

Synthesis of 6,9-Diazadibenzo[c,g]phenanthrene and 7,13-Diazadibenzo[c,i]phenanthrene through Double Benzyne Cyclisation¹.

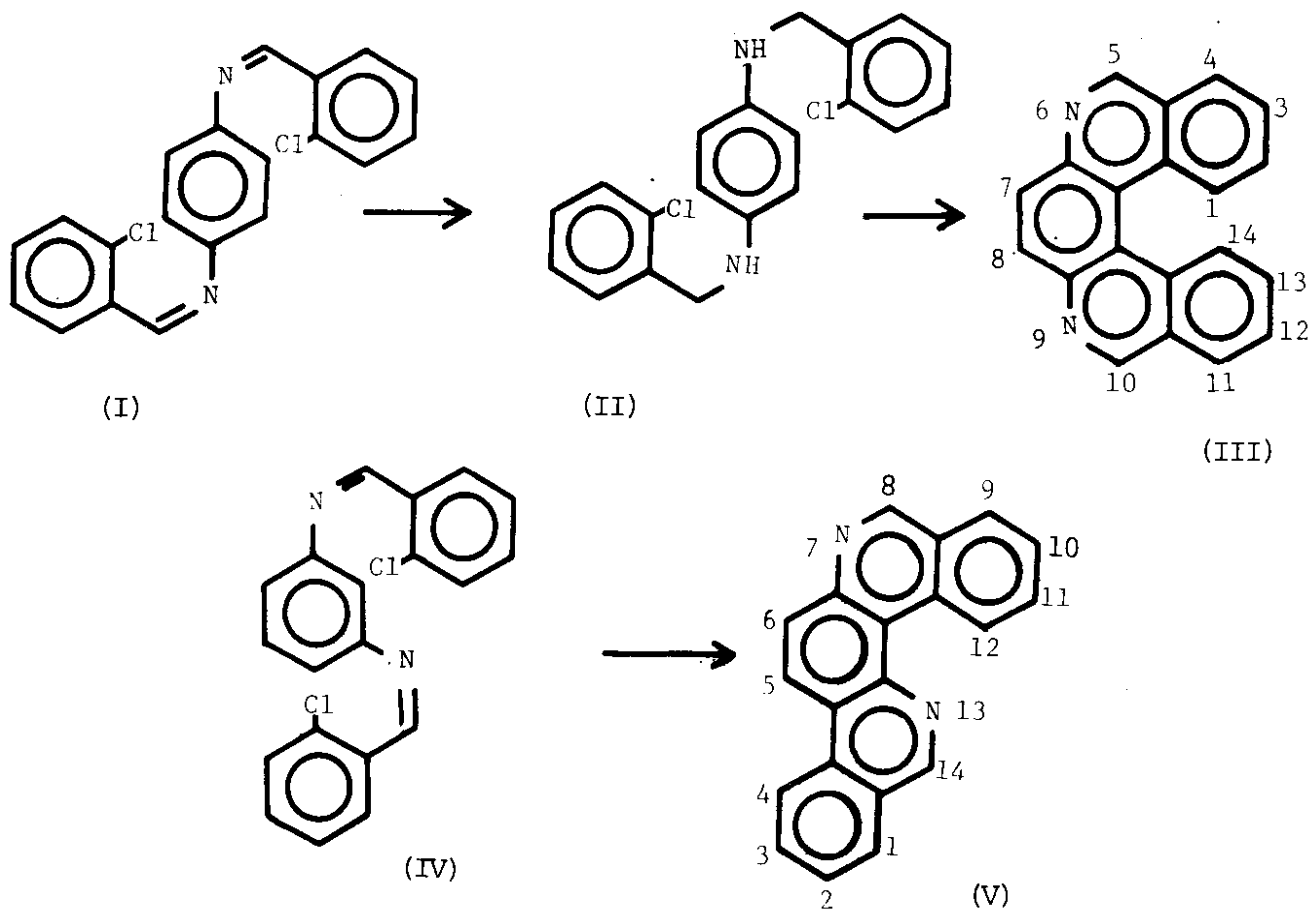
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Benzyne mediated cyclisation of ortho-halogenated Schiff bases or the corresponding dihydro compounds with KNH_2/NH_3 has been developed as a convenient route to a number of condensed polynuclear systems². It was of interest to find out if bis-Schiff bases derived from phenylenediamines can be made to undergo 'double' benzyne cyclisations. Reaction of I* (m.p. 139-140°C) with KNH_2 (8 molar) in liquid ammonia gave a very complex mixture. However, sodium borohydride reduction to II and immediate treatment with KNH_2/NH_3 readily furnished (40%) a pentacyclic base (m.p. 98-99°C) analysing for $\text{C}_{20}\text{H}_{16}\text{N}_2$. Stirring it with

MnO_2 suspended in chloroform afforded a completely aromatic product ($\text{C}_{20}\text{H}_{12}\text{N}_2$, m.p. 155-156°C); mass spectrum; m/e 280 (M^+), 253 ($\text{M}^+ - \text{HCN}$), 252 ($\text{M}^+ - \text{H}_2\text{CN}$), 140 (M^{++}); NMR (CDCl_3): 9.45 (S,2H,H-5, H-10), 8.31 (S,2H,H-7,H-8); UV (dioxane); λ_{max} 232 nm ($\log \epsilon$ 4.88), 270(4.51), 304(4.42), 330(4.07). This compound was assigned structure III on basis of the spectroscopic data, specially the ultraviolet absorption which was very similar to that of the carbocyclic analog dibenzo[c,g]phenanthrene³. Further, its physical constants differed from those reported⁴ for 6,13-diazadibenzo[a,h]anthracene, the alternate possible product of cyclisation.



*Satisfactory elemental analyses have been obtained for all new compounds.

Reaction of the anil IV with KNH_2/NH_3 gave a mixture from which the known⁵ 7,13-diazadibenzo[c,i]phenanthrene (V, m.p.183-184^o) could be isolated (10%) directly; mass spectrum : m/e 280 (M^+), 253 ($\text{M}^+ - \text{HCN}$), 252 ($\text{M}^+ - \text{H}_2\text{CN}$), 140 (M^{++}). Efforts to improve the overall yield by reduction of IV prior to cyclisation were unrewarding. Attempts to prepare, for cyclisation, bis-Schiff bases from o-phenylenediamine gave only imidazoles.

It may be concluded that synthesis of pentacyclic compounds through benzyne cyclisation of halogenated bis-Schiff bases is feasible. Surprisingly, such cyclisations occur to give angular rather than linear systems formation of which should be favourable on steric grounds.

References

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