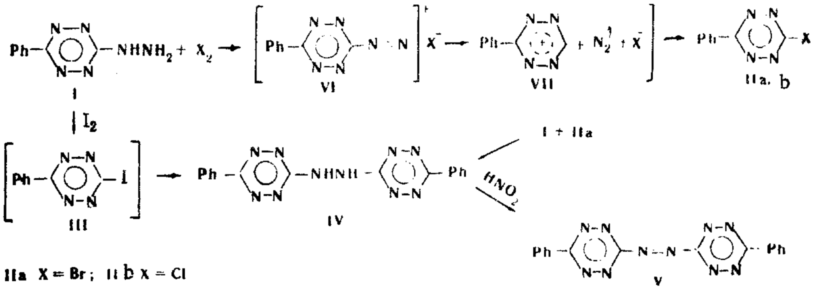
REACTION OF s-TETRAZINYLHYDRAZINE WITH HALOGENS

V. A. Ershov and I. Ya. Postovskii

UDC 547.883

In the process of studying the properties of s-tetrazine derivatives it was observed that direct replacement of the hydrazino group by halogen occurs during the action of halogens on 3-hydrazino-6-phenyl-s-tetrazine (I). Thus the reaction of I with bromine in glacial acetic acid at room temperature gave a quantitative yield of 3-bromo-6-phenyl-s-tetrazine (IIa), which was identical to that synthesized by the method in [1], while the action of chlorine gave 3-chloro derivative IIb, which could not be obtained by the method in [1].



The reaction of I with iodine proceeds slowly. The intermediate formation of iodotetrazine III is confirmed by chromatographic data, but 6,6'-diphenyl-3,3'-bistetrazinyl-1,2-hydrazine (IV), which is apparently formed by the reaction of I with III, was isolated. The structure of IV was confirmed by its synthesis from I and IIa. An investigation of the IR spectra of IV indicates the presence of NH groups (deformation vibrations of the NH_2 group are absent). A red-brown compound (V) with mp 295-298° was isolated when IV was oxidized with sodium nitrite in acetic acid. The replacement of the hydrazine group by halogen probably proceeds through diazonium compound VI, which is formed in the oxidation of I by halogen. Cleavage of a nitrogen molecule with subsequent formation of II is apparently facilitated by the possibility of the existence of stable cation radicals (VII) of the s-tetrazine ring [2].

Compound II readily nucleophilically exchanges a halogen atom for amino, hydroxy, hydrazino, and other groups. This was confirmed by an examination of the localization energies of IIa.

EXPERIMENTAL

3-Chloro-6-phenyl-s-tetrazine (IIb). Chlorine gas was passed at room temperature into a suspension of 0.5 g (2.6 mmole) of I in 10 ml of glacial acetic acid until nitrogen bubbles ceased to evolve. Finely crushed ice (20 g) was added to the resulting solution to give 0.48 g (94%) of a product with mp 125° [from

TABLE 1. Localization Energy of 3-Bromo-6-phenyl-s-tetrazine (IIa) (in β units)

Reactions	Ortho Ph	Para Ph	Meta Ph	Tetrazine C_3	C_6
Electrophilic	2,4578	2,4978	2,5428	2,6378	3,0353
Nucleophilic	2,3776	2,4176	2,5428	2,2288	2,5845
Radical	2,4177	2,4577	2,5428	2,4333	2,8099

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 571-572, April, 1971. Original article submitted November 12, 1970.

absolute alcohol−benzene (1 : 1)]. Found %: C 50.3; H 2.62; Cl 18.5; N 29.4. $C_8H_5ClN_4$. Calculated %: C 49.9; H 2.62; Cl 18.4; N 29.1.

Compound IIa was similarly obtained in 85% yield and had mp 132° (132° [1]).

6,6'-Diphenyl-3,3'-bistetrazinyl-1,2-hydrazine (IV). A. A mixture of 0.5 g (2.60 mmole) of I in 20 ml of acetic acid containing iodine was heated at 50° for 4 h to give 0.1 g (22%) of a product with mp 226-227° (from alcohol). Found %: C 55.9; H 3.51; N 41.3. $C_{16}H_{12}N_{10}$. Calculated %: C 55.8; H 3.51; N 40.7.

B. A mixture of 0.5 g (2.1 mmole) of IIa with 0.4 g (2.1 mmole) of I in 20 ml of alcohol containing 3 ml of pyridine was heated to give 0.6 g (65%) of product. IR spectrum, cm^{-1}: 3320 med, 3320 wk, 3066, 3050, 2940 m, 1601 wk, 1568, 1467, 1379, 1085, 1047, 948, 770, 698, and 582.

Diazonium Compound V. This was obtained from IV by treatment with sodium nitrite in acetic acid. Found %: C 55.9; H 3.2; N 40.95. $C_{16}H_{10}N_{10}$. Calculated %: C 56.1; H 2.9; N 40.92.

LITERATURE CITED

1. V. A. Grakauskas, A. Tomaševski, and J. P. Horwitz, J. Am. Chem. Soc., 80, 3155 (1958).
2. V. M. Tollies, W. R. McBride, and W. E. Thun, J. Am. Chem. Soc., 91, 2443 (1969).