chloride which separated was filtered off, the solvent distilled off, and the resinous residue dissolved in acetone, with addition of active charcoal. Yield 1 g (33%), colorless rhombic plates mp 214-215° (from alcohol). Soluble on heating in water, insoluble in benzene, chloroform, dioxane. Found: C 24.90; H. 3.32; N 15.64; S 15.59%. Calculated for $C_4H_6N_8S$: C 24.24; H 3.05; N 15.56; S 16.17%.

In the IR spectrum (IKS-14, NaCl prism) a strong narrow absorption band at 1076 cm^{-1} was observed, corresponding to vibration of the tetrazole ring.

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HETEROATOM DERIVATIVES OF AZIRIDINE.

II. Reaction of N, N'-Diaziridinylsulfide, -disulfide, -sulfoxide, and -sulfone with Methyl Iodide*

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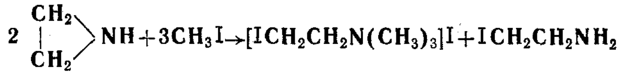
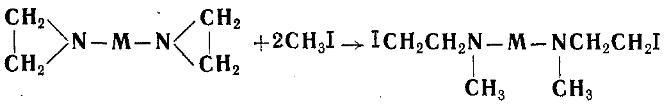
Reaction of N, N-diaziridinylsulfide, -disulfide, -sulfoxide, and -sulfone with methyl iodide, which takes place with opening of the ethyleneimine ring to give respectively N, N'-dimethylbis(β-iodoethylamino) sulfide, -disulfide, -sulfoxide, and sulfone, is investigated. The first three compounds are obtained in up to 70% yield, while the yields of the rest are inconsiderable. The properties of these substances are investigated, and their IR spectra determined. The higher alkyl iodides do not react similarly.

Ethyleneimine reacts very readily with methyl iodide, with opening of the aziridine ring, and formation of trimethyl-β-iodoethylammonium iodide [3]:



The present investigation of the reaction of methyl iodide with the previously described [1, 4] N, N'-diaziridinylsulfide (I), -disulfide (II), -sulfoxide (III), and -sulfone (IV) showed that in all cases enlargement of the ethyleneimine ring occurred. However, unlike the case of ethyleneimine, only one molecule of CH_3I added to each aziridine ring of I-IV. Reaction leads to formation of the corresponding N, N'-dimethylbis (β-iodoethylamino) derivatives V-VIII [2]:



I–IV V–VIII

$M=S(I,V);\ S_2(II,VI);\ SO(III,VII);\ SO_2(IV,VIII)$

The yields of addition products V-VII reach 70%, based on the starting ethyleneimine, and only VIII is formed in inconsiderable amount.

N, N'-dimethylbis (β-iodoethylamino) sulfide (V), -disulfide (VI), -sulfoxide (VII), and -sulfone (VIII) are rather stable, slightly yellow crystalline compounds, soluble in alcohol, acetone, and chloroform. Compounds VII and VIII are soluble in water.

The IR spectra of V-VIII (see Figure) support the structure put forward for them. The spectra show a new band characteristic of the C–I bond (490 cm^{-1}), and the characteristic bands of the ethyleneimine ring (1475, 3075 cm^{-1} and others) are absent. Insofar as, in consequence, a diaziridone structure for the products of addition of MeI to ethylene-

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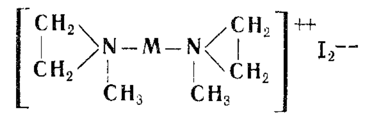
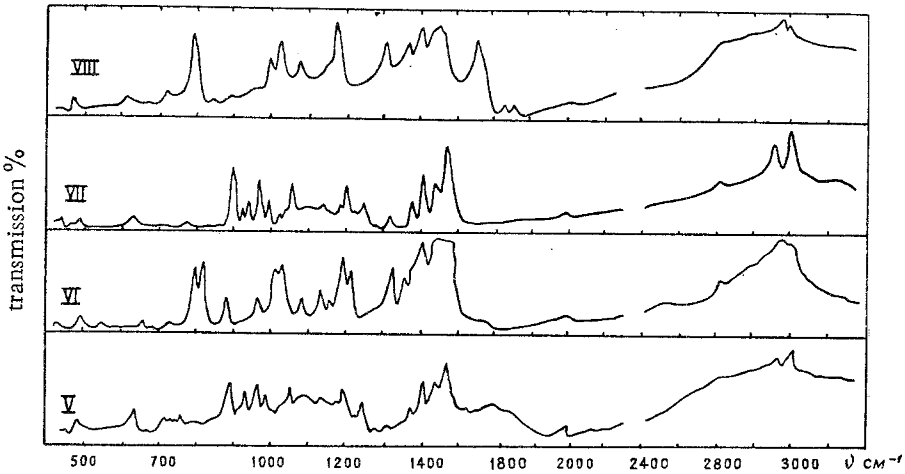
* For Part I see [1] and [2]. Presented at the Conference on Heterocyclic Rings in Organic Synthesis, Kiev, 1964.

imine is rather improbable, the possibility of the existence of a free radical ICH_2CH_2NS is of considerable interest.



Obviously its stability is conditioned by the considerable lowering of the capacity of the nitrogen atom to pass into the onium state, because of p_π -d_π interaction of its lone electron pair with the free 3-d orbitals of the sulfur atom.



IR spectra of V-VIII.

It proved impossible to prepare the addition products of I-IV with ethyl iodide and higher alkyl iodides, allyl bromide, and benzyl bromide, even by heating (only resinification observed).

The table below gives melting points, yields, and analytical data of the compounds V-VIII prepared.

$$ICH_2CH_2N(CH_3) - M - N(CH_3)CH_2CH_2I$$

Compound No.	M	Mp, °C	Molecular formula	Found, %			Calculated, %			Yield, %
				C	H	N	C	H	N	
V	—S—	170	$C_6H_{14}I_2N_2S$	18.92	3.99	6.60	18.01	3.52	7.00	43.0
VI	—S—S—	216	$C_6H_{14}I_2N_2S_2$	16.70	3.25	6.49	16.70	3.24	6.45	69.4
VII	—S(=O)—	215	$C_6H_{14}I_2N_2SO$	17.57	3.48	6.64	17.34	3.33	6.73	40.5
VIII	—S(=O)$_2$—	230	$C_6H_{14}I_2N_2SO_2$	16.63	4.00	6.21	16.68	3.26	6.48	3.0

N-N'-dimethylbis(β-iodoethylamino) sulfoxide possesses well defined physiological properties, data relating to which will be published separately.

Experimental

Starting materials. I-IV were prepared by the method previously described [1, 4]. The alkyl iodides were dried over calcium chloride, and distilled before being brought to reaction.

Analysis. Iodine was determined by Volhard titration. Carbon and hydrogen were determined as described in [5], that is, by the Dumas-Pregl procedure using nickel oxide as an oxidizing agent. The aziridine ring was estimated by titrating with 0.1 N HCl in the presence of sodium thiosulfate [6]. The IR spectra of VI-VIII were measured using a nujol suspension, but for the regions 1300-1500 and 2800-3300 cm^{-1} in hexachlorobutadiene, using a UR-10 spectrophotometer.

Two syntheses are described below, as typical examples.

N, N'-dimethylbis(β-iodoethylamino) disulfide (VI). A solution of N, N'-diaziridinyldisulfide was prepared from 0.2 mole ethyleneimine and 0.1 mole S_2Cl_2 [1, 4], and 50 ml methyl iodide added to it. The reaction mixture was left overnight in a refrigerator at 0°. The white precipitate of addition product formed was filtered off and washed with petrol ether, mp 215°, yield VI 30 g, or 69.4% based on the starting ethyleneimine. After recrystallizing from chloroform mp 265° (decomp). VI was soluble in chloroform, less soluble in acetone and alcohol, insoluble in water.

Preparation of N, N'-dimethylbis (β-iodoethylamino) sulfoxide (VII). To a solution of N, N'-diaziridinylsulfoxide, (prepared from 0.1 mole ethyleneimine and 0.05 mole $SOCl_2$) [1, 4], in 50 ml petrol ether was added 50 ml methyl iodide, and the mixture left overnight in a refrigerator at 0°. Next day the small white glistening crystals precipitated were filtered off, mp 210° (decomp). Yield of VII 8.4 g, or 40.5% based on the starting ethyleneimine. After recrystallization from alcohol it had mp 215°. Soluble in water, alcohol, chloroform.

Compounds V and VIII were prepared similarly.

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