10-Methyl-3-phenyl-2H-1,3,4-thiadiazino[3,2-*a*]benzimidazolium Bromide (VI, $C_{16}H_{14}BrN_3S$). Mp 233-234°C (from water.). PMR spectrum (DMSO-D_6): 4.05 (3H, s, NCH_3); 4.9 (2H, s, CH_2); 7.66 (5H, m, arom.); 8.1 ppm (4H, m, arom.). Yield 88%.

10-Methyl-3-phenyl-2H-1,3,4-selenodiazino[3,2-*a*]benzimidazolium Bromide (VII, $C_{16}H_{14}BrN_3S$). Mp 252-253°C (decomp., from water.). Yield 98%.

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1,3-DIPOLAR CYCLOFRAGMENTATION OF A SPIROANNELATED TETRAZOLE

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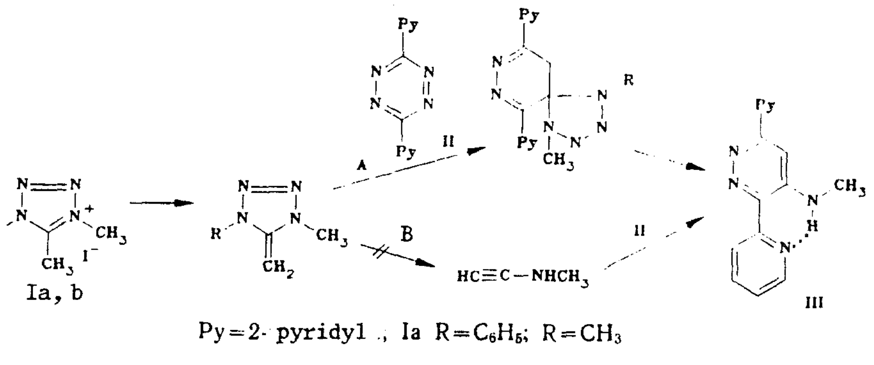
The anhydro-bases of six-membered heterocycles (acridines, xanthenes, thioxanthenes [1, 2], and quinoxalines [3]) have been shown to be capable of participating in cycloaddition reactions. The π-excessive nature of five-membered heterocycles reduces the acidity of their salts, thereby preventing the formation of anhydro-bases on treatment with tertiary amines (hydroxylic bases decompose s-tetrazines, but azolium cations usually convert them into the pseudobases). In the case of the five-membered heterocycle with the best acceptor properties, however (tetrazole), we have been able to carry out the reaction under the usual conditions. On boiling an alcoholic suspension of the tetrazolium iodide (I) and 3,5-di-(2-pyridyl)-s-tetrazine (II) in the presence of triethylamine, there was obtained 90% of 4-methylamino-3,6-di-(2-pyridyl)pyridazine (III) as bright yellow needles, mp 207-209°C (from heptane). PMR spectrum (in DMSO-D_6): 3.07 (3H, d, J = 5 Hz, N–CH_3); 9.85 (1H, m, NH); 7.5-8.9 ppm (protons of the α-pyridyl and pyridazine moieties). IR spectrum: 3235 cm^{-1} (ν_{NH}, intramolecular hydrogen bond). UV spectrum (in ethanol), λ_{max}, nm (log ε): 260 (4.03), 282 (4.32), 262 (3.93). M^+ 263.

GLC analysis of the reaction products of (Ia) with (II) showed the presence of substantial amounts of phenyl azide. However, when the salt (Ia) was treated with triethylamine in the absence of the tetrazine, phenyl azide was not formed, nor was methylaminoacetylene, which would be expected to be a synthon in cycloaddition to the tetrazine to give the pyridazine (III). The reaction may thus be described as the cycloaddition of the anhydro-base of the tetrazolium salt followed by 1,3-dipolar cyclofragmentation of the spiro-coupled tetrazole (route A).



Py=2- pyridyl ., Ia R=C_6H_5; R=CH_3

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A NOVEL s-TETRAZINE ASSEMBLY

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There have been no reports, either in reviews on sym-tetrazines [1-3] or in periodicals, of the synthesis of sym-tetrazines which are bonded directly to one another by C–C bonds. The preparation of the azo-compound (Ia) has been reported [4], but it was not possible to recrystallize this compound as a result of its low solubility.

We have found that on heating a suspension of (Ia) in DMF or o-dichlorobenzene to above 90°C, nitrogen is evolved rapidly with the formation of 77% of 6,6'-diphenyl-3,3'-bis-s-tetrazine (II) as a reddish-brown solid (λ_{max} 487 nm), mp 301-308°C (from DMF). M^+ 314.

IIa, b

Ia, b

I, II a $R=C_6H_5$; b $R=4-ClC_6H_4$

Alternative structures for (IIa) in which the sym-tetrazine ring is external with respect to R, which could arise by other modes of recombination of the phenyl-s-tetrazinyl radicals formed by elimination of nitrogen, are excluded by comparing the PMR spectra of (IIa) and the model 3-phenyl-s-tetrazine. In the latter, the tetrazine ring proton resonates at δ 10.6 ppm, whereas in (IIa) only a broadened multiplet centered on δ 7.7 ppm is seen for the phenyl protons. In addition, (Ib), obtained by the general method of Ershov and Postovskii [4], in which the p-positions of the benzene rings are occupied by chlorine atoms, also loses molecular nitrogen to give 75% of the bis-s-tetrazine (IIb) as a reddish-brown solid, mp 310-312°C, M^+ 382.

Unlike mono-s-tetrazines, which undergo cycloaddition with elimination of nitrogen [5], the bis-s-tetrazines (II) add to unsaturated compounds (enamines, acenaphthylene, tolane, ketones in the presence of triethylamine, and exomethylene anhydro-bases) without loss of nitrogen.

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