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HETEROATOM DERIVATIVES OF AZIRIDINE

I. Reaction of Ethyleneimine With Sulfur Chlorides and Chloroanhydrides of Sulfur Acids*

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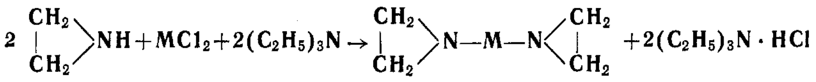
A method is worked out for synthesizing N, N'-diazirydinylsulfide, -disulfide, -sulfoxide, -sulfone, from ethyleneimine and, respectively, SCl_2, S_2Cl_2, $SOCl_2$, and SO_2CL_2 [1]. A study is made of these compounds, their IR spectra, and their complexes with picric acid and mercury salts.

Reactions of sulfur chlorides (SC_2, S_2Cl_2), and chloroanhydrides of sulfur acids ($SOCl_2$, SO_2Cl_2) with secondary aliphatic amines and some heterocyclic amines to give compounds containing the S-N link were described long ago [2-9]. They were usually effected at diminished temperature in the presence of excess amine, which latter was required to unite with the hydrogen chloride evolved.

At the same time, the reactions of ethyleneimine with sulfur halides and chloroanhydrides of sulfur acids have hitherto not been studied. Only the N-ethyleneimides of benzene and toluene sulfonic acids are known, and they are prepared by reacting ethyleneimine with benzene or toluene sulfonyl chlorides in the presence of aqueous NaOH [10, 11]. When that work was already finished, a short note was published about diaziridinylsulfoxide, which was synthesized by reacting ethyleneimine with thionylchloride in the presence of triethylamine at −80° and −20°.

It has now been found that in an inert solvent medium (ether) and at 0°, ethyleneimine reacts with sulfur mono- and dichlorides (SCl_2, S_2Cl_2) and with thionyl and sulfuryl chlorides ($SOCl_2$, SO_2Cl_2) in the presence of a hydrogen chloride acceptor (triethylamine), according to the general equation



where $M = S(I)$, $S_2(II)$, $SO(III)$. $SO_2(IV)$.

The reaction products were isolated practically pure after first removing the triethylamine hydrochloride, then distilling off volatile impurities under reduced pressure, either at room temperature or lower. Yields were 58-92% theory. Compounds I-III were further purified by high vacuum distillation.

The N, N'-diaziridinylsulfide (I), -disulfide (II), -sulfoxide (III), and -sulfone (IV) are unpeasant-smelling colorless liquids. They readily polymerize on standing or on heating, and are readily soluble in the usual organic solvents. I and II are insoluble in water, and not appreciably decomposed by it. Hence their preparation can be simplified by adding water or sodium carbonate solution to the reaction products after completion of reaction. Under those circumstances triethylamine hydrochloride dissolves, while I or II stays in the organic layer. III or IV dissolve in water, decomposing slowly.

On distilling I, II, and III at 1-3 mm, they mainly polymerize. They can be distilled only in a high vacuum. IV is even less thermally stable, polymerizing even at room temperature.

Table 1 gives physical constants, analytical data, and yields of the sulfur derivatives of aziridine.

The IR spectra of I-IV (see Figure) confirm the structures given above. Bands characteristic of the ethyleneimine ring [13], at 820, 955, 1020, 1087, 1137, 1220, 1460, and 3025 cm^{-1} are repeated in the spectra of all the compounds. The spectra also correspondingly contain bands characteristic of links S−N (680 cm^{-1}), −S−S− (415 cm^{-1}), S=O (1113 cm^{-1}), and O=S=O (1165 and 1340 cm^{-1}). All the ethyleneimine sulfur derivatives give crystalline picrates of formula

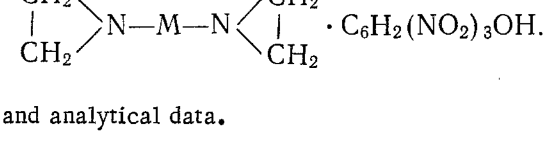


Table 2 gives their melting points and analytical data.

Compounds I-IV also form adducts with two molecules of mercurous chloride, and Table 3 gives melting points and analytical data for these.

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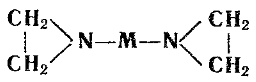
Table 1



Compound No.	M	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Formula	Found, %					Calculated, %					Yield, %
						C	H	N	S	Az*	C	H	N	S	Az*	
I	—S—	55(2) 14(0.02)	1.551	1.315	$C_4H_8N_2S$	41.00	6.78	23.01	27.33	73.50	41.41	6.89	24.13	27.62	72.32	70,7
II	—S—S—	75(2) 45(0.07)	1.587	1.285	$C_4H_8N_2S_2$	31.98	5.36	17.89	43.40	57.20	32.45	5.41	18.89	43.32	56.75	87
III	—S(=O)—	73(2) 60(0.1)	1.515	1.157	$C_4H_8N_2OS$	36.46	6.36	20.21	23.94	62.71	36.39	6.86	21.21	24.21	63.63	92
IV	—S(=O)$_2$—	—	1.451	1.0968	$C_4H_8N_2O_2S$	34.36	6.02	16.92	19.66	56.0	32.45	5.41	18.89	21.66	58.74	58**

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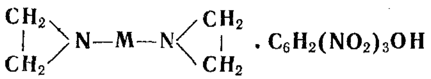
* Az – containing aziridine rings

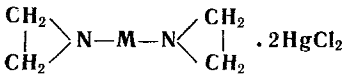
** Substance not purified (could not be distilled in a high vacuum)

Table 2



M	Mp, °C	Formula	Found, %			Calculated, %		
			C	H	N	C	H	N
—S—	175	$C_{10}H_{11}N_5O_7S$	35.20	3.63	19.81	34.82	3.21	20.30
—S—S—	154	$C_{10}H_{11}N_5O_7S_2$	31.81	3.12	18.11	31.83	2.93	18.56
—S(=O)—	137	$C_{10}H_{11}N_5O_8S$	34.93	2.98	19.40	33.27	3.07	19.41
—S(=O)$_2$—	160	$C_{10}H_{11}N_5O_9S$	31.01	3.12	18.91	31.87	2.93	18.58

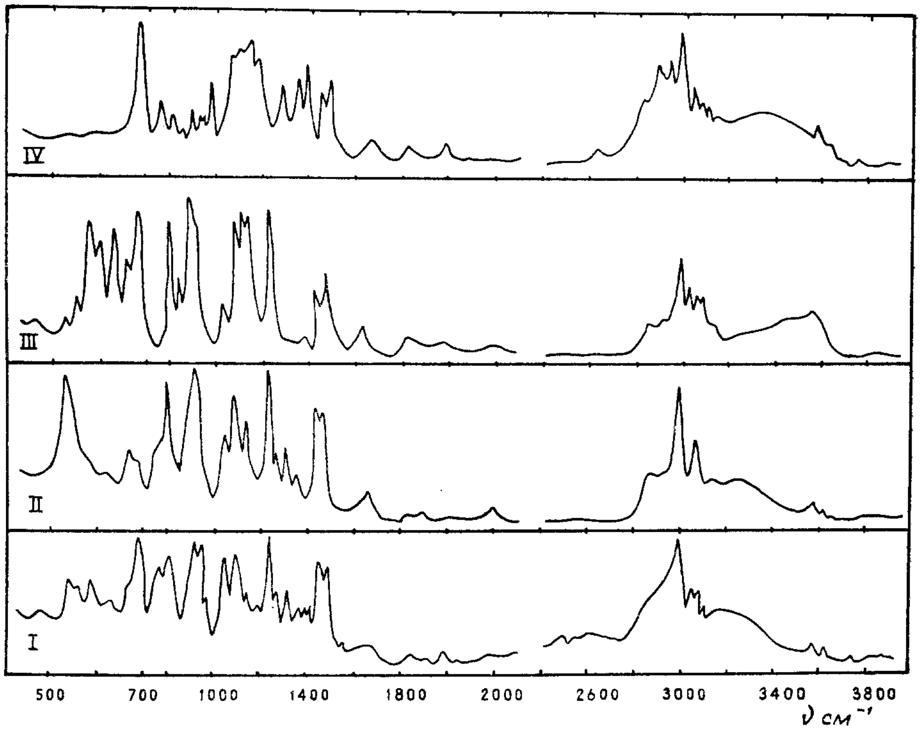
Table 3



M	Mp, °C	Formula	Found, %			Calculated, %		
			C	H	N	C	H	N
—S—	250	$C_4H_8Cl_4Hg_2N_2S$	7.30	1.20	3.59	7.29	1.22	4.25
—S—S—	215	$C_4H_8Cl_4Hg_2N_2S_2$	6.58	1.45	3.85	6.95	1.16	4.05
—S(=O)—	240	$C_4H_8Cl_4Hg_2N_2OS$	7.03	1.20	4.03	7.11	1.19	4.15
—S(=O)$_2$—	216	$C_4H_8Cl_4Hg_2N_2O_2S$	6.91	1.30	3.42	6.95	1.16	4.05

Experimental

Starting materials. The 97-98% ethyleneimine on sale was dried over sodium, and distilled. Bp 56-57°, n_D^{20} 1.4120. Sulfur mono- and dichlorides were prepared by chlorinating sulfur [14]. Thionyl chloride and sulfuryl chloride were bought. All were purified by distillation immediately before use. Triethylamine and ether were distilled over sodium.



IR spectra of N, N'-diaziridinylsulfide (I), -disulfide (II), -sulfoxide (III), and -sulfone (IV).

Analyses. Aziridine ring contents were found by titrating with 0.1 N hydrochloric acid in the presence of sodium thiosulfate [15]. Carbon, hydrogen and sulfur were determined in the microanalytical laboratory of the Institute of Organic Synthesis, AS LatvSSR, using Korshun's method [16], and nitrogen was determined by a modified Dumas-Pregl method, using nickel oxide as the oxidizing agent. IR spectra were measured with a UR-10 spectrophotometer.

N, N'-diaziridinylsulfide (I). A solution of 10.3 g (0.1 mole) sulfur dichloride in 50 ml ether was added dropwise, in 1 hr, to a solution of 8.6 g (0.2 mole) ethyleneimine and 20.2 g (0.2 mole) triethylamine in 100 ml ether cooled to 0°, and stirred, after which stirring was continued for 1 hr longer. The precipitate of triethylamine hydrochloride formed was filtered off with suction, and washed a few times with ether. From the united filtrates the ether was distilled off under reduced pressure, without heating, to a volume of 25-30 ml, this was then washed thrice with about 50 ml portions of 5-10% sodium carbonate solution to remove traces of hydrochlorides of triethylamine, ethyleneimine, and triethylamine, dried over anhydrous magnesium sulfate, filtered, and the ether completely distilled off under reduced pressure, without heating. Yield of I 8.2 g (70.7%). Yellowish oily liquid with sharp unpleasant smell, insoluble in water, but miscible with the ordinary organic solvents. Bp 55° (2 mm) (distillation accompanied by rapid polymerization), 14° (0.02 mm). Table 1 gives physical constants and analytical data.

On standing for a few days I was completely converted into water-insoluble polymer, which did not contain aziridine rings. I and picric acid gave a picrate which was bright yellow, insoluble in alcohol, acetone, and water, mp 175-177° (after heating first in alcohol, then with acetone). I and a mercuric chloride solution gave a 1 : 2 adduct, forming white crystals mp 250° (from alcohol).

N, N'-diaziridinyldisulfide (II). A solution of 13.5 g (0.1 mole) sulfur monochloride in 50 ml ether was added dropwise to a mixture of 8.6 g (0.2 mole) ethyleneimine, 20.2 g (0.2 mole) triethylamine, and 100 ml ether, which was cooled to 0° and stirred. The stirring and cooling were continued for 1 hr. The hydrochloride precipitated was filtered off, transferred to a beaker, and washed 3-4 times with portions of about 50 ml ether. The ether was distilled off from the total filtrated, under reduced pressure and without heating, till the volume was 25-30 ml. This solution was washed with 50 ml 10% sodium carbonate solution, or with water, dried over anhydrous magnesium sulfate, filtered, and the ether completely distilled off under reduced pressure, without heating. The distillation residue was practically pure II, yield 12.9 g (87%), of an oily liquid with an unpleasant smell, which readily polymerized on vacuum distilling, and on standing. Bp 75° (2 mm), distillation being accompanied by vigorous polymerization. II distilled at 45° (0.07 mm) undecomposed.

II was readily miscible with organic solvents, but was insoluble in water. Table 1 gives its physical constants and analytical data. II picrate was insoluble in water, alcohol, and acetone, and formed orange yellow needles, decomposing at 154° (after heating with alcohol and then with acetone). Mercuric chloride adduct II · $2HgCl_2$, was a white powder, consisting of small crystals, mp 215°.

N, N'-diaziridinylsulfoxide (III). 11.9 g (0.1 mole) thionyl chloride was added in an hour, with stirring, to a mixture of 8.6 g (0.2 mole) ethyleneimine, 20.2 g (0.2 mole) triethylamine, and 100 ml ether, kept at 0°, after which stirring at the same temperature was continued for a further hour. The triethylamine hydrochloride was filtered off, and washed thrice with about 50 ml 10% sodium carbonate solution, dried over anhydrous $MgSO_4$, and the ether distilled off under reduced pressure without heating. The residue was practically pure III, yield 12.15 g, or 92%, of oily, slightly yellowish liquid bp 73° (2 mm), polymerizing extensively on distillation. It distils at 60° (0.1 mm) without decomposition. Table 1 gives its physical constants and analytical data. III is readily soluble in water and organic solvents. It rapidly polymerizes on storage at room temperature. The picrate formed pale yellow needles mp 137° (from alcohol). Mercuric chloride adduct III · $2HgCl_2$, formed a white powder, mp 235-240° (decomp).

N, N'-diaziridinylsulfone (IV). A solution of 13.5 g (0.1 mole) sulfuryl chloride in 50 ml ether was added in an hour, with stirring, to a solution of 8.6 g (0.2 mole) ethyleneimine and 20.2 g (0.2 mole) triethylamine in 100 ml ether. After an hour the precipitate of triethylamine hydrochloride was filtered off, and washed with 3 lots of about 50 ml ether each. The bulked ether solutions were washed with 50 ml 10% sodium carbonate solution, dried over anhydrous $MgSO_4$, and the solvent distilled off under reduced pressure, without heating. The residue was IV, yield 8.6 g 58% theory. Oily mobile liquid, with an unpleasant smell, resinifying very rapidly on storing, or on attempting to distil it even in a high vacuum (0.01 mm). It was readily soluble in water, and organic solvents. The physical constants and analytical data are given in Table 1.

The picrate of IV was insoluble in water, alcohol, and acetone, and formed a dark yellow precipitate, mp 160-162° (after heating with alcohol, and then with acetone). Mercuric chloride adduct IV · $2HgCl_2$ had mp 216° (from hexane).

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