

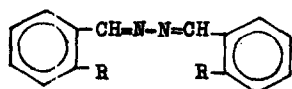
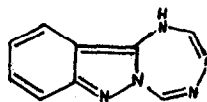
THE REACTION OF HYDRAZINE HYDRATE ON
BISFORMAMIDOBENZALDEHYDES;
CORRECTIONS TO OUR PAPER ON
"A NEW SYNTHESIS OF 1,2,4,6-TETRAZEPINES"¹

G.S. Sidhu, G. Thyagarajan and Nagabhushan Rao
Regional Research Laboratory, Hyderabad-9, India

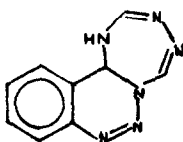
(Received 15 March 1965)

We recently published 'A New Synthesis of 1,2,4,6-Tetrazepines'¹. After this publication we had an opportunity to record the I.R. Spectra of the compounds reported by us and found that the spectra were not consistent with the structures proposed by us for different condensation products. We have now re-examined the reaction products and would like to correct our previous conclusions.

Condensation of bisformamido-*o*-nitrobenzaldehyde with 98% hydrazine hydrate does not result in the formation of 5,6-dihydro-2-*o*-nitrophenyl-4H-1,2,4,6 tetrazepine. The product on checking by TLC for purity was found to be a mixture. After purification it melted at 204° (from ethanol) and was identified as *o*-nitrobenzalazine (Ia); I.R. spectrum superimposable on that of an authentic sample².

Ia: R = NO₂Ib: R = NH₂

II



III

Its reduction product with ferrous sulphate and ammonia could, therefore, not be 5,6-dihydro-5-o-aminophenyl-4H-1,2,4,6 tetrazepine. It was identified as o-aminoazo-benzalazine, m.p. 238° (after recrystallisation from ethanol); I.R. spectrum superimposable on that of authentic sample².

We have now carried out the reaction of hydrazine hydrate with bisformamidobenzaldehyde, and its m- and p-nitro, o, m and p-methoxy, 3,4-methylenedioxy, o-, m- and p-chloro derivatives also. In each case, the product is the corresponding benzalazine. We shall report on the course of the reaction in a subsequent detailed communication in which we will also clarify the structures of the products erroneously claimed by us to be 1H-1,2,4,6 tetrazepino 4,5-b indazole (II) and the triazinotetrazepine (III).

The reaction may proceed through the intermediate formation of benzaldehyde involving an attack by water or ethanol on the benzylic carbon. It is also possible that the attacking species may be the hydrazine molecule which may attach itself to the benzylic carbon by the lone pair of electrons on the nitrogen. This can lead to the direct formation of the azine.

REFERENCES

1. G.S. Sidhu, G. Thyagarajan and Nagabhushan Rao, Tetrahedron Letters No. 24, 1637 (1963).
2. Kazuo Miyatake, Jour. Pharmac. Soc. Japan 72, 1162-4 (1952); Chem. Abs., 47, 6885c (1953).