### CHEMISTRY OF sym-TETRAZINE

### III.\* HYDROLYTIC CLEAVAGE OF sym-TRIAZOLO[4,3-b]-sym-TETRAZINE

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It was observed that unsymmetrically substituted sym-tetrazines give benzalazines during hydrolytic cleavage, while annelated sym-triazolo[4,3-b]-sym-tetrazines (III) give 4-benz-amido-1,2,4-triazoles. The results of calculations by the Pariser-Parr-Pople method made it possible to indicate the probable reason for the transfer of the reaction center during attack on the sym-tetrazine (I) ring by the OH anion on passing from I to III and to propose a mechanism for the hydrolysis. The level of the first  $\pi$ -antibonding orbital is lowered by annelation, which results in a shift of the first half-wave reduction potential to the positive region.

Recently [1] it was reported that 6-phenyl-3-tetrazinone (Ia) and its corresponding derivatives (Ib-e) in alkaline media readily undergo hydrolytic cleavage of the heteroring. Benalazine (II) is formed as a result of reaction with nitrogen evolution. Continuing the investigation, we found that 3-phenyltetrazine (If) is also cleaved to form II.



Calculations of the charges on  $C_{(3)}$  and  $C_{(6)}$  by the Pariser-Parr-Pople (PPP) method [2, 3, 4] demonstrated that for Ia the electron density on  $C_{(3)}$  is 0.814 and that on  $C_{(6)}$  is 0.851; for Ic, 0.822 on  $C_{(3)}$  and 0.858 on  $C_{(6)}$ ; for If, 0.828 on  $C_{(3)}$  and 0.835 on  $C_{(6)}$ . These results make it possible to assume that in the first phase of the hydrolysis  $C_{(3)}$  is attacked by the hydroxyl ion [1].

A two-ring compound, viz., 6-phenyl-sym-triazolo[3,4-b]-sym-tetrazine (III) [5], was obtained from 6-phenyl-3-hydrazino-sym-tetrazine (Ie). We have found that this compound also undergoes hydrolysis in alkaline media. A colorless substance with mp 235-236° and composition  $C_9H_8N_{40}^{\dagger}$  is formed as a result of reaction with nitrogen evolution.

It could be assumed that if the hydroxyl ion initially attacks  $C_{(9)}$ , which corresponds to  $C_{(3)}$  in I, the product of hydrolysis of III has the 4-benzalamino-1,2,4-triazol-3-one structure (IV). However, benzoic acid was isolated by refluxing this product with dilute hydrochloric acid. This result does not agree with structure IV. In addition, a compound with structure IV was described in [6] as having mp 178°, i.e., 60° lower than that of the hydrolysis product. It hence followed that the point of attack by the OH<sup>-</sup> anion in annelation to the tetrazine ring differs from the point of attack in the hydrolysis of I.

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<sup>\*</sup>See [1] for communication  $\Pi$ .

A compound of composition  $C_{9}H_{7}ClN_{4}O$  was obtained under similar conditions from 6-(p-chlorophenyl)sym-triazolo[4,3-b]-sym-tetrazine.

Calculations showed that the primary point of attack by hydroxyl ion in III is in all likelihood C  $_{(6)}$  rather than C  $_{(9)}$ , for here the electron density on C  $_{(9)}$  is 0.919 as compared with 0.835 on C  $_{(6)}$ . From this, it must be assumed that an isomer of IV, viz., 4-benzamido-1,2,4-triazole (V), is obtained as a result of the reaction. Difficulties are encountered in the alternative synthesis of this compound: the triazole ring is cleaved in the benzoylation of 4-amino-1,2,4-triazole [7].



Compound V could be obtained by employing the method used to synthesize sym-triazoles [8, 9]: the reaction of benzoic acid hydrazide with diformylhydrazine gave 10% of a compound with mp 235-236°, which was identical to the hydrolysis product of III.†

It follows from the quantum-chemical calculations by the PPP method that the different behavior of I and III during hydrolysis is bound up in the substantial change of the electron structure of the sym-tetrazine ring when a sym-triazole ring is annelated to it, which also shows up in the different colors of the compounds on passing from I to III. A pronounced hypsochromic shift of the absorption maxima of the  $n \rightarrow \pi *$  transitions is observed:  $\lambda_{max} 530$  nm (log  $\epsilon 2.62$ ) for Ie and  $\lambda_{max} 460$  nm (log  $\epsilon 2.64$ ) for III. This is probably induced by the appearance of a more accepting nitrogen atom of the pyrrole type instead of one of the pyridine type in the tetrazine heteroring during annelation. This also reduced the level of the lower  $\pi$ -antibonding orbitals. According to the calculations of the energies of the lower antibonding orbitals, If = -2.8026 eV, Ia = -2.6746 eV, Ic = -2.6101 eV, and III = -3.5727 eV. Since the energy of the lower antibonding orbital is a measure of the electron affinity, it should correlate with the first half-wave reduction potential [10]. This correlation was experimentally observed: III is more readily reduced than I. Thus, for the first wave,  $E_{1/2} = -0.03$  V for III, -0.48 V for Ie, -0.45 V for If, and -0.57 V for Ic.<sup>‡</sup>

# EXPERIMENTAL

<u>3-Phenyltetrazine (If)</u>. This was obtained by the method in [11] and had mp 125°. Under the conditions previously indicated for Ia [1], it was hydrolyzed to give 80% of benzalazine with mp 92-93°.

<u>4-Benzamido-1,2,4-triazole (V)</u>. A. A solution of 0.2 g of III in 4 ml of alcohol and 4 ml of 5% potassium hydroxide was refluxed for 5 min. After nitrogen evolution ceased, the solution was cooled and acidified with dilute HCl until it gave a weakly acid reaction; colorless needles of V with mp 235-236° (from 30% alcohol) precipitated in the process. The yield was 0.15 g (79%). Compound V was readily soluble in cold alcohol. Found %: C 57.7; H 4.1; N 30.  $C_9H_8N_4O$ . Calculated %: C 57.4; H 4.3; N 29.8.

B. A mixture of 1 g (11 mmole) of diformylhydrazine and 1.3 g (9.5 mmole) of benzoic acid hydrazide was heated slowly in vacuo to 200° with removal of the water formed. The readily soluble V was extracted from the reaction mass with cold alcohol. Removal of the alcohol gave 0.2 g (10%) of V with mp 235-236°. The slightly soluble residue of N,N'-dibenzoylhydrazine had mp 239-241° [12].

<sup>\*</sup>The major reaction product was N,N'-dibenzoylhydrazine.

<sup>†</sup> The potentials were measured relative to sludge mercury.

 $\frac{4-(p-Chlorobenzamido)-1,2,4-triazole.}{p-Chlorophenyl)-sym-triazolo[4,3-b]-sym-tetrazine.} Found \%: C 48.5; H 3.9; Cl 16.5; N 25.0. C_9H_7ClN_4O. Calculated \%: C 48.6; H 3.2; Cl 15.9; N 25.2.$ 

Polarographic reduction was carried out in dimethylformamide (c  $10^{-3}$  M) on a dropping mercury electrode with an LP-60 polarograph with a  $5 \cdot 10^{-2}$  M tetramethylammonium iodide background.

The spectra in the visible region of  $10^{-3}$  M solutions in alcohol were obtained with an SF-10 spectrometer.

The ionization potentials and electron affinities were taken from [13]. The two-electron integrals were calculated by the method in [14]. The *a* value was 0.06944. The following resonance integrals, which were employed repeatedly in the calculations, were taken within the PPP method:  $\beta_{c-N} = -2,576$  eV [2],  $\beta_{c-N} = -2,35$  eV [15],  $\beta_{c-C} = -2,388$  eV [2],  $\beta_{c-D} = -2.3$  eV,  $\beta_{N-N} = -2.61$  eV, and  $\beta_{N-N} = -2.35$  eV [16].

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