$ArCH_3$), 3.27 (9, 2, CH_2–Ph), 3.88 (m, 2, CH_2–O), 7.1–7.8 (m, 9, Ar). This crude solution could be kept for several days in the ice chest without appreciable polymerization and was used directly in the preparation of 1-benzyl-2-aziridinemethyl bromide. Evaporation of the crude benzene solution gave an oil which would not crystallize and after standing at room temperature overnight, had polymerized.

1-*t*-Butyl-2-aziridinemethyl Bromide.—1-*t*-Butyl-2-aziridinemethyl tosylate (7.0 g, 25 mmol, as a crude oil) and tetrabutylammonium bromide (10.0 g, 31 mmol) were refluxed in 100 ml of benzene for 12 hr. After cooling to room temperature, the reaction mixture was washed with two 100-ml portions of water, dried (K_2CO_3), and evaporated to an oil (4.0 g, 97% pure by analysis of the nmr spectrum, 81% yield) which was distilled to give an analytical sample of the aziridinemethyl bromide: bp 75–80° (0.3–0.5 mm); nmr (CCl_4) δ 0.97 [s, 9, $C(CH_3)_3$], 1.38 (d, 1, H_1), 1.62 (d, 1, H_2), 1.95 (m, 1, H_3), 2.96–3.44 (m, 2, CH_2–Br).

Anal. Calcd for $C_7H_{14}BrN$: C, 43.78; H, 7.34; N, 7.29. Found: C, 43.95; H, 7.47; N, 7.00.

1-Methyl-2-aziridinemethyl Bromide.—Tetrabutylammonium bromide (7.0 g, 22 mmol) was added with stirring to a solution of 1-methyl-2-aziridinemethyl tosylate (85 mg, ~18 mmol, freshly prepared from 1-methyl-2-aziridinemethanol) in 20 ml of benzene. Within 5 min, the nmr spectrum showed that ~50% of tosylate had been converted to the corresponding aziridinemethyl bromide. The reaction mixture was allowed to stand overnight, washed with two 25-ml portions of water, dried (K_2CO_3), and evaporated to an oil which was distilled with some decomposition to yield the 1-methyl-2-aziridinemethyl bromide (100 mg, 36%): bp 80–90° (40–50 mm); nmr (CCl_4) δ 1.24 (δ, 1, H_1), 1.3–1.7 (m, 2, H_2, H_3), 2.31 (s, 3, CH_3), 3.25–3.45 (m, 2, CH_2–Br).

1-Benzyl-2-aziridinemethyl Bromide.—Tetrabutylammonium bromide (7.0 g, 22 mmol) was added to a crude solution of 1-benzyl-2-aziridinemethyl tosylate (~10 mmol) in 35 ml of benzene. This mixture was stirred for 12 hr, then washed with two 25-ml portions of water, dried (K_2CO_3), and evaporated to an oil which was distilled to give 1-benzyl-2-aziridinemethyl bromide (1.2 g, 53%): bp 100° (0.5 mm); nmr (CCl_4) δ 1.3–2.0 (m, 3, H_1, H_2, H_3), 2.9–3.7 (m, 4, CH_2), 7.22 (s, 5, Ar).

1-*t*-Butyl-2-aziridinemethyl Methyl Ether.—1-*t*-Butyl-2-aziridinemethyl tosylate (5.6 g, 20 mmol) in 20 ml of methanolic sodium hydroxide (1 *N*, 20 mmol) was allowed to stand at room temperature and the reaction followed by observation of the *t*-butyl peaks in the nmr spectra. The reaction was approximately 50% completed in 22 hr. After 2 days, in order to complete the reaction, an additional 2 ml of methanolic sodium hydroxide (15% wt/total vol, 7.5 mmol) was added and the reaction allowed to stand for several additional days. The aziridinemethyl ether was the only product observed in the nmr spectrum of the crude reaction mixture which was filtered and evaporated to an oil. This oil was dissolved in 15 ml of ether, washed with 3 ml of water, dried (K_2CO_3), evaporated, and distilled to give an analytical sample of the aziridinyl ether (2.0 g, 65%): bp 85° (water aspirator); $n^{25}D$ 1.425; nmr (CCl_4) δ 0.95 [s, 9, $C(CH_3)_3$], 1.24 (d, 1, J = 3.0 Hz, H_c), 1.42 (d, 1, J = 6.5 Hz, H_b), 1.5–1.9 (m, 1, H_a), 3.20 (d, 2, CH_2), and 3.32 ppm (s, 3, OCH_3).

Anal. Calcd for $C_8H_{17}NO$: C, 67.09; H, 11.69; N, 9.78. Found: C, 67.16; H, 11.91; N, 9.69.

1-*t*-Butyl-2-aziridinemethyl Ethyl Ether from 1-*t*-Butyl-2-aziridinemethyl Tosylate.—Sodium (0.50 g, 22 g-atoms) in 70 ml of absolute ethanol was allowed to stand until all of the sodium had reacted. 1-*t*-Butyl-2-aziridinemethyl tosylate (1.25 g, 4.4 mmol) was added and the reaction mixture refluxed overnight under nitrogen. Flash evaporation gave an oil which was extracted with ether, washed with water, dried (K_2CO_3), flash evaporated, and distilled to give the aziridinemethyl ethyl ether (~0.4 g, ~50%), bp 60° (10 mm).

Anal. Calcd for $C_9H_{19}NO$: C, 68.75; H, 12.15; N, 8.92. Found: C, 69.02; H, 12.39; N, 9.08.

Registry No.—**1a**, 25662-13-9; **1b**, 25662-14-0; **2a**, 25662-15-1; **2a** (tosylate), 25662-16-2; **2b**, 25665-28-5; **2b** (tosylate), 23398-26-7; **2b** (nosylate), 25716-11-4; **2c** (tosylate), 25662-19-5; **3**, 25665-26-3; **4**, 25662-21-9; **6**, 25662-70-8; **7**, 25662-73-1; **9**, 25662-27-5; 1-*t*-butyl-2-aziridinemethyl bromide, 25662-22-0; 1-methyl-2-aziridinemethyl bromide, 25662-23-1; 1-benzyl-2-aziridinemethyl bromide, 25662-24-2; 1-*t*-butyl-2-aziridinemethyl methyl ether, 25662-25-3; 1-*t*-butyl-2-aziridinemethyl ethyl ether, 25662-26-4.

Reaction of Aziridinemethanols with Thionyl Chloride[1]

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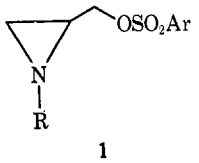
Aziridinemethanols react with thionyl chloride in the presence of base to yield aziridinemethyl chlorides (both rearranged and unrearranged), dihalamines, and 1,2,3-oxathiazolidines. The distribution among these products is a function of structure of the aziridinemethanol and the base used. The mechanisms of these reactions are discussed.

We have recently reported the investigation of the solvolytic behavior of primary aziridinemethyl sulfonates (**1**).[2] Our study of these compounds suggested



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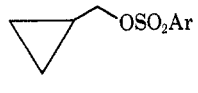

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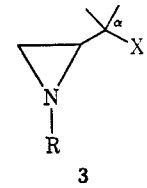
that reactivity was probably derived from classical (albeit sluggish) participation by the annular nitrogen, and thus little charge was developed on the primary carbon. These aziridines thus differ markedly from their cyclopropyl carbinyl analogs (**2**) in which participation is characterized by extensive charge delocalization. In hopes of obtaining more information concerning the interaction of the aziridine ring with adjacent cationic centers, we sought to prepare a variety of aziridinemethyl derivatives (**3**) substituted



3

at the α position by groups which would facilitate positive charge development. This paper describes various attempts to prepare these derivatives by the

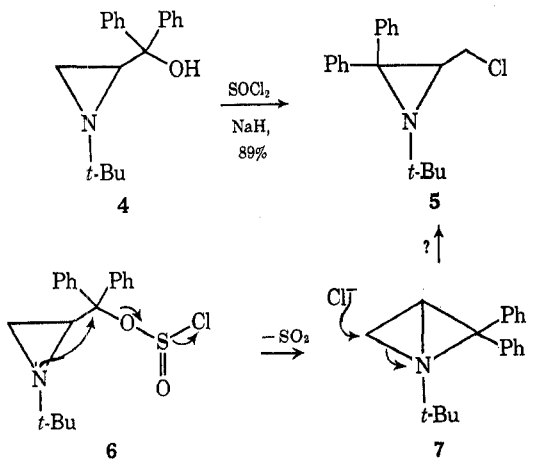
(1) Support of this research by National Science Foundation Grants GP-5531 and GP-8044 and by a Research Corporation Grant is gratefully acknowledged.

(2) J. A. Deyrup and C. L. Moyer, *Tetrahedron Lett.*, 6179 (1968).

reaction of aziridinemethanols[3] with thionyl chloride.

Results

The first such reactions studied were between **4** and $SOCl_2$ in THF with excess NaH. The latter reagent was added to consume the acid liberated during the reaction. Although the product had the proper empirical formula, it was possible to show (*vide infra*)



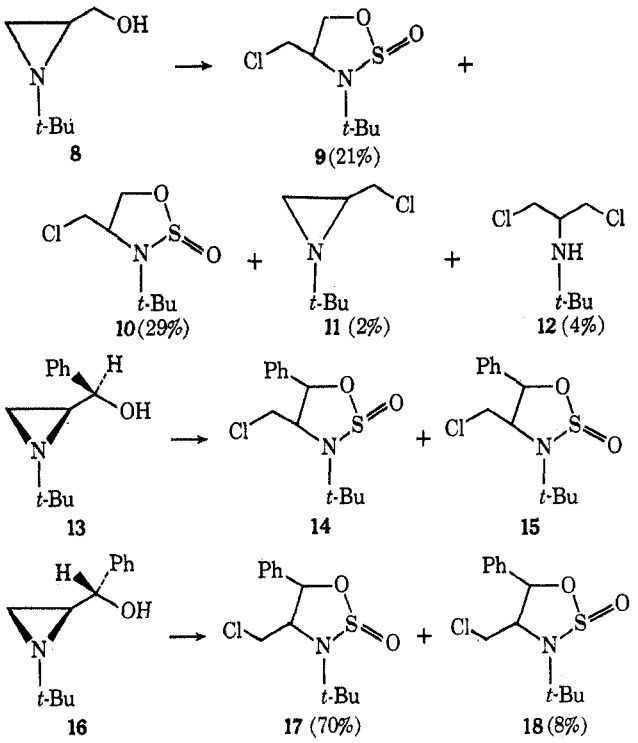
that it actually possesses rearranged structure **5**. A reasonable route to **5** would involve initial formation of chlorosulfite ester **6**. Since chlorosulfite esters apparently decompose by ion pair intermediates,[4] capture of the ion pair by the unshared nitrogen electrons could yield **7**. Nucleophilic atatck on **7** would then yield **5**. Attempted extension of this reaction revealed it to be more complex than expected. In each case, the major products were not aziridines but a mixture of isomeric 2-oxo-1,2,3-oxathiazolidines. The results of these reactions of aziridinemethanols with $SOCl_2$ and NaH in THF are summarized in Scheme I.[5]

The isolation of identifiable (**11**) and nonidentified (*e.g.*, from **13**) dichloramines indicated that the heterogeneous base NaH might not be totally effective in scavenging protons. For this reason, an alternative reaction procedure was used in which the aziridinemethanols were first converted to their lithium salts with an equivalent amount of BuLi and subsequently reacted with $SOCl_2$. The results of this procedure are summarized in Scheme II for the reaction aziridinemethanols **4**, **8**, and **13** with $SOCl_2$ in THF.

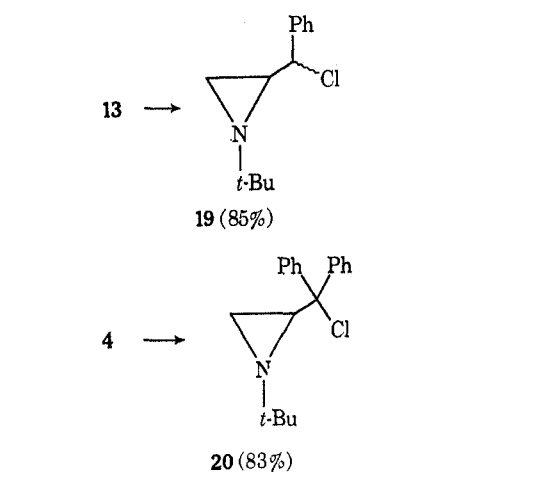
Structural Assignments.—The nmr spectra of the crude $SOCl_2$–NaH reaction mixtures were characterized by the presence of downfield (δ 1.25–1.45) *t*-Bu singlets. Separation of the reaction mixtures showed that these peaks were attributable to neutral substances which contained sulfur. These compounds have been assigned the 2-oxo-1,2,3-oxathiazolidine structure. This assignment is based partially on their elemental analyses and mass spectra. This structure is also supported by the close spectral correlation with oxathiazolidines previously prepared by an alternative route.[6] As would be expected from these earlier

(3) J. A. Deyrup and C. L. Moyer, *J. Org. Chem.*, **35**, 3424 (1970).
(4) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Wilson, New York, N. Y., 1959, p 294.
(5) The relative amounts of **9** and **10** varied somewhat from run to run.
(6) J. A. Deyrup and C. L. Moyer, *J. Org. Chem.*, **34**, 175 (1969).

SCHEME I



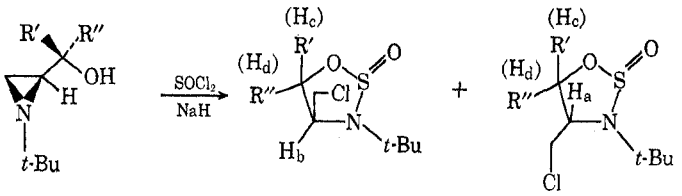
SCHEME II



results, asymmetry at sulfur results in the formation of two isomers from each aziridinemethanol. The stereochemistry is assignable on the basis of deshielding by the sulfoxide bond as previously discussed. The spectral properties of these oxathiazolidines are summarized in Table I. Open-chain dichloramine **12** was an unstable liquid which could not be isolated in pure form or fully characterized. It gave an immediate precipitate with silver nitrate and showed mass spectral peaks for the expected molecular weight (see Experimental Section). Reaction of this material with Et_3N converted it to chloroaziridine **11**. Although the nmr specturm was in agreement with the proposed structure, the N-*t*-Butyl-2,3-dichloropropylamine structure could not be excluded.

The mass spectra, elemental analyses, and infrared and nmr spectra of **5** and **20** were consistent with the aziridine structure.[3] Comparison of the nmr spectra

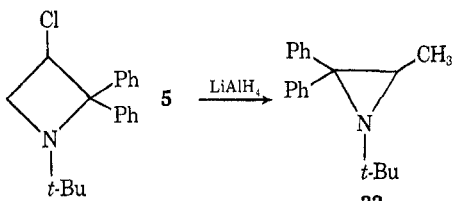
TABLE I
2-OXO-3-*t*-BUTYL-4-CHLOROMETHYL-1,2,3-OXATHIAZOLIDINES FROM AZIRIDINEMETHANOLS. INFRARED AND NMR SPECTRAL PROPERTIES



Compd no.	R	R′	Ir (S=O), cm⁻¹	Nmr, ppm Ha	Hb	Hc	Hd	CH₂Cl	R,R′	C(CH₃)₃
9	H	H	1148		3.5–4.1	4.4–4.9[a]		3.5–4.1		1.33
10	H	H	1152	3.6–4.0		4.5–5.0[a]		3.3–3.5		1.40
14	H	Ph	1170		4.04		5.55	3.1–3.8	7.33	1.45
15	H	Ph	1159	3.94		6.16		2.9–3.6	7.3–7.4	1.45
17	Ph	H	1170		3.5–4.1	6.03		3.5–4.1	7.32	1.25
18	Ph	H					5.66			1.33

[a] Two-proton unresolved multiplet.

of **4**, **20**, and **5** showed the first two to be very similar to each other and quite different from **5**. The relationship between **20** and **4** was also demonstrated by the hydrolysis of **20** to **4**. In contrast, **5** was inert under the same hydrolysis conditions. On this basis, **20** was assigned the unrearranged structure. Chemical proof (including exclusion of structure **21**) for the structure of **5** was obtained by its reduction with $LiAlH_4$ to methylaziridine **22**. The aziridinemethyl chloride **11** was

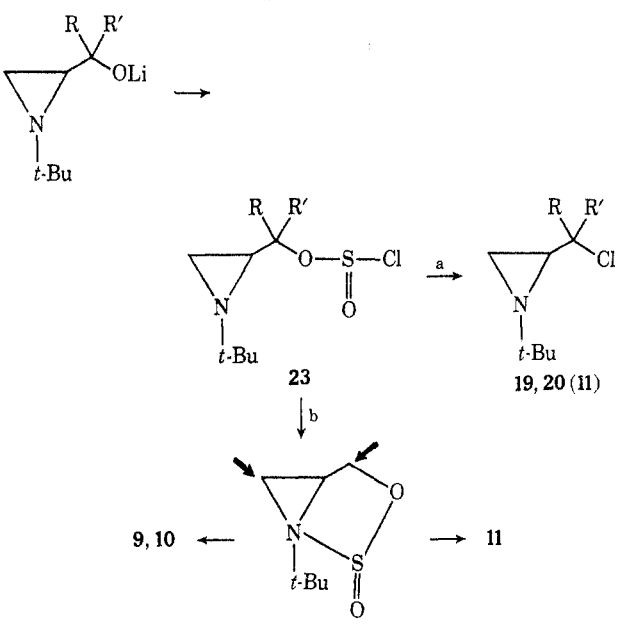


identified by comparison of its mass and nmr spectra with the corresponding bromide prepared by an alternative procedure.[2] The structure assigned to **19** (an apparent epimeric mixture) is tentative owing to our inability to separate or purify this high boiling liquid. This assignment is based on the mass spectrum of the mixture, the presence of the characteristic ring hydrogen shift and pattern of 1,2-disubstituted azirdines as well as the chemical shift of the downfield doublets.

Discussion

A consistent picture of the above observations must account for the striking difference between the behavior of NaH and BuLi as bases. The stability of the aziridine ring toward the attack by acid chlorides has been established in numerous cases.[7] It is probable, therefore, that the initial reaction step is formation of a chlorosulfite ester. It is not possible, however, that the same chlorosulfite ester can give different products as a function of its mode of formation. *A priori*, it is most likely that the homogeneous solutions which resulted from the reaction of aziridinemethanols with BuLi would yield chlorosulfite ester **23**. Decomposition of this chlorosulfite ester to a carbonium ion would be facilitated by the phenyl groups (path a of Scheme III). The apparent lack of stereospecificity in formation of **19** is in agreement with capture of an ion pair intermediate. The increased stability of primary chlorosulfite esters would allow competitive attack at sulfur by nitrogen to produce a bicyclic intermediate (path b of Scheme III). This intermediate could then undergo bimolecular attack at either position to yield the observed products **9–11**.

SCHEME III

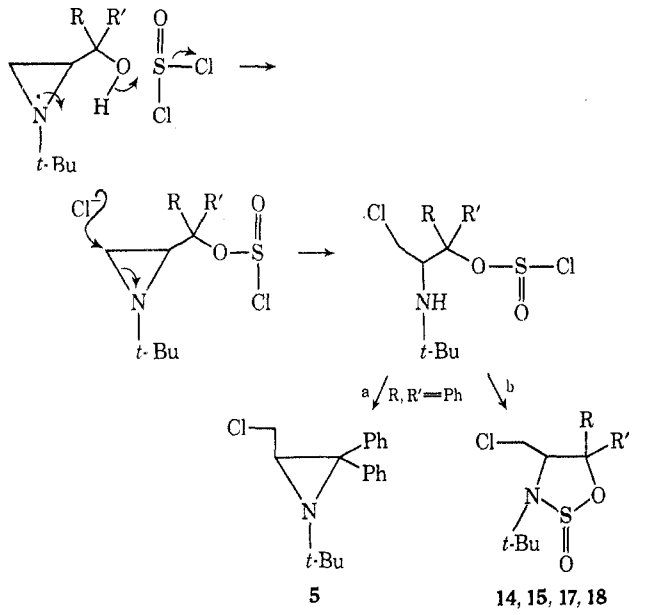


If the above picture is correctly drawn for the BuLi reactions, it is reasonable to postulate that the heterogeneous base, NaH, is a less efficient proton scavenger than the aziridine ring. The protonated chlorosulfite ester is now susceptible to nucleophilic ring opening by chloride (Scheme IV). The fate of this ring-opened intremediate is apparently governed by the substituents. Ionization (path a of Scheme IV) can result in carbonium ion capture by nitrogen to yield aziridine. Diminished ease of ionization allows nitrogen attack at sulfur with concomitant formation of oxathiazolidine

(7) The aziridine ring has been shown to be stable toward a variety of acid chlorides in the presence of base.[2,8] Even in the absence of base, **22** was recovered in 75% yield after 12 hr at room temperature with $SOCl_2$ in THF.

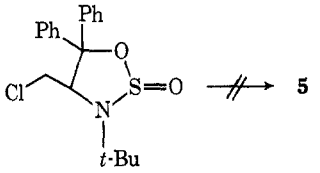
(8) C. L. Moyer, S. C. Clough, unpublished results.

SCHEME IV

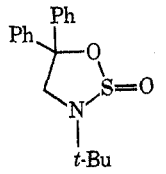


5 14, 15, 17, 18

(path b of Scheme IV). An alternative route to **5** from **24** was excluded by the finding that model compound **25**[6] was stable under the reaction conditions.



24



25

The reactions discussed in this paper open up a new route to substituted aziridines as well as alternative paths to the oxathiazolidine ring system. A search for additional examples of these and similar reactions as well as chemical studies of the compounds described in this paper is now in progress.

Experimental Section

Melting points and boiling points are uncorrected. Liquid samples of less than 5 g were molecularly distilled using a hot air bath and the boiling point reported was the temperature of the air bath. Routine infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer and the expanded infrared spectra were run on a Perkin-Elmer 337 spectrophotometer. All nmr spectra were recorded on a Varian A-60A spectrometer. Chemical shifts of nmr spectra run in organic solvents are reported in parts per million downfield from internal TMS (δ). Chemical shifts run in D_2O are reported in parts per million downfield from a point 4.99 ppm upfield from the DOH peak. Mass spectra were obtained on a RMU 6E mass spectrometer for all compounds reported in this paper except **4**. In each case molecular weights in agreement with theory were obtained. Fragments are reported as *m/e* (relative intensity). Infrared spectra obtained on the aziridines and oxthiazolidines reported in the Experimental Section were consistent with expected absence of N–H and unsaturation implicit in the assigned structure. Microanalyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tenn.

Reactions of 1-*t*-Butyl-2-aziridinemethanol (8) with Thionyl Chloride. (1) Sodium Hydride in Tetrahydrofuran.—Tetrahydrofuran (600 ml) was distilled directly from lithium aluminum hydride into a flask containing sodium hydride (19.2 g, 50% in mineral oil, 400 mmol, washed with three 150-ml portions of hexane). 1-*t*-Butyl-2-aziridinemethanol (**8**, 20 g, 155 mmol) was added in several portions with stirring at room temperature. A solution of thionyl chloride (24.8 g, 15 ml, 208 mmol) in 110 ml of tetrahydrofuran was added at room temperature at a rate which avoided noticeable temperature change (1.5 hr) and the reaction was then stirred overnight. It was evaporated to a paste and taken up in 200–300 ml of hexane. After 100 ml of water had been added with caution, the reaction mixture was washed with 50 ml of saturated sodium bicarbonate solution. The hexane layer was dried (K_2CO_3) and evaporated to an oil (20–25 g) which was fractionally distilled using a 20-cm Vigreux column to give fraction 1 (1.5 g, 5.5%), a mixture of ~25% 1-*t*-butyl-2-aziridinemethyl chloride (**11**) and 75% 1,3-dichloro-2-*t*-butylaminopropane (**12**) (by analysis of the nmr spectrum) [bp 31° (0.5–0.3 mm); mass spectrum (mixture, 70 eV) *m/e* (relative intensity) 187 (0.09), 185 (0.5), 183 (0.85), 172 (8.5), 170 (46), 168 (68), 149 (1.4), 147 (2.8), 134 (28), 132 (63), 112 (26), 57 (97), 56 (100)] and fractions 2–4 (16.5 g, 50%), mixtures of *cis* and *trans*-oxathiazolidines **9** and **10** (*cis/trans* ratios: fraction 2, 0.24; fraction 4, 0.71, by analysis of the nmr spectra). Elemental analysis was obtained on a mixture of the *cis*- and *trans*-oxathiazolidines.

Anal. Calcd for $C_7H_{14}ClNO_2S$: C, 39.77; H, 6.68; N, 6.62. Found: C, 39.94; H, 6.80; N, 6.54.

A sample of fraction 4 (1.0 g) was separated on a column of 5% deactivated alumina (2.5 × 30 cm) packed in hexane and eluted with 200 ml of hexane, 200 ml of 1:1 hexane–benzene, and 250 ml of benzene. Fractions of 50 ml were collected. Fraction 11 was evaporated several times from carbon tetrachloride and rotary evaporated under high vacuum to give a pure sample of the *trans*-oxathiazolidine (**10**). Fraction 13, treated in the same manner, gave a pure sample of *cis*-oxathiazolidine (**9**).

(2) Butyllithium in Tetrahydrofuran.—About 75 ml of tetrahydrofuran was distilled directly from lithium aluminum hydride into a flask containing 1-*t*-butyl-aziridinemethanol (**8**, 3.4 g, 13 mmol). Butyllithium (26 ml, 1.4 m, 36 mmol) was added through a syringe over 3 min with stirring in an ice–water bath. A solution of thionyl chloride (1.9 ml, 36 mmol) in 10 ml of tetrahydrofuran was then added over 0.25 hr. The reaction was allowed to warm to room temperature, stirred for an additional 0.5 hr, evaporated to a paste, and taken up in ~100 ml of hexane. The hexane layer was washed with 50 ml of water and 50 ml of aqueous sodium bicarbonate solution, dried (K_2CO_3), and evaporated to an oil (2.0 g, 40%). Analysis of the nmr spectrum of this oil showed that it contained ~50% 1-*t*-butyl-2-aziridinemethyl chloride (**12**), 12% *cis*-2-oxo-3-*t*-butyl-4-chloromethyl-1,2,3-oxathiazolidine (**9**), and 36% *trans*-2-oxo-3-*t*-butyl-4-chloromethyl-1,2,3-oxathiazolidine (**10**).

Ring Closure of 1,3-Dichloro-2-*t*-butylaminopropane (12) to 1-*t*-Butyl-2-aziridinemethyl Chloride (11).—Fraction 1 from the fractional distillation of the product mixture from the reaction of thionyl chloride with 1-*t*-butyl-2-aziridinemethanol (1.5 g, 75% 1,3-dichloro-*t*-butyl-aminopropane; see procedure above) was added to 10 ml of triethylamine and allowed to stand at room temperature for several weeks. The crude reaction mixture was evaporated to a paste and extracted with 15 ml of carbon tetrachloride and 10 ml of water. The organic layer was washed with 10 ml of water, dried (K_2CO_3), and evaporated to an oil which was distilled to give the aziridinemethyl chloride (**11**) (600 mg, 48%): bp 85–100° (water aspirator); nmr (CCl_4) 3.30 (q, 2, CH_2Cl), 1.87 (m, 1, C_2 H), 1.53 (d, 1, C_3 H_{trans}), 1.36 (d, 1, C_3 H_{cis}), 0.96 (s, 9, *t*-Bu).

Reactions of *erythro*-1-*t*-Butyl-α-phenyl-2-aziridinemethanol (13) with Thionyl Chloride. (1) Sodium Hydride in Tetrahydrofuran.—Thionyl chloride (0.50 ml, 6.9 mmol) in 20 ml of tetrahydrofuran was added to a solution of sodium hydride (0.75 g, 50% in mineral oil, 15.5 mmol, washed with three 20-ml portions of hexane) and *erythro*-1-*t*-butyl-α-phenyl-2-aziridinemethanol (**12**, 1.00 g, 4.9 mmol) in 60 ml of tetrahydrofuran over 0.75 hr at room temperature. After stirring for 4 hr, the reaction mixture was evaporated to a paste which was taken up in 150 ml of hexane. Water was added with caution and the hexane solution was washed with 50 ml of water and 50 ml of sodium

bicarbonate solution, dried (K_2CO_3), and evaporated to an oil (1.4 g, 100%). The nmr spectrum of this oil showed the presence of ~75% a mixture of the *cis,syn-* (**14**) and *cis,anti*-2-oxo-3-*t*-butyl-4-chloromethyl-5-phenyl-1,2,3-oxathiazolidine (**15**) and 20% unidentified *t*-butyl species. This crude oil was taken up in carbon tetrachloride, washed with dilute hydrochloric acid and water, dried (K_2CO_3), and evaporated to an oil which precipitated solids and contained only the isomeric oxathiazolidines **14** and **15**. About 1–2 ml of hexane was added to the oil and the supernatant solution removed from the solids. Recrystallization of these solids from hexane gave *cis,syn*-oxathiazolidine **14** (~100 mg, 7%), mp 116–117.5°.

Anal. Calcd for $C_{13}H_{18}NO_2SCl$: C, 54.28; H, 6.31; N, 4.87. Found: C, 54.54; H, 6.46; N, 4.94.

The filtrate from the *cis,syn*-oxathiazolidine (**14**) was evaporated to an oil which contained ~15% *cis,syn-* and 85% *cis,anti*-oxathiazolidine (**15**). The oil was rotary evaporated (1.0 mm) for 4 hr to yield an analytical sample of the mixture of oxathiazolidines **14** (15%) and **15** (85%).

Anal. (*cis,trans* mixture). Calcd for $C_{13}H_{18}NO_2SCl$: C, 54.28; H, 6.31; N, 4.87. Found: C, 54.06; H, 6.35; N, 4.75.

(2) **Butyllithium in Tetrahydrofuran.**—Thionyl chloride (0.35 ml 4.9 mmol) in 10 ml of tetrahydrofuran was added to a solution of *erythro*-1-*t*-butyl-α-phenyl-2-aziridine methanol (**13**, 1.00 g, 4.9 mmol) and butyllithium (5 ml, 1.4 g, 7 mmol) in 75 ml of tetrahydrofuran over 0.25 hr at room temperature. The reaction mixture was stirred for 0.5 hr and evaporated to a paste which was taken up in 50 ml of hexane, washed with water, dried (K_2CO_3), and evaporated to an oil (0.85 g, 77%). The nmr spectrum of this oil showed *ca.* a 2:1 mixture of two compounds: δ 0.67 and 0.72 (*t*-Bu), 4.17 and 4.62 (CHCl). Attempts to further purify and assign stereochemistry to these compounds were not successful.

Reactions of *threo*-1-*t*-Butyl-α-phenyl-2-aziridinemethanol (16) with Thionyl Chloride. (1) Sodium Hydride in Tetrahydrofuran.—A solution of thionyl chloride (0.25 ml, 3.5 mmol) in ~10 ml of tetrahydrofuran was added to a solution of sodium hydride (0.5 g, 50% in mineral oil, 10 mmol, washed with three 20-ml portions of hexane) and *threo*-1-*t*-butyl-α-phenyl-2-aziridine methanol (**16**, 550 mg, 2.7 mmol) in 50 ml of tetrahydrofuran over 0.5 hr at room temperature. After stirring for 4 hr, the reaction mixture was evaporated to a paste and taken up in ~50 ml of hexane. The excess sodium hydride was destroyed by the careful addition of water and the hexane layer washed with water, dried (K_2CO_3), and evaporated to an oil (0.6 g, 85%). The nmr spectrum of this oil showed it to contain ~85–90% a 1:10 mixture of oxathiazolidines **18** and **17**. The oil was dissolved in 50 ml of carbon tetrachloride and washed with 5% aqueous hydrochloric acid and water, dried (K_2CO_3), and evaporated to an oil which showed only the oxathiazolidines in its nmr spectrum. The two isomers were not separated but the major isomer was identified as the *trans,syn*-2-oxo-3-*t*-butyl-4-chloromethyl-5-phenyl-1,2,3-oxathiazolidine (**17**) and the minor isomer was identified as *trans,anti* isomer **18**. Rotary evaporation under high vacuum (1.0 mm) for 1 hr gave an analytical sample which still contained some hydrocarbon impurities. The mass spectrum of this mixture was virtually identical with that obtained from the *cis,anti* compound **15**.

Reactions of 1-*t*-Butyl-α,α-diphenyl-2-aziridinemethanol (4) with Thionyl Chloride. (1) Sodium Hydride in Tetrahydrofuran.—Thionyl chloride (1.5 ml, 21 mmol) in 30 ml of tetrahydrofuran was added to a solution of sodium hydride (1.5 g, 50% in mineral oil, 31 mmol, washed with three 30-ml portions of hexane) and aziridinemethanol (**4**) (5.6 g, 20 mmol) in 125 ml of tetrahydrofuran over 0.5 hr with stirring in an ice–water bath. The reaction mixture was stirred overnight, evaporated to a paste, and extracted with 100 ml of low boiling petroleum ether and 45 ml of sodium bicarbonate solution. The petroleum ether layer was dried (K_2CO_3), stirred overnight with 10 g of 10% deactivated alumina,[9] and then evaporated to give 1-*t*-butyl-3,3-diphenyl-2-aziridinemethyl chloride (**5**) as an oil which would not solidify (5.7 g, 89%): bp 110–120° (0.01 mm); nmr ($CDCl_3$) δ 6.9–7.5 (m, 10, ArH), 2.8–3.3 (m, 3, $-CH_2-$, and C_2 H), 0.93 (s, 9, *t*-Bu).

Anal. Calcd for $C_{19}H_{22}ClN$: C, 76.13; H, 7.40; N, 4.67. Found: C, 76.12; H, 7.31; N, 4.56.

(2) **Triethylamine in Hexane.**—Thionyl chloride (0.72 ml, 10 mmol) in 20 ml of hexane was added to a solution of triethylamine (1.1 g, 11 mmol) and aziridinol (**4**) (2.8 g, 10 mmol) in 200 ml of hexane over 0.5 hr at room temperature, washed with 50 ml of water and 50 ml of sodium bicarbonate solution, dried (K_2CO_3), and evaporated to give 1-*t*-butyl-α,α-diphenyl-2-aziridinemethyl chloride (**20**) as an oil (83%) which would not crystallize. Rotary evaporation for 2 hr (0.2 mm) yielded an analytical sample: nmr (CCl_4) δ 6.9–7.7 (m, 10, ArH), 2.57 (q, 1, C_2 H), 1.56 (q, 1, C_3 H_{trans}) 1.24 (q, 1, C_3 H_{cis}), 0.90 (s, 9, t-Bu).

Anal. Calcd for $C_{19}H_{22}ClN$: C, 76.20; H, 7.40; N, 4.68. Found: C, 76.27; H, 7.56; N, 4.72.

(3) **Butyllithium in Tetrahydrofuran.**—Thionyl chloride (1.15 ml, 16 mmol) in 10 ml of tetrahydrofuran was added to a solution of butyllithium (10 ml, 1.4 m, 14 mmol) and aziridinol **4** (2.81 g, 10 mmol) in 50 ml of tetrahydrofuran over 2 min at 0°. The reaction mixture was stirred for 10 min and evaporated to a paste which was taken up in 50 ml of hexane and washed with 30 ml of water and 30 ml of sodium bicarbonate solution. The hexane layer was dried (K_2CO_3) and evaporated to an oil (2.5 g, 82%). The nmr spectrum of this oil showed only the 1-*t*-butyl-α,α-diphenyl-2-aziridinemethyl chloride (**20**).

1-*t*-Butyl-2,2-diphenyl-3-methylaziridine (22).—A mixture of 3.5 g of 1-*t*-butyl-α,α-diphenyl-2-aziridinemethyl chloride and 5 g of $LiAlH_4$ in 250 ml of THF was refluxed for 30 hr. The reaction mixture was cooled and 2.2 g additional $LiAlH_4$ was added. The mixture was then heated at reflux for 24 more hr and cooled, and the excess $LiAlH_4$ carefully decomposed. After removal of inorganic salts by filtration, the filtrate was concentrated to a crude oil which still contained some starting material. Final purification was affected by thick layer chromatography and molecular distillation [110–120 (0.5 mm)]: nmr (CCl_4) δ 7.0–7.4 (10, m, ArH), 2.82 (1, q, C_3 H), 0.86 (3, d, CH_3) 0.90 (9, s, *t*-Bu).

Anal. Calcd $C_{19}H_{23}N$: C, 85.98; H, 8.74; N, 5.28. Found: C, 86.14; H, 8.95; N, 5.31.

Hydrolysis of 1-*t*-Butyl-α,α-diphenyl-2-aziridinemethyl Chloride (20).—A solution of 1-*t*-butyl-α,α-diphenyl-2-aziridinemethyl chloride (**20**) (3.0 g, 10 mmol) and sodium hydroxide (0.5 g, 12 mmol) in 50 ml of tetrahydrofuran and 30 ml of water was refluxed for 4 days. Evaporation gave an oil which was extracted with 50 ml of ether, washed with 25 ml of water, dried (K_2CO_3), and evaporated to an oil. The only product apparent in the nmr spectrum of this oil was 1-*t*-butyl-α,α-diphenyl-2-aziridinemethanol (**4**).

Attempted Hydrolysis of 1-*t*-Butyl-3,3-diphenyl-2-aziridinemethyl Chloride (5).—A solution of 1-*t*-butyl-3,3-diphenyl-2-aziridinmethyl chloride (**5**) (2.0 g, 6.7 mmol) and sodium hydroxide (0.5 g, 12 mmol) in 50 ml of tetrahydrofuran and 30 ml of water was refluxed for 4 days. The reaction mixture was evaporated to an oil which was extracted with 25 ml of carbon tetrachloride, washed with 15 ml of water, dried (K_2CO_3), and evaporated to an oil (1.6 g, 80%). The only material apparent in the nmr spectrum of this oil was the starting aziridinemethyl chloride (**5**).

Registry No.—**4**, 25665-26-3; **5**, 25665-27-4; **8**, 25665-28-5; **9**, 25662-68-4; **10**, 25662-69-5; **11**, 21452-72-2; **12**, 25665-30-9; **13**, 25662-70-8; **14**, 25662-71-9; **15**, 25662-72-0; **16**, 25662-73-1; **17**, 25662-74-2; **18**, 25662-75-3; **20**, 25665-31-0; **22**, 25716-07-8; thionyl chloride, 7719-09-7.

(9) This treatment was necessary to remove trace amounts of acid and/or acid-forming products which led to the slow decomposition of the product.