

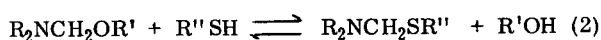
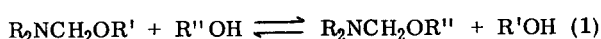
Research Laboratories, Eastman Kodak Company

Heterocyclic Azonia Derivatives Including New Spiro Ring Systems

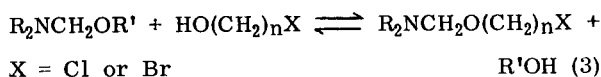
Bernard C. Cossar and Delbert D. Reynolds

A variety of heterocyclic azonia derivatives have been prepared by reaction of alkoxy-methylamines with haloalcohols and haloalkylthiols. Many of these represent new heterocyclic azoniaspiro ring systems. Evidence has been presented for structural assignments.

Alkoxy-methylamines and their thio analogues undergo transesterification (1) when allowed to react with alcohols or mercaptans (Eq. 1 and 2).



Application of these reactions to the preparation of ω -haloalkoxymethylamine (Eq. 3) has led to a



method for preparing a variety of new heterocyclic azonia derivatives. Of particular interest are the heterocyclic spiroazonia compounds all of which represent new heterocyclic ring systems.

When $n > 3$ (Eq. 3), the ω -haloalkoxymethylamines are readily obtained and, interestingly enough, they are quite resistant to intermolecular quaternization. However, when $n = 2$ or 3, the transesterification step is followed rapidly by an intramolecular displacement of the halogen to form five-membered (I) or six-membered (II) rings, respectively.

Analogous compounds (III, IV) are obtained when the corresponding haloalkylthiols react with alkoxy-methylamines.

Compounds of the foregoing type which have been synthesized and characterized are shown in Tables I-III, where X, Y, and R are defined.

Alkoxy-methylamines derived from heterocyclic secondary amines have yielded a variety of heterocyclic spiroazonia compounds. General structures of such compounds are represented by V through X, where A = O, CH₂ or CH₃N; Z = O or S; X = Cl, Br, or ClO₄ and Y is as shown in Tables IV through XI.

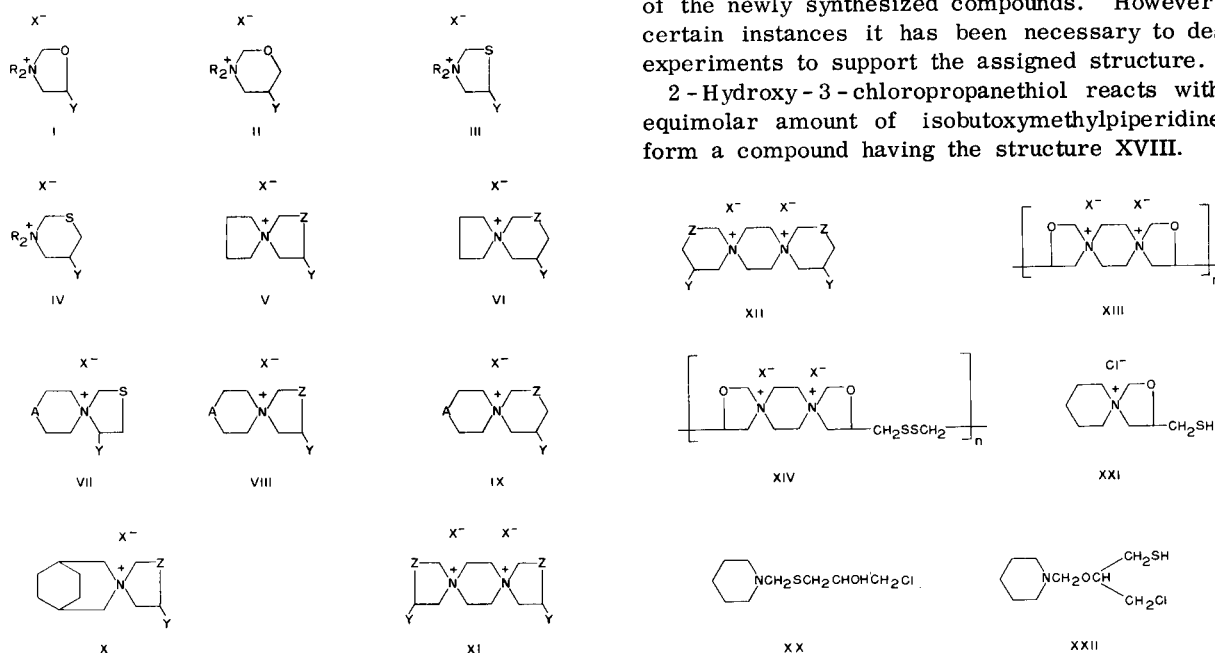
1,4-Bisalkoxymethylpiperazine reacts with ethylene- or propylene halohydrins or their thio analogues to yield tricyclic systems XII and XIII. (See Tables XII and XIII.)

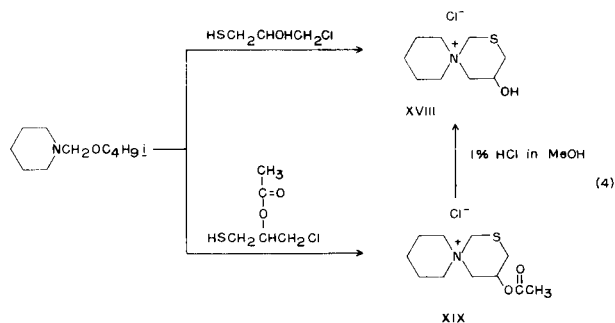
Bishalohydrins, 2,3-dihydroxy-1,4-dichlorobutane or 1,8-dichloro-3,7-dihydroxy-4,5-dithiaoctane yield the bis-type structures shown in Tables XIV and XV, respectively. These bis-halohydrins react with bisalkoxymethylpiperazine to yield structural units XIII and XIV.

Structure Assignments.

Unambiguous structures can be assigned to most of the newly synthesized compounds. However, in certain instances it has been necessary to design experiments to support the assigned structure.

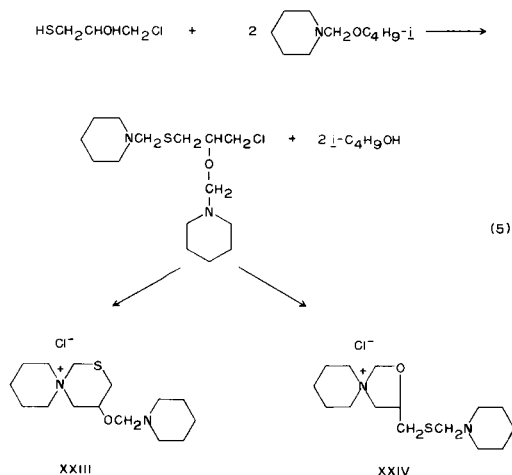
2-Hydroxy-3-chloropropanethiol reacts with an equimolar amount of isobutoxymethylpiperidine to form a compound having the structure XVIII.



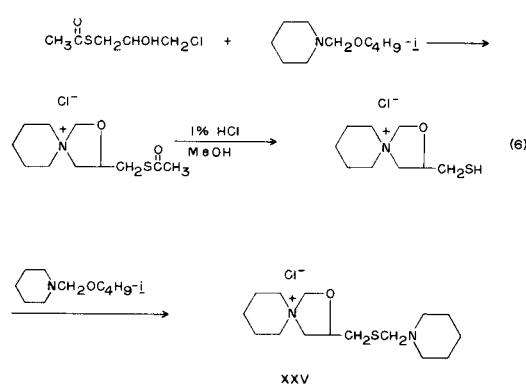


The fact that this compound does not decolorize an iodine solution supports the assigned structure. The isomeric structures XX, XXI, and XXII would react instantly with iodine. A compound identical with XVIII, as verified by melting point and infrared spectra, has been prepared by the reaction of 2-acetoxy-3-chloropropanethiol with isobutoxymethylpiperidine to produce XIX, which, upon treatment with 1% hydrochloric acid in methanol, gave a high yield of XVIII (Eq. 4). Similar proofs of structure were carried out with the corresponding morpholine and pyrrolidine derivatives.

When 2-hydroxy-3-chloropropanethiol is allowed to react with two molar equivalents of isobutoxymethylpiperidine, a transesterification occurs at both the mercapto and the hydroxy reaction sites. Subsequent intramolecular quaternization might lead to one or both of the isomeric structures XXIII, XXIV, as shown in the following scheme.

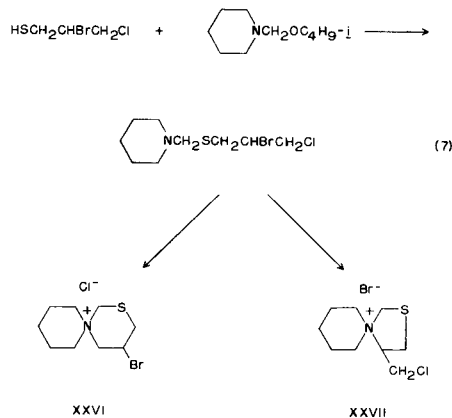


From the relative rates of formation of the five- and six-membered rings, one would predict structure XXIV. That this is correct was proved by the following transformations.



The identity of XXIV and XXV is supported by elemental analysis, infrared spectra, and iodometric titration. The corresponding structures for the morpholine and pyrrolidine derivatives are supported by analogous reactions and analytical data.

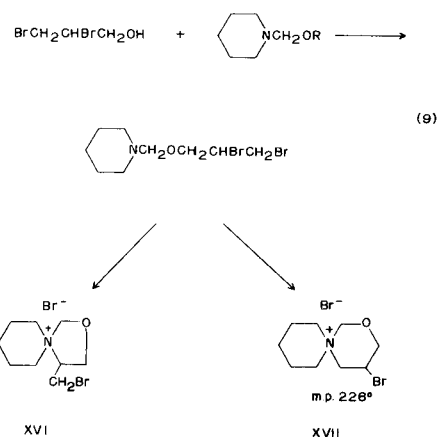
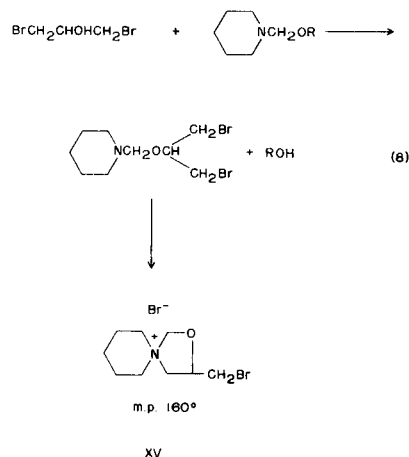
The intermediate formed by the reaction of 2-bromo-3-chloropropanethiol with isobutoxymethylpiperidine might undergo ring closure by intramolecular displacement with either the chlorine or the bromine atom. The two possible isomeric structures are represented by XXVI and XXVII.



Two strong influences, the greater ease of forming a five-membered ring and the fact that the bromine atom is a more effective leaving group, favor the formation of XXVII. These factors apparently dominate any which favor the six-membered ring (XXVI) since conversion of the products to perchlorate or tetraphenylborides by anion exchange yields salts, the analysis of which indicates that the structures are represented by XXVII.

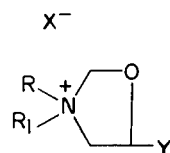
When 1,3-dibromo-2-propanol reacts with an alkoxymethylpiperidine, subsequent displacement of either bromine results in the formation of 3-bromo-

methyl-2-oxa-5-azoniaspiro-4,5-decane bromide (XV) (m.p. 160°). On the other hand, ring closure of the condensation product of 2,3-dibromo-1-propanol with an alkoxymethylpiperidine might conceivably yield XVI or its isomer XVII.

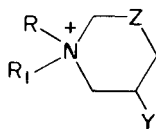


Structure XVII (m.p. 226°) is being tentatively assigned, without rigorous proof, because of the relatively greater ease of displacement of the primary *versus* the secondary bromine atom. Support for the assigned structure is found in the fact that the compounds prepared from 1,3-dibromo-2-propanol are readily quaternized by pyridine, whereas those prepared from 2,3-dibromo-2-propanol do not react under similar conditions. This behavior is in accord with the assigned structures.

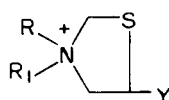
TABLE I



R	R ₁	Y	X	M. p., °C	% Calcd.		% Found	
					X	N	X	N
C ₂ H ₅	C ₂ H ₅	H	Cl	223	21.4	8.5	21.7	8.3
C ₂ H ₅	C ₂ H ₅	H	ClO ₄	194	15.4	6.1	15.8	6.3
<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	H	ClO ₄	70	10.4	4.1	10.6	4.1
CH ₃	C ₆ H ₁₁	H	ClO ₄	124	13.1	5.2	13.5	5.3
C ₂ H ₅	C ₂ H ₅	CH ₂ Cl	Cl	126	33.1	6.5	33.1	6.4
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	CH ₂ Cl	Cl	102	26.3	5.2	26.2	4.9
CH ₃	C ₆ H ₁₁	CH ₂ Cl	Cl	130	27.9	5.5	27.8	5.3
C ₂ H ₅	C ₂ H ₅	CH ₂ Br	Br	117	52.7	4.6	53.0	4.8
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	CH ₂ Br	Br	104	44.5	3.9	44.1	3.8
CH ₂ =CHCH ₂	CH ₂ =CHCH ₂	CH ₂ CN	Cl	140	15.5	12.3	14.7	11.9
CH ₃	C ₆ H ₁₁	CH ₂ CN	Cl	189	14.5	11.5	14.9	11.3
CH ₃	C ₆ H ₁₁	CH ₂ OH	Cl	wax	15.1	5.9	14.8	5.8
C ₂ H ₅	C ₂ H ₅	CH ₂ SO ₃ Na	Cl	221	12.6	5.0	12.5	4.6
CH ₃	C ₆ H ₁₁	CH ₂ SCH ₂ N(CH ₃)C ₆ H ₁₁	Cl	112	9.4	7.4	9.8	7.0

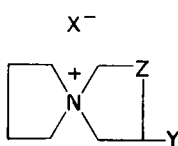
TABLE II
X⁻

R	R ₁	Z	Y	X	M. p., °C		C	H	Cl	N	S
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	O	H	ClO ₄	69	Calcd.	48.1	8.7	-	4.7	-
						Found	48.5	9.0	-	4.7	-
CH ₃	C ₆ H ₁₁	O	H	ClO ₄	159	Calcd.	46.6	7.8	12.4	4.9	-
						Found	46.3	7.7	12.8	5.2	-
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	S	H	Cl	132	Calcd.	57.2	10.4	14.1	5.6	12.7
						Found	57.1	10.0	14.5	5.7	12.4
<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	S	H	Cl	226	Calcd.	62.4	11.1	-	4.5	-
						Found	62.1	11.2	-	4.0	-
CH ₃	C ₆ H ₁₁	S	H	Cl	259	Calcd.	56.0	9.4	15.1	5.9	13.6
						Found	56.4	9.7	15.3	6.0	13.4
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	S	H	ClO ₄	110	Calcd.	45.6	8.3	11.2	4.4	10.1
						Found	45.2	8.0	11.6	4.6	9.8
<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	S	H	ClO ₄	50	Calcd.	51.7	9.2	9.5	3.8	8.6
						Found	52.2	9.4	9.8	3.7	8.2
CH ₃	C ₆ H ₁₁	S	H	ClO ₄	230	Calcd.	44.1	7.4	11.8	4.7	10.7
						Found	44.1	7.7	12.3	4.6	10.6
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	S	OH	Cl	Oil	Calcd.	53.8	9.8	-	5.2	-
						Found	52.9	9.8	-	4.8	-

TABLE III
X⁻

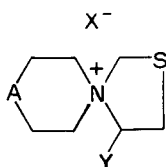
R	R ₁	Y	X	M. p., °C		C	H	Cl	N	S
C ₂ H ₅	C ₂ H ₅	H	Cl	224	Calcd.	46.3	8.9	19.5	7.7	17.6
					Found	45.8	8.9	19.9	8.0	17.4
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H	Cl	58	Calcd.	55.5	10.2	14.9	5.9	13.5
					Found	55.4	10.3	15.4	6.1	13.1
CH ₃	C ₆ H ₁₁	H	Cl	120	Calcd.	-	-	16.0	6.3	14.5
					Found	-	-	16.4	6.3	14.3
CH ₃	C ₆ H ₅	H	Cl	55 (dec.)	Calcd.	55.6	6.5	16.4	-	14.9
					Found	55.2	7.2	16.5	-	14.7
C ₂ H ₅	C ₂ H ₅	H	ClO ₄	216	Calcd.	34.2	6.5	14.4	5.7	13.1
					Found	33.9	6.3	14.6	5.9	12.9
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H	ClO ₄	159	Calcd.	43.8	8.0	11.7	4.6	10.6
					Found	43.8	7.8	12.1	4.7	10.3
CH ₃	C ₆ H ₁₁	H	ClO ₄	151	Calcd.	41.9	7.0	12.4	4.9	11.2
					Found	41.5	6.7	12.5	5.4	10.8
CH ₃	C ₆ H ₁₁	CH ₂ Cl	ClO ₄	165	Calcd.	-	-	21.2	4.2	9.6
					Found	-	-	21.1	3.9	9.4
C ₂ H ₅	C ₂ H ₅	CH ₂ SCH ₂ N(C ₂ H ₅) ₂	Cl	134	Calcd.	49.9	9.3	-	9.0	20.4
					Found	50.5	8.9	-	8.9	20.3

TABLE IV



Z	Y	X	M. p., °C		C	H	Br or Cl	N	S
O	CH ₂ Cl	Cl	162	Calcd.	45.3	7.1	33.5	6.6	-
				Found	45.1	7.1	33.6	6.4	-
O	CH ₂ Br	Br	194	Calcd.	31.9	5.0	53.0	4.7	-
				Found	32.3	5.0	52.8	4.5	-
O	CH ₂ CN	Cl	159	Calcd.	53.3	7.4	17.5	13.8	-
				Found	53.0	7.6	17.8	13.4	-
O	CH ₂ SO ₃ Na	Cl	180	Calcd.	34.4	5.4	-	5.0	-
				Found	34.5	5.4	-	4.8	-
O	CH ₂ N ⁺ ClO ₄ ⁻	ClO ₄	172	Calcd.	-	4.8	16.9	-	-
				Found	-	5.0	17.1	-	-
O	-CH ₂ SCH ₂ N	Cl	75	Calcd.	53.3	8.6	-	9.6	10.9
				Found	52.9	8.0	-	9.6	10.8
O	CH ₂ SCOCH ₃	Cl	154	Calcd.	47.7	7.2	14.1	5.6	12.7
				Found	47.5	7.0	14.3	5.7	12.6
O	CH ₂ SH	Cl	106	Calcd.	45.8	7.7	16.9	-	15.3
				Found	45.5	7.4	17.1	-	14.8
S	CH ₂ Cl	Br	175	Calcd.	35.2	5.5	-	5.1	-
				Found	34.8	6.1	-	4.8	-

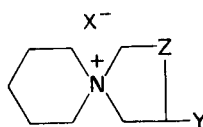
TABLE V



A	Y	X	M. p., °C	C	Calcd.				Found			
					H	N	S	C	H	N	S	
CH ₂	CH ₂ Cl	Br	235	-	-	4.9	11.2	-	-	4.6	10.9	
CH ₂	CH ₂ Cl	ClO ₄	132	-	-	4.6	10.5	-	-	4.4	10.2	
CH ₃ N	CH ₂ Cl	(C ₆ H ₅) ₄ B	178	73.3	7.1	5.2	-	73.6	7.1	5.2	-	
O	CH ₂ Cl	Br	218	-	-	4.8	11.1	-	-	4.7	10.9	
O	CH ₂ Cl	(C ₆ H ₅) ₄ B	185	-	-	2.7	6.1	-	-	2.5	6.2	

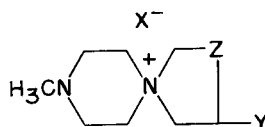
(dec.)

TABLE VIII



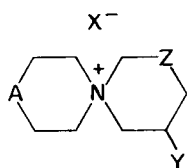
Z	Y	X	M. p., °C	Br or Cl	Calcd.			Found	
					N	S	Br or Cl	N	S
O	H	Cl	147	20.0	7.9	-	19.6	8.1	-
S	H	Cl	212	18.3	7.2	-	18.7	7.3	-
S	H	ClO ₄	126	13.8	5.4	12.4	14.2	5.4	12.2
O	CH ₂ Cl	Cl	195	31.4	6.2	-	31.3	6.2	-
S	CH ₂ SCH ₂	Cl	167	10.5	8.3	19.0	10.4	8.1	18.9
O	CH ₂ Br	Br	160	50.8	4.4	-	50.9	4.4	-
O	CH ₂ CN	Cl	197	16.2	12.9	-	16.7	12.6	-
O	CH ₂ OH	Cl	115	17.1	6.7	-	17.4	6.7	-
O	CH ₂ SO ₃ Na	Cl	248	-	4.8	10.9	-	4.6	10.6
O	CH ₂ SH	Cl	165	15.8	-	14.3	16.1	-	13.9
O	CH ₂ SCH ₂	Cl	165	11.1	8.7	10.0	11.3	8.4	10.3

TABLE IX



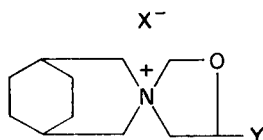
Z	Y	X	M. p., °C	C	Calcd.			Found	
					H	N	C	H	N
S	H	Cl	>200	46.0	8.2	13.4	45.9	8.6	13.5
O	CH ₂ CN	Cl	179	51.8	7.8	18.2	51.9	8.2	17.8
O	CH ₂ SO ₃ Na	Cl	113	35.0	5.9	9.1	35.4	6.2	8.7
O	CH ₂ OCH(CH ₃) ₂	(C ₈ H ₅) ₄ B	144	78.8	8.3	5.1	78.4	8.5	5.1

TABLE X



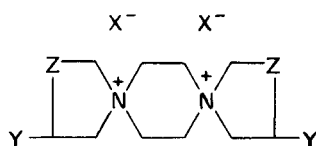
A	Z	Y	X	M. p., °C		C	H	Br or Cl	N	S
CH ₂	O	H	ClO ₄	172	Calcd.	-	-	13.9	5.5	-
					Found	-	-	13.9	5.6	-
O	O	H	ClO ₄	157	Calcd.	37.3	6.3	13.8	5.4	-
					Found	36.8	6.3	14.1	5.3	-
CH ₂	S	H	Cl	278	Calcd.	52.0	8.7	17.1	6.7	15.4
					Found	51.9	8.7	17.5	6.5	15.0
O	S	H	Cl	225	Calcd.	45.8	7.7	16.9	6.7	15.3
					Found	46.2	7.2	17.3	6.4	15.2
CH ₃ N	S	H	Cl	232	Calcd.	48.5	8.6	15.9	12.6	14.4
					Found	48.6	8.9	16.1	12.6	14.4
CH ₂	S	H	ClO ₄	145	Calcd.	39.8	7.7	13.1	5.2	11.8
					Found	40.2	7.0	13.4	5.2	11.5
CH ₂	O	Br	Br	228	Calcd.	34.3	5.4	50.7	4.4	-
					Found	34.9	5.4	50.4	4.2	-
O	O	Br	Br	205	Calcd.	30.3	4.8	-	4.4	-
					Found	30.5	4.8	-	4.1	-
CH ₃ N	O	Br	Br	130	Calcd.	32.7	5.5	48.4	8.5	-
					Found	32.5	5.4	48.3	8.4	-
CH ₂	S	OH	Cl	222	Calcd.	48.3	8.1	15.9	6.3	-
					Found	48.1	8.2	16.0	6.0	-
CH ₂	S	OCOCH ₃	Cl	258	Calcd.	49.7	8.0	13.4	5.3	12.1
					Found	49.9	7.9	13.7	5.2	12.0
O	S	OH	Cl	223	Calcd.	42.6	7.1	15.7	6.2	14.2
					Found	42.7	7.2	16.0	5.9	14.1
CH ₃ N	S	OH	(C ₆ H ₅) ₄ B	172	Calcd.	75.7	7.5	-	5.4	-
					Found	75.2	7.7	-	5.7	-

TABLE XI



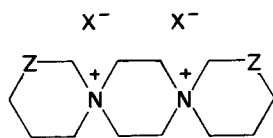
Y	X	M. p., °C		C	H	Br or Cl	N	S
H	ClO ₄	141	Calcd.	46.9	7.2	-	-	-
			Found	46.7	7.2	-	-	-
CH ₂ Cl	Cl	196	Calcd.	54.1	8.0	26.6	5.3	-
			Found	53.8	7.8	27.0	4.9	-
CH ₂ Br	Br	201	Calcd.	40.6	6.0	45.1	3.9	-
			Found	40.1	5.7	45.0	3.6	-
CH ₂ SCOCH ₃	Cl	174	Calcd.	55.0	7.9	11.6	4.6	10.5
			Found	55.4	7.7	11.6	4.5	10.1

TABLE XII



Z	Y	X	M.p., °C		C	H	Br or Cl	N	S
S	H	Cl	>200	Calcd.	-	-	23.4	9.2	21.1
				Found	-	-	23.5	9.6	21.1
S	H	ClO ₄	>255	Calcd.	27.9	4.7	-	6.5	14.9
				Found	28.1	4.8	-	6.5	14.7
S	CH ₂ Cl	Br	>200	Calcd.	29.5	4.5	-	5.7	-
				Found	29.4	4.7	-	5.6	-
S	CH ₂ Cl	ClO ₄	>230	Calcd.	27.3	4.2	26.7	5.3	-
				Found	26.7	3.7	26.4	5.0	-
O	H	ClO ₄	262	Calcd.	30.1	5.1	17.8	7.0	-
				Found	29.7	5.0	17.5	7.2	-
O	CH ₂ OH	Cl	115	Calcd.	43.5	7.3	21.4	8.4	-
				Found	43.6	7.2	21.1	8.0	-
O	CH ₂ SO ₃ Na	Cl	>215	Calcd.	28.6	4.4	-	5.6	12.8
				Found	28.2	4.6	-	5.4	12.5

TABLE XIII



Z	X	M.p., °C	C	H	Calcd.			Found				
					Cl	N	S	C	H	Cl	N	S
O	ClO ₄	272	33.8	5.7	16.6	6.6	-	33.8	5.9	16.1	6.7	-
S	ClO ₄	235	-	-	15.4	6.1	13.9	-	-	15.8	6.5	14.2
S	Cl	302	43.5	7.3	21.4	8.5	19.4	43.7	7.5	21.7	8.2	19.0

TABLE XIV

$$\text{ClCH}_2\text{CHOHCHOHCH}_2\text{Cl} + 2\text{R}_2\text{NCH}_2\text{O}-\text{C}_4\text{H}_9 \longrightarrow \text{R}_2\text{N}^+\text{C}_4\text{H}_8\text{O}^-\text{C}_4\text{H}_8\text{O}^-\text{NR}_2 + 2\text{i-C}_4\text{H}_9\text{OH}$$


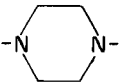
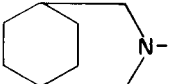
Compound	R ₂ N-	M. p. °C	Calcd.		Found	
			N	Cl	N	Cl
		>250 (dec.)	7.9	20.2	8.0	20.3
		>220 (dec.)	7.9	19.9	7.6	20.0
		>200 (dec.)	14.6	18.5	14.2	18.4
		>190 (dec.)	8.6	21.8	8.2	21.8

TABLE XV

$$\text{R}_1\text{N}^+\text{C}_4\text{H}_8\text{O}^-\text{CH}_2\text{SSCH}_2\text{C}_4\text{H}_8\text{O}^-\text{NR}_1$$

R	R ₁	M. p., °C		N	Cl
CH ₃ -	C ₆ H ₁₁ -	104	Calcd. Found	5.6 5.9	14.1 13.7
	-(CH ₂) ₅ -	>200 (dec.)	Calcd. Found	6.3 6.2	15.9 15.8
	-(CH ₂) ₂ O(CH ₂) ₂ -	114- 117	Calcd. Found	6.2 5.9	15.8 15.1
	-(CH ₂) ₄ -	50- 55	Calcd. Found	6.7 6.2	16.9 16.5

TABLE XVI

$R_2NCH_2OC_4H_9-i$							
$-NR_2$	% Yield	B. p., °C	n_D^{25}		C	H	N
$(CH_2=CHCH_2)_2N-$	82	87-88/19 mm.	1.4349	Calcd.	72.1	11.6	7.6
				Found	72.1	12.0	7.4
$(n-C_4H_9)_2N-$	89	119/19 mm.	1.4247	Calcd.	72.5	13.6	6.5
				Found	72.6	14.0	6.4
$CH_3(C_6H_{11})N-$	86	120/19 mm.	1.4497	Calcd.	72.3	12.6	7.0
				Found	72.6	12.7	6.9
	78	80/21 mm.	1.4350	Calcd.	68.7	12.2	8.9
				Found	69.1	12.2	8.6
	89	123/1.2 mm.	1.4477	Calcd.	65.1	11.7	10.8
				Found	65.0	11.9	10.8
	83	91-92/1.2 mm.	1.4736	Calcd.	73.9	11.9	6.6
				Found	74.5	12.1	6.6

EXPERIMENTAL

Isobutoxymethylamines.

These compounds were prepared according to the method of Mason and Zief (2). The morpholine (2), piperidine (3), and diethylamine (3) derivatives have been reported. Those not previously described are shown in Table XVI.

Haloalcohols.

The following compounds were purchased from Distillation Products Industries, Rochester, New York 14603: ethylene chlorohydrin, 3-chloro-1-propanol, 3-chloro-1,2-propanediol, 1,3-dichloro-2-propanol, 1,3-dibromo-2-propanol, 2,3-dibromo-1-propanol, and 4-chloro-3-hydroxybutyronitrile.

1-Methoxy-2-hydroxy-3-chloropropane and 1-isopropoxy-2-hydroxy-3-chloropropane were prepared according to the method of Flores-Gallardo and Pollard (4).

1-Chloro-2-hydroxy-sodium propanesulfonates were prepared as described by Tsunoo (5).

1,4-Dichloro-2,3-dihydroxybutane was obtained by the method of Miller (6).

Haloalkylthiols.

(a) The following chemicals were prepared by previously described methods. 2-Chloroethanethiol (7), 3-chloropropanethiol (8), 2-acetoxy-3-chloropropanethiol (8), and 2-mercapto-3-chloropropanethiol (9).

(b) 1,8-Dichloro-2,7-dihydroxy-4,5-dithiaoctane. A solution prepared from 166 g. of potassium iodide, 255 g. of iodine, and 250 ml. of water was added to a solution containing 126.5 g. (1 mole) of 2-hydroxy-3-chloropropanethiol until the iodine color just persisted. Evaporation of the benzene layer yielded the disulfide which was purified by recrystallization from toluene; yield, 64%; m.p. 49-50°.

Anal. Calcd. for $C_8H_{12}Cl_2O_2S_2$: C, 28.7; H, 4.8; Cl, 28.2. Found: C, 28.6; H, 4.9; Cl, 28.4.

(c) 2-Bromo-3-chloropropanethiol. Ninety grams of phosphorus tribromide was added to 126 g. of 2-hydroxy-3-chloropropanethiol which was stirred at 0°. After one hour, the reaction mixture was dissolved in 500 ml. of chloroform and washed well with cold water. The chloroform layer was separated, dried over anhydrous magnesium sulfate, and distilled; yield, 94 g.; b.p. 75-76°/10 mm., n_D^{25} 1.5525.

Anal. Calcd. for C_3H_6BrClS : C, 19.0; H, 3.2; Br, 42.1. Found: C, 20.9; H, 3.3; Br, 42.8.

This crude product was used without purification.

General Procedure for the Preparation of Azonia Heterocycles.

Five hundred milliliters of anhydrous benzene and 0.25 mole of haloalcohol (or haloalkylthiol) were stirred together under reflux. One-fourth mole of isobutoxymethylamine was added over a 5-minute period. Stirring and heating were continued for 30 minutes. In those cases where either reactant had two sites at which condensation could occur, the proper stoichiometric adjustments were made. The quaternary salts which precipitated from the reaction mixture were separately washed with benzene and dried.

General Procedure for the Preparation of Perchlorates.

Two-tenths of a mole of the azonia halide was dissolved in 40 ml. of water and a solution of 26 g. of sodium perchlorate in 30 ml. of water was added. The crystalline perchlorate which separated was washed thoroughly with cold water and dried.

General Procedure for the Preparation of Tetraphenylborides.

Two-tenths of a mole of azonia halide was dissolved in 20 ml. of water and treated with an equivalent of sodium tetraphenylboride. The crystalline product was washed thoroughly with cold water and dried.

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