3b, yield 1.24 grams (50%). Recrystallization from warm glacial acetic acid yielded a product having m.p. 203-204° and containing one molecular proportion of acetic acid, lit. (*10*) m.p. 203°, 203-205° (*7*), and 202-203° (*6*); recrystallization of 3b from warm ethyl acetoacetate afforded the unsolvated product, m.p. 218-220°, lit. (*1*) m.p. 222°.

The dark-red filtrate (ca. 100 ml.) was treated with 1.5*M* barium chloride (5 ml.) and then carefully neutralized at 50° with sodium carbonate; the resulting greenish red precipitate was filtered off, washed with water, and dried (yield 0.2 gram). A sample (0.1 gram) of this material was digested for 10 minutes at 50° with 2*M* hydrochloric acid (10 ml.) to give insoluble, lustrous yellow plates (0.01 gram) of barium croconate (*5*). The small amount of croconic salt (*5*) isolated from the reaction mixture presumably resulted from a benzilic acid-type of rearrangement of rhodizonic acid in the presence of air and base; this type of rearrangement was discovered by Nietzki (*10, 11*). The neutralized filtrate gave red crystals of barium rhodizonate (*5*) (0.08 gram).

Similarly, the following esters of benzenehexol (3a) were prepared: hexapropionate 3c, m.p. 140-141° (from ethanol), lit. (*1*) m.p. 137°; hexabutyrate 3d, m.p. 137-139° (from ethanol), lit. (*1*) m.p. 135°.

For the hexaisobutyrate 3e, m.p. 169-170° shrinking at 157° (from ethanol), lit. (*1*) m.p. 157°, Anal. Calcd. for $C_{30}H_{42}O_{12}$: C, 60.59; H, 7.12. Found: C, 60.50; H, 7.05.

To facilitate the isolation of the acyl derivatives 3c, 3d, and 3e, decomposition of the reaction mixture was performed with aqueous ethyl alcohol.

Acetylation of 2b into 3b and 1b. A mixture of diacetate 2b (1 gram), acetic anhydride (20 ml.), and pyridine (3 ml.) was treated according to the procedure already described. The crude reaction mixture was dried and extracted with warm ethanol (15 ml.); the undissolved solid was 3b (47%). Addition of water (5 ml.) and cooling of the filtrate gave 1b (42%). By use of different anhydrides with compound 2b, this procedure may be employed for the preparation of mixed acyl derivatives.

Formation of Tetraacetate (1b) from Rhodizonic Acid (4). Rhodizonic acid dihydrate [4, 1 gram (*5*)] was thoroughly mixed with ice-cold acetylating mixture (*3*) (25 ml.; 5 ml. of 100% phosphoric acid and 20 ml. of acetic anhydride) and kept in a refrigerator (3°) for 48 hours; decomposition of the light-yellow solution with ice water yielded light-yellow crystals of 1b (0.32 gram, 20%).

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RECEIVED for review April 19, 1968. Accepted June 25, 1968.

Preparation of Substituted Aziridinium Salts

PATRICK J. FOLEY, Jr.[1] and ROBERT S. NEALE
Union Carbide Research Institute, Box 278, Tarrytown, New York 10591

Cyclizations of several β-substituted β-chloramines, $R_2NCH_2CR(Cl)X$, to the corresponding, novel aziridinium salts have been carried out in 30 to 90% yields with silver perchlorate in benzene or acetone when X was H, alkyl, CH_2Cl, CH_2OR, CH_2SO_2R, or $Si(CH_3)_3$. However, no cyclization products could be isolated, although the chloramines did decompose, when X was Cl, Br, F, or CF_3.

RECENT REPORTS of the synthetic usefulness of simple alkyl aziridinium salts (*5, 6, 10*) prompted this study of some novel, ring-substituted analogs from the β-chloramines, I, which were readily available via the free radical addition of *N*-chloramines to substituted olefins (*8, 9*). Using substantially the method of Leonard and Paukstelis (*7*), several of the desired salts were isolated in high yield (Table I and Equations 1 through 3).

The structures of compounds IIa-h, IV, VI, VIII, and IX were assigned on the basis of their NMR spectra and combustion analyses (Tables II and III). The NMR absorptions due to the $\geqslant NCH_2$— protons at τ 6.5-6.9 appear at unusually high field and are characteristic of the aziridinium ring protons (*5*). An illustration of this is provided by the aziridinium salt IIa, which had a broad singlet at τ 6.6, and the 6-membered ring dimer (piperazinium salt, IX), which showed the singlet at τ 6.2. Although the absorption patterns in the τ 6-7 region were highly complex in the spectra of the other aziridinium salts, the absorption near τ 7 was definitive (*5*) in all cases (see Table II). The non-equivalence of the *N*-alkyl groups (except in IIa) confirmed the presence of an unsymmetrical quaternary structure, and conclusive evidence of the presence of aziridinium rings was obtained from the following chemical behavior of the salts.

Aziridinium salts react rapidly with water, methanol, and lithium chloride (*5*), in contrast to piperazinium salts such as IX, which was quantitatively recovered after 24 hours of boiling in water or methanol, or from lithium chloride in acetonitrile at room temperature. Therefore the last reaction was applied as a facile diagnostic test for the presence of the aziridinium ring in the five representative compounds IIe, IIf, IIh, IV, and VI; all except IIh afforded only the corresponding original β-chloramine (Ie, If, III, and V), as judged by NMR and thin-layer chromatography.

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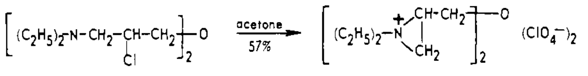
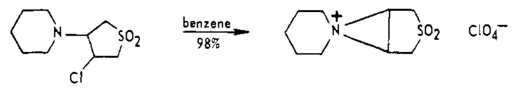
[1] Present address: Harry Diamond Laboratories, U. S. Army Materiel Command, Washington, D. C. 20438



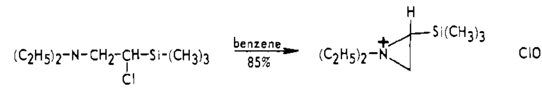
(1)

III IV



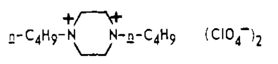
(2)

V VI



(3)

VII VIII



IX

Compound IIh gave a mixture of two products, but the major was identified from the NMR spectrum as the expected β-chloramine, Ih. The minor product, not identified, probably resulted from either chloride ion ring opening at the less hindered position or from displacement of 2,4-dichlorophenoxide ion from Ih. This clean reversal of the cyclization reaction agrees with earlier results which demonstrated the propensity of chloride ion to react with aziridinium salts at the more substituted carbon atom (*1, 3, 4, 5*).

Unfortunately, the desired aziridinium salts containing a ring halogen atom could not be isolated from reactions of β,β-dihalamines—e.g. compounds Ii-In. Thus, work-up of the tar from the reaction of Ii gave only Ii·$HClO_4$, which was identified by comparision with an authentic sample. Similarly, peaks characteristic of compound In·$HClO_4$ were observed in the NMR spectrum of the crude reaction product of compound In. A different reaction involving a cleavage of the β,β-dihalamines occurred with compounds Ij, Ik, and Im. A 45% yield of piperidinium perchlorate was isolated from the reaction of Ik, and peaks due to diethylammonium perchlorate were found in the NMR spectra of the crude reaction mixtures from compounds Ij (method 1) and Im. These reactions were not investigated further.

The behavior of compounds Ii-In apparently reflects the inability of the aziridinium ring to tolerate a strongly electronegative group in the 2-position. This is substantiated by the fact that the trifluoromethyl compound Io also produced only tar, whereas the β-trimethylsilyl compound VII reacted normally to give a high yield of the salt VIII.

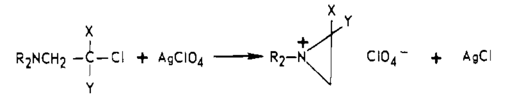
EXPERIMENTAL SECTION

Preparation of Aziridinium Salts. METHOD 1. A solution of one equivalent of the chloramine in 15 times its weight of acetone was added over a 20-minute period to one equivalent of anhydrous silver perchlorate in an equal volume of acetone at 0° C. The mixture was then allowed to warm to room temperature and was stirred overnight. The precipitated silver chloride was removed by filtration and the filtrate diluted with five times its volume of ether to precipitate the aziridinium salt, which was then collected, usually in pure form (Table III).

METHOD 2. A solution of one equivalent of the chloramine in 15 times its weight of benzene was added over 20 minutes to one equivalent of anhydrous silver perchlorate in an equal weight of benzene at about 5° C. (just warm enough to keep the solution from freezing). The mixture was then allowed to come to room temperature and was stirred overnight. The benzene was decanted from the crude solid residue, which was triturated a number of times with acetone and filtered to remove silver chloride. The acetone filtrates were combined and diluted with 5 times their volume of ether and the precipitated aziridinium salt removed by filtration.

Most of the salts were obtained analytically pure by either of these methods, but, when necessary, they could be reprecipitated from a mixture of warm isopropanol and acetone on addition of ether.

Table I. The Cyclization of β-Substituted β-Chloramines with Silver Perchlorate



Io–o IIa–h

Compound	R_2	X	Y	% Yield II	Method[a]
a	$(n\text{-}C_4H_9)_2$	H	H	70	2[b]
b	$(C_2H_5)_2$	CH_3	H	63	2
c	$(n\text{-}C_4H_9)_2$	C_2H_5	H	92	1
d	$(C_2H_5)_2$	$t\text{-}C_4H_9$	H	33	2
e	$(C_2H_5)_2$	$CH_2C_6H_5$	H	Oil	1 and 2
f	$(C_2H_5)_2$	CH_2Cl	H	82	1
g	$(CH_2)_5$	$CH_2OC_2H_5$	H	Oil	1 and 2
h	$(CH_2)_5$	$CH_2OC_6H_3Cl_2(o,p)$	H	74	1
				91	2
i	$(C_2H_5)_2$	Cl	H	Tar	1 and 2
j	$(C_2H_5)_2$	Cl	CH_3	Tar	1 and 2
k	$(CH_2)_5$	Cl	CH_3	Tar	1
l	$R_1 = t\text{-}C_4H_9$; $R_2 = C_2H_5$	Cl	CH_3	Tar	2
m	$(C_2H_5)_2$	F	H	Tar	2
n	$(CH_2)_5$	Br	H	Tar	2
o	$(C_2H_5)_2$	CF_3	H	Tar	1 and 2

[a] See Experimental Section. [b] When acetone was used as solvent, the piperazinium salt IX was isolated in 77% yield; this solvent effect has been observed previously (*2*).

Table II. NMR Spectra of Aziridinium Salts[a]

Compound	Solvent	$\overset{+}{N}$—C—H	C—CH_2—X	C—CH_2—C	C—CH_3
IIa	d_6DMSO	6.78 t, 6.60 bs (8)		8.50 bm (8)	9.02 t (6)
IIb	d_6Acetone	6.35-7.05 (7)			8.63 t, 8.60 t (6) 8.25 d (3)
IIc	$CDCl_3$	6.85 bm (7)		8.40 bm (10)	8.80 m (9)
IId	d_6Acetone	5.90-7.30 (7)			8.68 s 8.55 t, 8.50 t } (15)
IIe[b]	d_6Acetone	——6.10-7.15 (9)——			8.77 t, 8.59 t (6)
IIf	d_6Acetone	——5.35-7.30 (9)——			8.55 t, 8.50 t (6)
IIg	d_6Acetone	——5.60-6.95 (11)——		8.15 bm (6)	8.80 t (3)
IIh[c]	d_6Acetone	5.80-6.75 (7)	4.75-5.55 (2)	8.10 bm (6)	
IV	d_6Acetone	——5.45-7.30 (18)——			8.60 t, 8.55 t (12)[d]
VI[e]	d_6DMSO	——5.50-7.05 (9)——		8.30 bm (7)	
VIII[f]	$CDCl_3$	6.10-7.60 (7)			8.63 t, 8.57 t (6)
IX[g]	d_6DMSO	6.50 bm, 6.20 s (16)		8.50 bm (16)	9.04 t (12)

[a] Chemical shifts in τ-values relative to internal tetramethylsilane; s = singlet, bm = broad multiplet, etc; hydrogen count in parentheses. Boundaries for complex, unsymmetrical sharp line patterns are given without indication of multiplicity. [b] Aromatic hydrogens: 2.66 m (5). [c] Aromatic hydrogens: 2.53 m (1), 2.67 m (2). [d] The presence of but two, clean triplet methyl group absorptions suggests that IV may consist of only one of the two possible diasteromeric forms. [e] The high-field N—C—H is suggested by models to be the piperidinium α-hydrogen which lies above the aziridinium ring and projects toward one of the sulfone S—O bonds; if the S—O magnetically shields the proximate hydrogen, as might result were a C=O group involved, the observed up-field shift of one N—C—H hydrogen can be rationalized. [f] $Si(CH_3)_3$ hydrogens: 9.66 s (9). [g] Piperazinium salt.

Table III. Melting Points and Analyses of New Compounds

Compound	M.P., °C.	% Carbon		% Hydrogen		% Chlorine		% Nitrogen	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
IIa	240 d	46.96	47.21	8.67	8.67	13.86	13.67	5.48	5.06
IIb	197-8	39.35	39.76	7.55	7.64	16.59	16.44	6.55	6.46
IIc	74-5	50.79	50.83	9.23	9.32	12.49	12.40	4.93	4.86
IId	164-5	46.96	46.48	8.67	8.60	13.86	14.17	5.48	5.34
IIe	Oil								
IIf	85-6	33.89	33.68	6.09	6.16	28.58	28.39	5.64	5.66
IIg	Oil								
IIh	104-5	43.49	43.64	4.69	4.80	27.51	27.28	3.62	4.03
IV	106-9	38.10	38.18	6.86	6.84	16.07	15.89	6.35	6.53
VI[a]	168-9	35.82	35.92	5.34	5.50	11.75	11.80	4.64	4.63
VIII	164-5	39.78	39.77	8.12	8.26	13.05	13.23	5.15	5.01
IX	>280	46.96	47.20	8.67	8.81	13.86	14.19	5.48	5.51

[a] Calcd. S, 10.63; found, 10.98.

Reaction of Aziridinium Salts with Lithium Chloride. A solution of 250 mg. of the salt in 3 ml. of acetonitrile containing three equivalents of lithium chloride was stirred under 30 ml. of pentane overnight at room temperature. The pentane layer was decanted and evaporated to give the chloramine. Yields were uniformly above 80%.

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RECEIVED for review April 19, 1968. Accepted July 19, 1968.