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NEW ROUTES TO CONDENSED POLYNUCLEAR COMPOUNDS, II
DIRECT BENZYNE CYCLISATION OF N-CHLOROBENZYLIDENE ARYLAMINES

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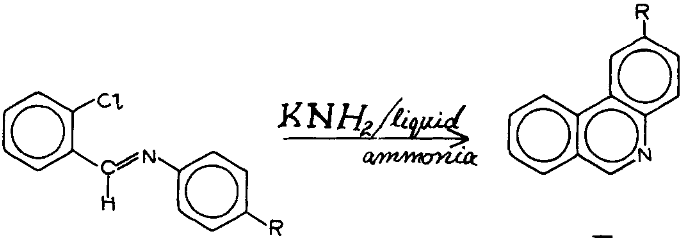
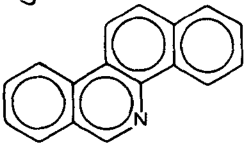
Reduction and subsequent dehydrogenation steps involved in our recently reported route (1) to phenanthridines could be avoided by direct benzyne cyclisation of anil **1a**. This, however, did not seem feasible in view of the known trans geometry (2). Reaction through trans-cis equilibration also appeared unlikely on basis of the kinetic data from thermal relaxation of photoisomerised anil solutions (3,4,5). Nevertheless, cyclisation could occur if an intermediate allowing change in the original disposition of the rings got formed during the course of the reaction.



I a, R = H

b, R = CH_3

II



III

Experimentally it was found that treatment of anil Ia with excess potassium amide in liquid ammonia gave phenanthridine (IIa) in excellent yield. Similar reaction of Ib afforded IIb, while the anil from α-naphthylamine gave (6) benzo(c) phenanthridine (III, 35%) identical with an authentic sample. Numerous previous attempts (7) to obtain the latter system by direct cyclisation had proven unsuccessful.

This new method, besides its synthetic utility, has considerable mechanistic interest. Its scope and mechanism are under investigation.

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5. This is only valid if formation of benzyne does not lead to appreciable redistribution of electronic charge and hence changed mobility with respect to-C=N-bond.
6. The reaction requires ether as cosolvent with liquid ammonia. Use of other solvents like hexamethyl phosphoramide having good dissolving power for large organic molecules is under investigation.
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