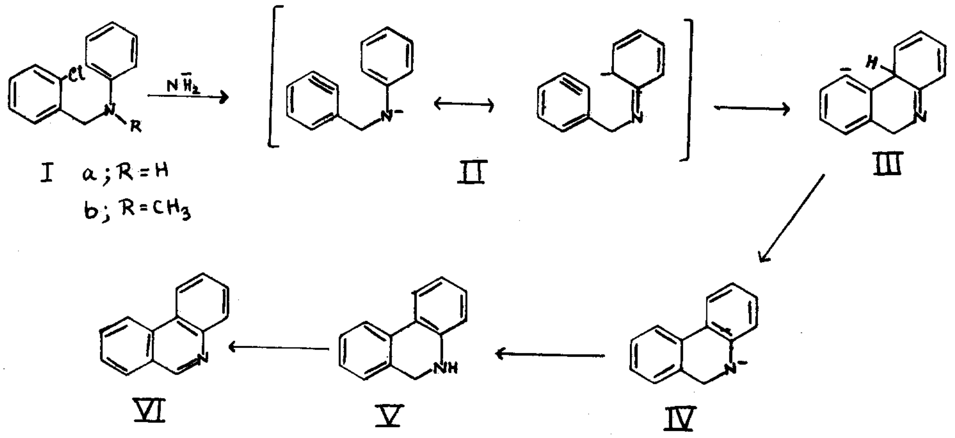
Development of a good method to effect intramolecular linkage of aromatic rings, for building polynuclear systems, is a long standing problem in synthetic organic chemistry (1). Such a union could conceivably be brought about by intramolecular reaction of a dehydrobenzene with an aromatic ring. No doubt benzene itself is somewhat inert towards dehydrobenzene (2), yet attachment to a nitrogen or oxygen carrying a negative charge may confer sufficient reactivity on it. For example, ambident character is expected from anion II and it may show requisite nucleophilicity at positions ortho and para to nitrogen. To test these ideas a synthesis of phenanthridine was envisaged along the following lines.



The amine Ia was prepared by sodium borohydride reduction of the anil from o-chlorobenzaldehyde. Its reaction with excess potassium amide in liquid ammonia gave crystalline V, identical with authentic dihydrophenanthridine (3) (mixed m.p., t.l.c., IR), which on dehydrogenation afforded phenanthridine (4) (VI). A similar reaction with N-methyl derivative Ib, leads to a complex mixture (at least five components as adjudged by t.l.c.). It seems, therefore, that in absence of strong anionic activation the attack of aromatic nucleus by dehydrobenzene does not proceed as well.

The near quantitative yield in cyclisation of Ia is very gratifying. Absence of products corresponding to reaction on nitrogen (5) suggests effective nucleophilicity (6) of the ortho carbon in the ambident anion II, although ease of 6-membered ring formation may be a contributing factor.

This method opens routes to a variety of polynuclear compounds and natural products like α-naphthaphenanthridine alkaloids (7). A similar dehydrobenzene cyclisation on ortho or para position of phenoxides, if successful, would also be of wide applicability. These aspects are currently under investigation.

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