

Experimental evidence indicates that the cerium-bearing inhibitor entity may be present as small macromolecules formed by crosslinking one cerium-MHS molecule with one or several siloxane molecules, as larger crosslinked clusters containing several molecules of each kind, or as colloidal ceric oxide particles a micron or more in diameter. The latter are stabilized by surface linking to silicone or cerium-MHS molecules. Clear dispersions and maximum inhibition are obtained with the smaller units; the procedures for the preparation of the inhibited silicone are dictated largely by the need to secure small inhibitor molecules or aggregates.

ACKNOWLEDGMENT

The authors thank Ralph Little of the Surface Chemistry Branch for his molecular weight determinations. They are also indebted to C. R. Singleterry for suggestions on the interpretation of experimental data.

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RECEIVED June 7, 1965. Accepted November 4, 1965.

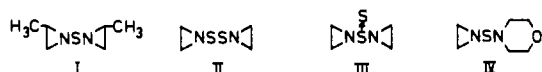
Aziridines. XIV. *N*-Organomercaptoaziridines, a New Class of Aziridine Derivatives

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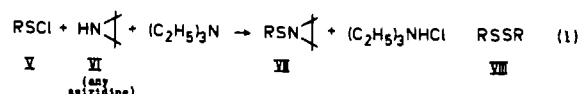
By using five sulfenyl chlorides and three aziridines, 14 *N*-organomercaptoaziridines, representing a new class of aziridine derivatives have been prepared. One of the new compounds, 1-phenylmercaptoaziridine, is effective as a chemosterilant of the screw worm fly.

ONLY A FEW EXAMPLES of aziridine derivatives containing a nitrogen-divalent sulfur bond have been reported in the literature. For example, the reaction of sulfur dichloride with 2-methylaziridine gives the diaziridine sulfide I in poor yield (1). Reaction of ethylenimine with sulfur monochloride, S₂Cl₂, gives a 1,1'-dithiodiaziridine, but it is not clear whether the structure should be represented as II or III (1). The preparation of some mixed aziridine-cyclic secondary amine sulfides, such as IV, has been reported in a German patent (3).



In view of the reports of the biological activity of aziridine derivatives, it appeared desirable to attempt the preparation of some representative examples of the previously unreported class of aziridine derivatives, the *N*-organomercaptoaziridines

VII, for testing as insect chemosterilants. The desired preparation was readily accomplished by addition of an organosulfenyl halide V to a solution of an aziridine VI in an inert solvent in the presence of triethylamine, according to Equation 1. In this way, 14 different organomercaptoaziridines were prepared, using five different halides and the three aziridines, ethylenimine, 2-methylaziridine, and cyclohexenimine. The products were isolated in satisfactory yields of 50-98%. A disulfide, VIII, was sometimes formed in small yield as a by-product in the preparation.



The phenyl, *p*-chlorophenyl, *p*-bromophenyl, and trichloromethylmercaptoaziridines were isolated as colorless liquids having a persistent, characteristic odor. They were sufficiently stable to heat to permit purification by vacuum distillation at

Table I. Properties of the *N*-Organomercaptoaziridines, Formula VII

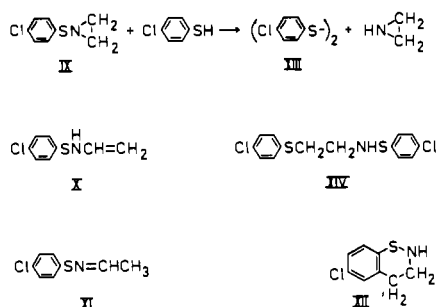
Group R	Formula	Yield, %	B.P., °C./Mm. of Hg and n_D^{25} or M.P., °C.		Analyses					
					Calculated			Found		
					C	H	N	C	H	N
FROM ETHYLENIMINE										
Phenyl	C ₈ H ₉ NS	66	72/0.04	1.5909	63.54	6.00	9.26	63.02	6.00	8.93
<i>p</i> -Chlorophenyl	C ₈ H ₈ NSCl	50	78/0.03	1.6055	51.75	4.34	7.55	51.87	4.25	7.80
<i>p</i> -Bromophenyl	C ₈ H ₈ NSBr	69	108/0.05	1.6260	41.75	3.50	6.09	41.41	3.47	5.68
2,4-Dinitrophenyl	C ₈ H ₇ N ₃ O ₄ S	81	146-7		39.83	2.93	17.42	40.20	3.01	17.11
FROM 2-METHYLAZIRIDINE										
Trichloromethyl	C ₄ H ₆ NSCl ₃	98	52/0.15	1.5245	23.26	2.93	6.78	23.38	3.18	6.78
Phenyl	C ₉ H ₁₁ NS	57	70/0.03	1.5736	65.41	6.71	8.48	65.51	6.66	8.72
<i>p</i> -Chlorophenyl	C ₉ H ₁₀ NSCl	72	90/0.02	1.5850	54.12	5.05	7.01	54.32	5.11	7.11
<i>p</i> -Bromophenyl	C ₉ H ₁₀ NSBr	89	89/0.03	1.6031	44.27	4.13	5.74	43.72	4.11	5.14
2,4-Dinitrophenyl	C ₉ H ₉ N ₃ O ₄ S	76	98-100		42.35	3.55	16.96	42.94	3.78	16.57
FROM CYCLOHEXENIMINE										
Trichloromethyl	C ₇ H ₁₀ NSCl ₃	67	66/0.04	1.5415	34.09	4.09	5.68	34.22	3.91	5.82
Phenyl	C ₁₂ H ₁₆ NS	61	95/0.02	1.5846	70.20	7.36	6.82	69.78	7.10	6.43
<i>p</i> -Chlorophenyl	C ₁₂ H ₁₄ NSCl	72	120/0.04	1.5910	60.11	5.89	5.85	60.37	5.92	5.95
<i>p</i> -Bromophenyl	C ₁₂ H ₁₄ NSBr	65	127/0.02	1.6113	50.70	4.97	4.93	50.65	4.92	5.13
2,4-Dinitrophenyl	C ₁₂ H ₁₃ N ₃ O ₄ S	82	160-1		48.80	4.44	14.23	48.69	4.40	13.86
					S,10.86			S,10.94		

50°-130° C. The 2,4-dinitrophenylmercaptoaziridines were orange solids which were readily recrystallized from alcohol. Properties and analyses of the new compounds are listed in Table I.

In view of the frequently observed ring-opening and isomerization reactions of aziridines (2), it seemed advisable to secure alternative evidence for the assigned structures. The determination of the nuclear magnetic resonance spectrum proved to be particularly suitable for this purpose. For example, the spectrum illustrated in Figure 1 clearly supports structure IX for 1-(*p*-chlorophenylmercapto)-aziridine, and excludes such isomeric structures as X, XI, and XII.

Many *N*-substituted aziridines characteristically undergo ring-opening reactions with retention of the bond to the *N*-substituent. However, the nitrogen-sulfur bond in the *N*-organomercaptoaziridine was readily cleaved. For example, 1-(*p*-chlorophenylmercapto)-aziridine IX reacted with *p*-chlorobenzenethiol to give *S,S'*-bis-(*p*-chlorophenyl) disulfide XIII, rather than the anticipated product, XIV. Ethylenimine is assumed to be the other product of this reaction. On treatment of compound IX with methyl iodide in ethanol, a crude, crystalline product was obtained which contained no sulfur and appeared to be a mixture of *N,N,N*-trimethyl-(2-iodoethyl) ammonium iodide and *N,N*-dimethyl-(2-iodoethyl) amine.

Studies of 1-phenylmercaptoaziridine, conducted by the U.S. Department of Agriculture, Beltsville, Md. indicate that it is moderately effective as an oral chemosterilant on the screwworm fly at 0.1% concentration, but is not effective against the Mexican fruit fly.



EXPERIMENTAL

Reagents Ethylenimine, 2-methylaziridine, and 2,4-dinitrobenzenesulfonyl chloride were obtained from commercial sources. Cyclohexenimine (7-azabicyclo [4.1.0] heptane) was prepared as described (5). Perchloromethyl mercaptan was obtained from the Hooker Chemical Company. The other arenosulfonyl chlorides were prepared by treatment of the corresponding benzene thiols with chlorine in carbon tetrachloride solution.

Preparation of *N*-Organomercaptoaziridines. The following procedure was typical. A solution of 36.2 grams of benzenesulfonyl chloride in 50 ml. of ether was added dropwise with stirring and cooling to a solution of 14 ml. of ethylenimine and 27.5 grams of triethylamine in 200 ml. of ether, and the reaction mixture was stirred for two more hours at 0° C., then warmed to room temperature. The precipitate of triethylammonium chloride was removed by filtration and rinsed with 10 ml. of ether. Ether was removed from the filtrate by distillation and the residue was distilled at low pressure. After 1-phenylmercaptoaziridine had been collected, a small, higher-boiling fraction was identified as *S,S'*-diphenyldisulfide, m.p. 60-61° C. after recrystallization from hexane. (lit. (4), m.p. 61° C.).

Anal. Calcd. for C₁₂H₁₀S₂: C, 66.01; H, 4.62; N, 0.0.

Found: C, 65.63; H, 4.61; N, <0.3.

Similarly, recrystallization of the still-pot residue from the preparation of 1-(*p*-chlorophenylmercapto)-aziridine gave *S,S'*-

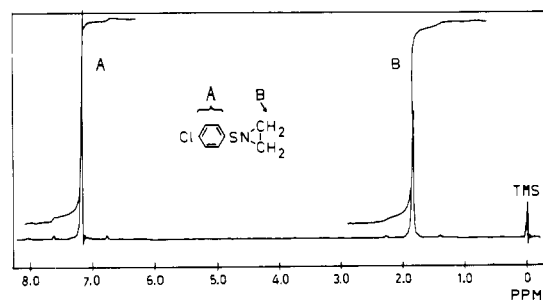


Figure 1. Nuclear magnetic resonance spectrum of 1-(*p*-chlorophenylmercapto)-aziridine IX, including integration curves

di-(*p*-chlorophenyl)-disulfide, m.p. 70–71° (lit. (6), m.p. 70–71°).

Anal. Calcd. for C₁₂H₈Cl₂S₂: C, 50.02; H, 2.81; N, 0.0.

Found: C, 50.37; H, 3.02; N, <0.3.

The *N*-2,4-dinitrophenylmercaptoaziridines were not distilled, but were purified by recrystallization from ethanol.

Reaction of 1-(*p*-Chlorophenylmercapto)-aziridine with *p*-Chlorobenzenethiol. A solution of 1.108 grams of 1-(*p*-chlorophenylmercapto)-aziridine and 0.871 grams of *p*-chlorobenzenethiol in 20 ml. of benzene was allowed to stand for several hours at 30° C. Evaporation of the benzene and recrystallization of the residue from hexane gave 1.473 grams of *S,S'*-di-(*p*-chlorophenyl)-disulfide, m.p. 71–72°, undepressed on admixture with an authentic sample.

Reaction of 1-(*p*-Chlorophenylmercapto)-aziridine with Methyl iodide. A solution of 1.0 grams of 1-(*p*-chlorophenylmercapto)-aziridine and 2.0 ml. of methyl iodide in 10 ml. of ethanol was allowed to stand at room temperature for several days. The solution became deep purple and a crystalline solid separated, which melted with decomposition at 236° C. and appeared to decompose on attempted recrystallization. The crude material was analyzed.

Anal. Calcd. for C₅H₁₃NI₂ + 0.3 C₄H₁₀NI: C, 18.58; H, 4.03; N, 4.55.

Found: C, 18.94; H, 4.05; N, 4.24.

ACKNOWLEDGMENT

This investigation was supported in part by Public Health Service Grant No. GM-11883 from the National Institute of General Medical Sciences.

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RECEIVED for review June 14, 1965. Accepted November 9, 1965.

Boiling Points and Boiling Point Numbers of Perfluoroalkyl Compounds Containing Chlorine, Bromine, Iodine, Nitrogen, and Oxygen

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Application of the Kinney equation: b.p. in °C. = 230.14(total boiling point number)^{1/3} - 543 and of the new equation: total boiling point number = a + b (number of carbon atoms) + c furnishes satisfactory results (a simple average error of 1.2° and a maximum error of 4.4°) in calculations of normal boiling points of 175 compounds. These compounds include 108 perfluoroalkyl chlorides, bromides, and iodides and also 67 perfluoroalkyl compounds in 10 different series: acyl chlorides, primary, secondary, and tertiary amines; azomethines, diazo compounds, ethers, ketones; perfluoro (β -alkoxypropionic) acids; and nitro compounds. Thirty-five values for constants *a*, *b*, and *c*, including a value for the ring—and also seven atomic boiling point numbers for carbon and the four halogens in perfluoroalkyl chlorides, bromides, and iodides—are given.

ACCCEPTABLE RESULTS occur in application of the Kinney equation (34):

$$\text{b.p. in } ^\circ\text{C.} = 230.14(\text{total boiling point number})^{1/3} - 543 \quad (1)$$

in calculations of the normal boiling points of hydrocarbons (34–36), silanes and organosilicon compounds (37), boranes and alkylboron compounds (1), alkyl derivatives of bivalent sulfur, selenium, and tellurium (1), organic derivatives of trivalent phosphorus (1) and arsenic (1), perfluoroalkanes, perfluorocycloalkanes, and perfluoroalkenes (1), and some substituted perfluoroalkanes. These substituted perfluoroalkanes include linear perfluoro monocarboxylic acids, perfluoro (β -alkoxypropionyl) fluorides, and also lone hydrogen, isocyanate, nitroso, perfluorooxacyclobutyl, sulfonyl fluoride, and the SF₄ or SF₅ groups (1).

Different methods (23, 46) are available for calculation of the normal boiling points of 6 or 13 linear perfluoroalkanes.

In the immediately previous publication on some substituted perfluoroalkanes (1), there is an adequate fit of 83 compounds

in ten series with increments in boiling point number (b.p.n.) per CF₂ group in the range 2.22–2.29 through use of Equation 1 and the new general equation:

$$\text{total boiling point number} = -1.83A + 2.04B + Y \quad (2)$$

in which *A* is the number of carbon atoms in the perfluoroalkyl group or groups, *B* is the number of fluorine atoms attached to carbon, and *Y* is a substituted atom or group such as isocyanate.

Now, in turn, the present manuscript continues the study of substituted perfluoroalkanes in which the increments in b.p.n. per CF₂ group are outside the range 2.22–2.29 and thus not suited by Equation 2 above. Extensive data on the boiling points of perfluoroalkyl compounds containing chlorine, bromine, iodine, nitrogen, and oxygen offer ample ground for further study. As shown later, the development of suitable mathematical methods allows a very satisfactory fit between calculated normal boiling points and observed boiling points of 175 compounds of these types. Further equations related to Equation 2 are the backbone of the new methods.