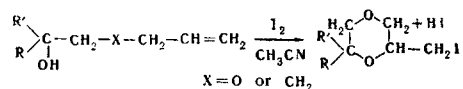


sists in that the starting material, which contains a double bond and a hydroxy group, is cyclized under the action of iodine in acetonitrile in accordance with the following scheme:



The reaction takes place by stirring a solution of iodine in acetonitrile with the appropriate compound at room temperature for 2-3 days. In the case of 1,4-dioxane derivatives, the reaction mixture may be boiled, which shortens the reaction time to 7-8 hr. By this method, we have obtained 2-iodomethyl-1,4-dioxane and 6-hydroxymethyl-2-iodomethyl-1,4-dioxane, the constants of which agree with those given previously [1, 3]. The structure of 2-iodomethyl-6,6-dimethyltetrahydropyran [bp 89° C (7 mm),  $n_D^{20}$  1.5115,  $d_4^{20}$  1.4867] has been confirmed by analyses and the IR spectrum.

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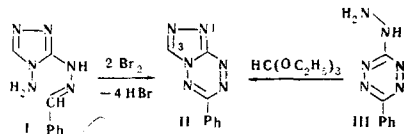
### SYNTHESIS OF COMPOUNDS CONTAINING A NEW BIHETEROCYCLIC SYSTEM (s-TRIAZOLO [3,4-b]-s-TETRAZINE)

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To study the fine structure and color of *s*-tetrazine, we have synthesized *s*-tetrazine with a fused *s*-triazole ring. First 4-amino-3-benzylidenehydrazino-1,2,4-triazole (I) [1] was brominated in chloroform at room temperature (1 mole of bromine per mole of I). The dibromide obtained (Found, %: Br 44.64. Calculated for C<sub>9</sub>H<sub>6</sub>N<sub>6</sub> · 2HBr, %: Br 44.40), without further purification, was heated in chlorobenzene for 2 hr and the precipitate was filtered off. After the evaporation of the filtrate, 6-phenyl-*s*-triazolo[3,4-*b*]-*s*-tetrazine (II) was obtained. Yield 12%, small yellow plates, mp 229-230° C (a mixture of dimethylformamide and benzene).  $\lambda_{\text{max}}$  264 nm (log  $\epsilon$  4.32), 338 (3.65), 460 (2.64) in ethanol. Found, %: C 55.03; H 3.08; N 42.56. Calculated for C<sub>9</sub>H<sub>6</sub>N<sub>6</sub>, %: C 54.54, H 3.05; N 42.41.



The structure of II was shown by independent synthesis. 3-Hydrazino-6-phenyl-*s*-tetrazine (III) [2] (crimson red needles), mp 178° C (decomp.) (from ethanol),  $\lambda_{\text{max}}$  305 (4.57), 410 (3.13), 530 (log  $\epsilon$  2.62) (in ethanol) was heated with an excess of orthoformic ester for 3 hr. The II was filtered off and recrystallized, mp 229-

230° C. Yield 54%. Identical with that described above in respect to its spectra in the UV, visible, and infrared regions.

In spite of the difficulty of obtaining the initial hydrazine and its derivatives, the synthetic route III → II proved to be more suitable for obtaining compounds of the new biheterocyclic system with an aryl substituent in position 6. The route I → II may find use for the production of compounds II with substituents in position 3.

Attention is attracted by the considerable hypsochromic shift of the spectrum on passing from III to II which is apparently due to the fact that because of ring fusion the  $\pi$ -electronic system of tetrazine, which is distinguished by a high equivalence of the limiting structures, is disturbed.

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