Tetrahedron Letters No.6, pp. 471-472, 1971. Pergamon Press. Printed in Great Britain.

NEW ROUTES TO CONDENSED POLYNUCLEAR COMPOUNDS,VI
SYNTHETIC SCOPE OF THE BENZYNE CYCLISATION OF SCHIFF BASES

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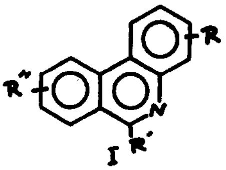
(Received in UK 21 December 1970; accepted for publication 4 January 1971)

We have recently reported[1] that N-(o-chlorobenzylidene)-arylamines can be readily cyclised with excess amide ions in liquid ammonia. To explore the synthetic scope of this procedure it was necessary to find out (a) what functional groups are compatible with the conditions of this reaction, (b) whether it succeeds when arynes of lower selectivity are involved as intermediates and (c) if it is possible to affect cyclisation onto hetrorings also.



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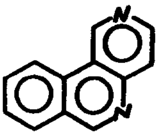

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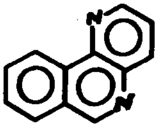

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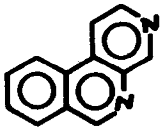

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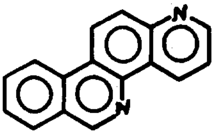

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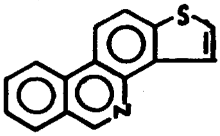

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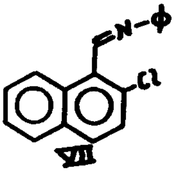

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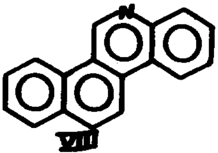

VIII

It has now been found that good (ca 50%) to excellent (ca 90%) yields of phenanthridines bearing a variety of electron-supplying or electron-withdrawing substituents(R=o-, m- or p-alkoxy,alkyl,chloro, cyano,carbethoxy and carbonyl) can be readily obtained[2]. Further 6-substituted (R'=alkyl or aryl) phenanthridines could also be obtained by this method though the yields were slightly inferior. As expected Schiff bases from meta arylamines afforded mixtures of 1- and 3-substituted phenanthridines.

In case of anil VII reaction should proceed through a 2,3-naphthyne which can be expected to have poor selectivity, due to less effective overlap between aryne orbitals across a bond of lower order[3]. Cyclisation of this anil indeed afforded only 35% of benzo (i)phenanthridine (VIII, m.p. 182-3)[4]. The lower yield, however, is not a consequence of poor selectivity since the dihydro derivative of anil VII on cyclisation and dehydrogenation afforded VIII almost quantitatively. Reaction of anils Ia (R'=3:4-dimethoxy) and Ib (R"=3:4-methylenedioxy) were also studied since it is known that arynes having alkoxy substituents exhibit[5] poor selectivity. Again the cyclisation proceeded in moderate yield (40% and 30%) and here no significant improvement resulted on using the dihydro compounds.

Reaction of the condensation product from 4-amino pyridine and o-chloro-benzaldehyde gave diazaphenanthrene (II) ($C_{12}H_8N_2$, m.p. 114-15°, 67%) whereas that of the corresponding 3-isomer afforded a mixture of III ($C_{12}H_8N_2$, m.p. 99-102°, 20%) and IV ($C_{12}H_8N_2$, m.p. 102-4, 45%). The diazachrysene V($C_{16}H_{10}N_2$, m.p. 155-6, 72%) and the thiopheno compound VI ($C_{15}H_9NS$, m.p. 144-5, 65%) could also be readily obtained from appropriate anils. All these seem to be new heterocyclic systems which by conventional routes would be accessible with difficulty. Thus, a new versatile method by which two aromatic synthons, one in the form of a halogenated carbonyl compound and the other as an amine, can be fused together to a polycondensed system seems at hand.

References

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