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A NEW SYNTHESIS OF 1,2,4,6-TETRAZEPINES

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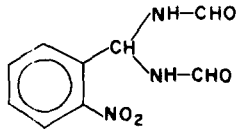
During our work on the synthesis of substituted quinazolines we had occasion to prepare several bisformamido-o-nitrobenzaldehydes[1]. These intermediates appear to offer a suitable frame-work for novel and relatively facile syntheses of a variety of heterocyclic ring systems and condensed rings derived therefrom. In this communication we report a new method for the synthesis of 4H- [1,2,4,6] tetrazepines from which the new condensed rings, 1H [1,2,4,6] tetrazepino [4,5,-b] indazole and 1H [1,2,4,6] tetrazepino [4,5-c] bensotriazine, could be obtained. The only record in literature of a 1,2,4,6-tetrazepine derivative refers to a compound obtained by Ottensooser[2] by the action of dilute potassium hydroxide solution on isobutyl chlorourea.

Condensation of bisformamido-o-nitrobenzaldehyde (I) with 98 % hydrazine hydrate in ethanolic solution gave directly in 80 % yield, 5,6-dihydro-5-o nitrophenyl-4H- [1,2,4,6] tetrazepine (IIa) which was crystallised from benzene-light petroleum as yellow shining needles, m.p.118°. It was reduced with ferrous sulphate and aqueous ammonia to the corresponding amino compound (IIb) (82%) m.p.228° (from benzene).

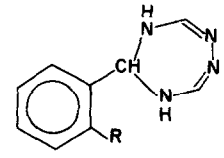
1H- [1,2,4,6] tetrazepino [4,5-b] indazole (III) was obtained by oxidising IIb with ferric chloride following the procedure described by Naqui and Srinivasan[3]. Yield 64 %. It had melting point 102-105° (from benzene-light petroleum).

The triazinotetrazepine (m.p.151°) (IV) separated out as tiny yellow needles when a solution of IIb in glacial acetic acid was treated with sodium nitrite solution. It could be crystallised only with difficulty from tetrahydro-

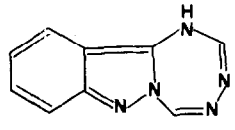
furan being insoluble in most of the common organic solvents.



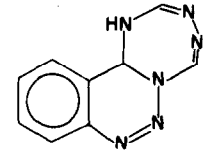
I



IIa : R=NO$_2$
IIb : R=NH$_2$



III



IV

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

This approach appears amenable to extension for the synthesis of other azahetrocyclics by a suitable choice of the condensing components and conditions of reaction. This aspect is receiving our attention.

We thank Dr. Leonard T. Capell for advice on the nomenclature and numbering of the new systems synthesised now.

REFERENCES

1. G.S. Sidhu, G. Thyagarajan and Nagabhushan Rao, Indian Journal of Chemistry (in press).

2. M.R. Ottensooser, Bull. soc. chim. 4, 45 1013 (1929); Chem. Abstr. 24, 3755 (1930). It is a derivative of 1H-1,2,4,6-tetrazepine, a hydrogen isomer of the system reported in the present communication.

3 S. Naqui and V.R. Srinivasan, J. Sci. industr. Res. 21B, 456 (1962).