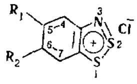

Compound	R_1	R_2	λ_{max}, nm (log ε)	Empirical formula	Found, %		Calculated, %		Yield, %
					S	Cl	S	Cl	
I	H	H	425 (3.285)	$C_6H_4ClNS_2$	34.01	18.47	33.86	18.69	56
II	H	Cl	423 (3.595)	$C_6H_3Cl_2NS_2$	28.88	31.31	28.61	31.52	100
III	CH_3O	H	420 (2.935)	$C_7H_6ClNOS_2$	29.31	16.25	29.12	16.15	79
IV	CH_3O	Cl	450 (3.291)	$C_7H_5Cl_2NOS_2$	25.31	28.00	25.23	27.91	100
V*	H	C_6H_5NH	520 (4.279)	$C_{12}H_9ClN_2S_2 \cdot ZnCl_2$	15.27	25.61	15.38	25.52	100
VI*	CH_3O	C_6H_5NH	512 (4.103)	$C_{13}H_{11}ClN_2OS_2 \cdot ZnCl_2$	14.58	23.65	14.33	23.79	100

*Double salts with zinc chloride: V · $ZnCl_2$; VI · $ZnCl_2$.

thionyl chloride on o-aminothiophenol gives compound **I** only when these substances are allowed to react briefly (1 min). The more prolonged interaction described by Huestis leads to the partial formation of the product of chlorination in position 6 (about 4% after 4 hr), the amount of which increases with an increase in the duration of the process (12% after 8 hr).

If compound I is treated with sulfur monochloride in thionyl chloride solution, chlorination in position 6 takes place quantitatively. These observations indicate that in the Herz reaction chlorination in the nucleus takes place, contrary to the statements of Huestis and Gompper [3 and 4], after the formation of **I**. Taking the high reactivity of benzothiazathionium salts to the action of nucleophiles and their incapacity for electrophilic reactions into account, it may be considered that chlorination in position 6 takes place by a nucleophilic mechanism, the sulfur monochloride or, more feebly, the thionyl chloride acting as hydride ion acceptor. Confirmation of this is the analogous reaction of 2-amino-4-methoxythiophenol which we have performed; under the action of thionyl chloride this gave 5-methoxybenzo-1,3,2-thiazathionium chloride (on brief reaction) and the product of its chlorination in position 6, which takes place considerably more easily than in the preceding case.

The content of products of chlorination in position 6 was determined by spectrophotometry of the products of the nucleophilic displacement of the chlorine atom by aniline, since the products unchlorinated in the nucleus do not react with aniline.

The table gives the analytical and spectral characteristics of the benzo-1,3,2-thiazathionium salts (**I–VI**) obtained.

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HYDROLYTIC CLEAVAGE OF THE HETERO RING OF 6-PHENYLTETRAZIN-3-ONE

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UDC 547.883

In the study of the lactam-lactim tautomerism of tetrazinone, we have made an attempt to methylate a comparatively accessible tetrazinone derivative—6-phenyltetrazin-3-one (I)—in order to obtain a derivative with a fixed tautomeric form. Methylation was carried out with methyl iodide in an aqueous alkaline medium. Instead of the expected methylation product we obtained a yellow substance with the composition $C_{14}H_{12}N_2$, mp 92° C, which proved to be benzaldehyde azine (V). The same substance was formed by heating I with aqueous alkali in the absence of methyl iodide. It was also obtained under the same conditions from 3-bromo-*, 3-amino-*, and 3-dimethylamino-6-phenyltetrazines. Evidently, in an aqueous alkaline medium all these compounds are converted into I and then undergo cleavage and give V. Cleavage does not take place in ethanolic alkali.

The mechanism of this reaction can be deduced by taking into account the results of calculations that we have carried out by the MO LCAO method in Hückel's approximation using Pullman's parameters. For **I**, the charge on $C^3 = +0.2189$ and that on $C^6 = +0.0508$. For the tautomeric hydroxy form, 3-hydroxy-6-phenyl-s-tetrazine, the charge on $C^3 = +0.0812$ and that on $C^6 = +0.0002$. It is obvious from the results of calculation (with the question of tautomerism still remaining open*), that there is a considerable positive charge on C_3,

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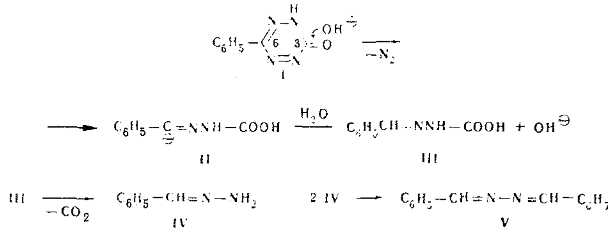
*Obtained according to Grakauskas et al. [1].

*A separate report will be made on the lactam-lactim tautomerism of the compound.

which determines the position of attack of the hydroxyl ion. From the anion **II** arising as a result of the splitting out of N_2 is formed benzylidenecarbazic acid (**III**) which undergoes decarboxylation and gives benzaldehyde hydrazone (**IV**). The latter, as is well known [2], is unstable, and two molecules disproportionate to give V and hydrazine.



Hydrolytic cleavage of I. A solution of 0.35 g (0.002 mole) of **I** in 10 ml of 5% KOH was heated in the water bath for 30 min. The color of the solution changed from dark red to yellow. The cooled solution was diluted with 100 ml of water and acidified with dil HCl to a weakly acid reaction. Yellow prisms from ethanol, mp 92° C. Yield 0.19 g (45%). Found, %: C 80.98; H 5.93; N 13.93. Calculated for $C_{14}H_{12}N_2$, %: C 80.74; H 6.81; N 13.45. The reaction product was identified as benzaldehyde azine by a comparison of the IR spectra and by a mixed melting point test with an authentic sample of benzaldehyde azine.

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AMINATION OF 5, 6-DIHYDROIMIDAZO[4, 5, 1-i, j]QUINOLINE

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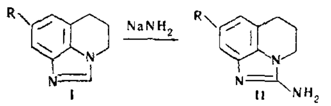
In spite of statements that the preparative importance of the Chichibabin [Tschitschibabin] reaction is limited to the production of amino derivatives of six-membered nitrogen heterocycles [1], derivatives of some five-membered systems—benzimidazole and naphthimidazole substituted in the NH group—smoothly undergo amination under the action of sodium amide [2]. We have found that 5, 6-dihydroimidazo[4, 5, 1-i, j]quinoline (I) and its derivatives can be subjected to direct amination. Compound **I** aminates at 160° C in dimethylaniline, forming the 2-amino derivative with a yield of 47%. When a methoxy group is present in position 8, the reaction takes place even at 120° C and the yield rises to 75%.



R = H, CH_3O

2-Amino-5, 6-dihydroimidazo[4, 5, 1-i, j]quinoline (IIa). Colorless crystals with mp 199–200° C (from water) (according to the literature [3], 201–202° C). p-Nitrobenzylidene derivative, yellow crystals with mp 151–153° C (from aqueous ethanol). Found, %: N 18.49. Calculated for $C_{17}H_{14}O_2N_4$, %: N 18.29.

2-Amino-8-methoxy-5, 6-dihydroimidazo[4, 5, 1-i, j]quinoline (IIb). Colorless prisms with mp 229–230° C (from water). Found, %: C 65.06; H 6.67; N 20.45. Calculated for $C_{11}H_{13}ON_3$, %: C 65.00; H 6.45; N 20.67. With p-nitrobenzaldehyde it forms an anil. Red prisms with mp 210–211° C (from ethanol). Found, %: N 16.36. Calculated for $C_{18}N_{16}O_3N_4$, %: N 16.62.

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