HETEROATOMIC DERIVATIVES OF AZIRIDINE

VII. N-Organylthioaziridines*

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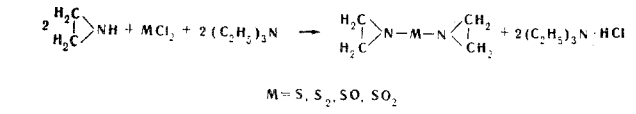
The reaction of ethyleneimine with sulfenyl chlorides RSCl at −10° C in the presence of a hydrogen chloride acceptor (triethylamine) leads to the formation of N-organylthioaziridines $RSN\overline{CH_2CH_2}$. Compounds with R = n-C_5H_{11}, C_6H_5, o-$O_2NC_6H_4$, and $C_6H_6CH_2$ have been obtained by this method. $(CH_3)_3SSN\overline{CH_2CH_2}$ and $(C_2H_5)_2NSN\overline{CH_2CH_2}$ have been synthesized analogously.

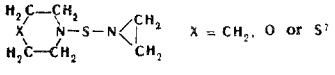
The properties and IR spectra of these compounds have been studied. The action of methyl iodide on N-phenylthioaziridine leads to disproportionation of the molecule with the formation of diphenyl disulfide, β-iodoethyltrimethylammonium iodide, and free iodine.

Aziridine derivatives containing an S–N bond have yet been little studied. Di-1-aziridinyl sulfide, disulfide, sulfoxide, and sulfone have been obtained by the reaction of ethyleneimine (I) with sulfur halides or halides of sulfur acids [2–5].



M = S, S_2, SO, SO_2

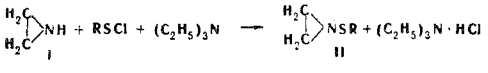
The reaction of I with trichloromethylsulfenyl chloride leads to N-trichloromethylthioaziridine $Cl_3CSN\overline{CH_2CH_2}$, which possesses marked insecticidal activity [6]. Pharmacologically active compounds of type



are also known.

We have studied the reaction of I with aliphatic, aromatic, and araliphatic sulfenyl chlorides, and also with $(C_2H_5)_2NSCl$ and $(CH_3)_3CSSCl$ [8] in order to obtain new sulfur-containing aziridine derivatives and to study their properties and physiological activity.

The reaction of I with RSCl in the presence of a hydrogen chloride acceptor (triethylamine) performed in an inert solvent at −10° C takes place in the following way:



R = n-C_5H_{11} (III), C_6H_5 (IV), o-$O_2NC_6H_4$ (V), $C_6H_5CH_2$ (VI), $(C_2H_5)_2N$ (VII), $(CH_3)_3CS$ (VIII).

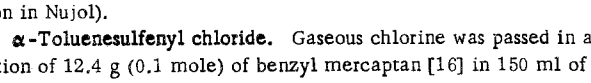
All the compounds II so formed (yields 27–76%), apart from the crystalline V with R = o-$NO_2C_6H_4$, consist of colorless liquids with a characteristic unpleasant smell which are soluble in the usual organic solvents. Their yields, physical properties, and analytical data, are given in Table 1.

Compound VIII is a representative of previously unknown substances containing the $-S-S-N\overline{CH_2CH_2}$ grouping.

The IR spectra of III–VIII satisfactorily confirm their structure. In all cases, they have bands of C–H stretching vibrations (3070 cm^{-1}) and of C–C deformation vibrations (at 850–890 and 1225 cm^{-1}) in the aziridine ring, and also of S–N stretching vibrations at 780–795 cm^{-1} (see figure). As was to be expected, this band is considerably stronger in the spectrum of VIII than in the case of the other compounds II.

The IR spectra of IV–VI have absorption bands at about 700–730, 1030, 1095, 1450, 1580, and 3050 cm^{-1} that are characteristic for aromatic compounds. The IR spectrum of V also has two bands characteristic for a nitro group attached to an aromatic nucleus (1338 and 1510 cm^{-1}). In the spectra of III, VII, and VIII there is strong absorption at about 1370–1380 and 1450 cm^{-1} (δ_{as} of CH in the CH_3–C group) and at 2930 and 2970 cm^{-1} (ν C–H).

N-Phenylthioaziridine (IV) is decomposed by CH_3I (cf. also [9]), being converted into β-iodoethyltrimethylammonium iodide (IX) and diphenyl disulfide (X) with the liberation of free iodine.



EXPERIMENTAL

Starting materials. Commercial 97–98% ethyleneimine was dried over metallic sodium and distilled. Bp 56–57° C; n_D^{20} 1.4120. The carbon tetrachloride was dried over anhydrous calcium chloride and redistilled. The initial organylsulfenyl chlorides were obtained by the chlorination of the corresponding mercaptans or disulfides with chlorine in CCl_4 [10–12] and were purified by vacuum distillation.

tert-Butylthiosulfenyl chloride $(CH_3)_3CSSCl$ was prepared by chlorinating $(CH_3)_3CSH$ under analogous conditions [13] and o-nitrophenylsulfenyl chloride by the reaction of bis(o-nitrophenyl) disulfide with sulfuryl chloride [14].

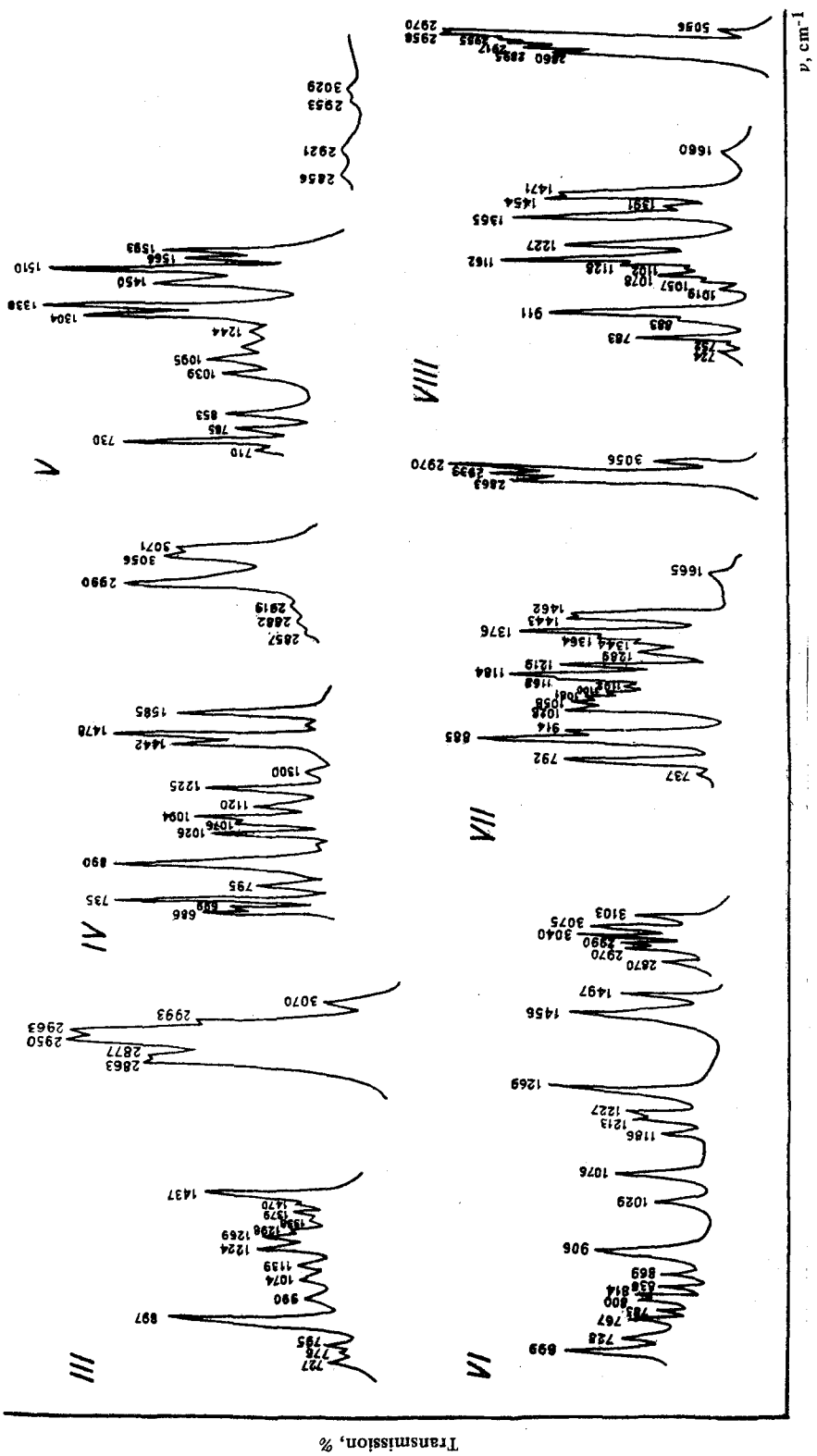
The physical constants of the initial RSCl are given in Table 2.

The IR spectra of the II were taken on an IKS-14 or a UR-10 spectrophotometer (III, IV, and VI–VIII as liquid films and V as a suspension in Nujol).

α-Toluenesulfenyl chloride. Gaseous chlorine was passed in a solution of 12.4 g (0.1 mole) of benzyl mercaptan [16] in 150 ml of CCl_4 cooled to −10° C until the increase in weight reached 7.5 g (0.106 mole). The solvent was driven off and the residue was distilled in vacuum. The yield of α-toluenesulfenyl chloride with bp 52–55° C (2 mm), n_D^{20} 1.5427, was 5.3 g (33.5%).

In the chlorination of dibenzyl disulfide under the same conditions, the yield of α-toluenesulfenyl chloride was about 10% (chlorine atoms simultaneously entered the CH_2 group).

*For communication VI, see [1].



IR spectra of N-organylthioaziridines RSNCH$_2$CH$_2$:

R=*n*-C_5H_{11} (III); C_2H_5 (IV); *o*-$O_2NC_6H_4$ (V); $C_6H_5CH_2$ (VI); $(C_2H_5)_2N$ (VII); $(CH_3)_3CS$ (VIII).

Table 1

Compound	R	bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Empirical formula	Found, %				Calculated, %				Yield, %
						C	H	N	S	C	H	N	S	
III	n-C_5H_{11}	66.9(5)	1.486	0.986	$C_7H_{15}NS$	57.84	9.91	9.83	21.49	57.90	10.40	9.64	22.08	34.2
IV	C_6H_5	95(2)	1.596	1.109	C_8H_9NS	63.28	6.01	9.48	21.21	63.57	5.95	9.26	21.17	76.3
V	o-$O_2NC_6H_4$	mp 147°	—	—	$C_8H_8N_2O_2S$	48.38	4.08	13.28	16.35	48.17	4.25	13.25	16.60	27.2
VI	$C_6H_5CH_2$	56—58 (3)	1.539	1.112	$C_9H_{11}NS$	65.21	6.36	8.12	18.93	65.44	6.66	8.47	19.41	29.3
VII	$(C_2H_5)_2N$	51—54(8)	1.479	—	$C_6H_{14}N_2S$	49.15	9.28	19.17	21.94	49.38	9.57	19.19	21.94	50.0
VIII	$(CH_3)_3CS$	77—80(8)	1.497	—	$C_6H_{13}NS_2$	43.85	7.90	8.33	37.81	44.15	7.90	8.57	39.29	46.9

tert-Butylthiosulfenyl chloride. A solution of 21.8 g (0.24 mole) of tert-butyl mercaptan was slowly added to a solution of 17.2 g (0.24 mole) of chlorine in 160 ml of CCl_4 cooled to −20° C. The solvent was distilled off at reduced pressure, and the residue was distilled in vacuum. The yield of tert-butylthiosulfenyl chloride with bp 78–83° C (10 mm) was 5.7 g (19.8%). In addition, 10.1 g of a substance with bp 105–112° C (10 mm), n_D^{20} 1.525, not further investigated, was obtained.

Table 2

Physical Constants of the Initial RSCl*

R	Bp, °C (pressure, mm)	n_D^{20}	Yield, %
n-C_5H_{11}	66—67 (6)	1.480	26.6
C_6H_5	61.5 (5)	1.612	91.0
o-$O_2NC_6H_4$	т. пл. 75	—	63.0
$C_6H_5CH_2$	52—55 (2)	1.480	33.5
$(C_2H_5)_2N$	60—65 (13)	1.499	70.1
t-C_4H_9S	78—80 (10)	1.512	22.3

*Literature data: n-$C_5H_{11}SCl$, bp 85° (7 mm), n_D^{20} 1.4829[15]; C_6H_5SCl, bp 61.5° (5 mm), n_D^{20} 1.6120[10]; o-$O_2NC_6H_4SCl$, mp 73–74.5°[12]; $(C_2H_5)_2NSCl$, bp 62–64° (13mm)[13].

N-Phenylthioaziridine (IV). A solution of 20.0 g (0.14 mole) of benzenesulfenyl chloride in 100 ml of dry carbon tetrachloride was added dropwise to a solution of 5.83 g (0.14 mole) of I and 14.4 g (0.14 mole) of triethylamine in 200 ml of the same solvent cooled to −10° C. After the end of the reaction, the mixture was stirred for 1 hr and the precipitate of triethylamine hydrochloride was filtered off (16.9 g, 96.5%). The solvent was distilled off under reduced pressure and the residue was distilled in vacuum. The yield of **IV** with bp 95–96° C (2 mm), d_4^{20} 1.1090, n_D^{20} 1.5965, was 15.8 g, or 76.3%.

Compounds **III** and **VI–VIII** were obtained similarly.

o-Nitrophenylthioaziridine (V). Synthesized in the same way as **IV**. The residue from the distillation of the solvent (oil) was treated with ether. The crystalline mass formed was filtered off and washed with ether. Light yellow crystals with mp 146–147° C failed to recrystallize.

Reaction of N-phenylthioaziridine with CH_3I. 4.3 g (0.03 mole) of CH_3I was gradually added to an ethereal solution of 1.5 g (0.01 mole) of **IV**. Lustrous brown crystals deposited from the light brown solution, and these were filtered off with suction and carefully washed with a large amount of ether (100 ml). Mp 150–160° C. After recrystallization from aqueous ethanol, faintly yellowish crystals of **IX** melting with decomposition at 222–225° C were obtained. A mixture with the β-iodoethyltrimethylammonium iodide obtained from ethyleneimine [17] and having mp 228° C melted without depression. Found, %: C 18.03; H 4.20; N 3.83; I 76.45. Calculated for $C_5H_{13}I_2N$, %: C 17.61; H 4.75; N 4.01; I 74.46.

When the filtrate was evaporated, white crystals of **X** separated out with mp 58° C. Found, %: C 68.70; H 4.27; S 27.56. Calculated for $C_{12}H_{10}S_2$, %: C 69.42; H 4.13; S 26.50.

A mixture with diphenyl disulfide melted without depression.

The ether used for washing the **IX** was found by titration with 0.1 N sodium thiosulfate solution to contain 1.01 g (0.004 mole) of free iodine.

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