higher aggregates apparently dispose themselves about the HCl molecule in such a way as to reduce its free energy of ionization. The group of observations as a whole presents many features which have little precedent in hydroxylic media, and it is our hope that they may provide an understanding of the great penetration of electrostatic forces in hydrophobic media as well as in fused salts.

The Solvolysis of 1-Chloroaziridines[1]

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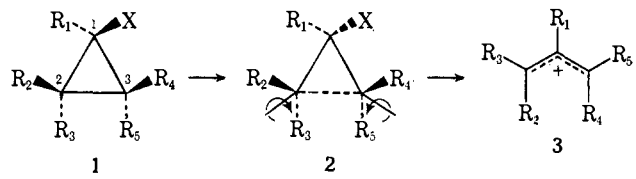
Abstract: The solvolytic behavior of N-chloroaziridine and five methyl-substituted N-chloroaziridines has been investigated. The fate of the N-chloroaziridines under solvolytic conditions was found to be very similar to that observed for the acetolysis of cyclopropyl tosylates. For all of the N-chloroaziridines investigated the ionization of the N–Cl bond was accompanied by cleavage of the aziridine ring. The relative rates of solvolysis correlated quite well with the anticipated results based on the theory that N-chloroaziridines would solvolyze with an electrocyclic disrotatory ring opening as predicted by the Woodward–Hoffmann molecular orbital symmetry considerations. Rate accelerations as large as 1.5×10^5 resulted from the substitution of two methyl groups on the aziridine ring. A detailed comparison of the solvolysis of N-chloroaziridines with the solvolysis of cyclopropyl tosylates has been made. In general, methyl substitution in the aziridine system results in a larger rate acceleration than analogous methyl substitution in the cyclopropyl system.

Although the ring opening of cyclopropyl derivatives to give allylic cations has been known for some time,[3] it was only with the advent of the Woodward–Hoffman molecular orbital symmetry considerations[4] that a theoretical basis was provided for the apparent anomalous behavior of the incipient cyclopropyl cation.[5–7] As shown by a variety of labeling experiments, including isotopic studies,[8] the bond of the three-membered ring which is cleaved in the formation of the allylic cation is not attached directly to the carbon bearing the leaving group. In accord with molecular orbital symmetry considerations for the electrocyclic opening of cyclopropanes it should be the C_2–C_3 bond of **1** which is broken as the X group leaves with its pair of bonding electrons. The elegant studies of DePuy,[5] Schleyer,[6,7] and Schöllkopf[6,7] have established that, as the X group of **1** starts to leave as shown in **2**, concerted cleavage of the C_2–C_3 bond occurs with a disrotatory motion about the C_1–C_2 and C_1–C_3 bonds. As indicated in structure **2** this rotation is stereospecific with the groups *cis* to the leaving group both rotating inward and the groups *trans* to the leaving group rotating outward to eventually produce the allyl cation **3**.



1 **2** **3**

Our recent studies of the nitrogen analog of the carbonium ion[1,9] suggested to us that the nitrenium analog of the cyclopropyl cation should show the same properties of ring cleavage and stereospecific disrotatory movement of substituents. For an aziridine such as **4** the concerted cleavage would be expected to proceed as shown in **5** with the group *cis* to the leaving group (R_1 and R_4) rotating inward and the groups *trans* to X rotating outward. If the aziridine system behaved exactly like the cyclopropyl system the cleavage of **4** should lead initially to **6** either as a discrete intermediate or as a point along the reaction pathway. As shown, **6** would be a planar molecule. However, a 90° rotation of either the C_1–N bond or the C_2–N bond of **6** would give **7**, the isoelectronic nitrogen analog of an allene. Both **6** and **7** might be expected to be short-lived under the reaction conditions and both would be expected to yield the product mixture **8**. The direct conversion of **5** into **7** also requires

(1) Paper X in a series on The Chemistry of Nitrenium Ions. For the previous paper in this series see P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, 91, 5176 (1969). See also P. G. Gassman, *Accounts Chem. Res.*, 3, 26 (1970).

(2) Alfred P. Sloan Foundation Research Fellow, 1967–1969.

(3) For some initial studies in the area of cyclopropyl cation chemistry see P. Lipp and C. Padberg, *Ber.*, 54B, 1316 (1921); P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, 499, 1 (1932); J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, 73, 5034 (1951); D. E. Applequist and G. F. Fanta, *ibid.*, 82, 6393 (1960); H. Hart and R. A. Martin, *ibid.*, 82, 6362 (1960); R. Pettit, *ibid.*, 82, 1972 (1960); and J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, 28, 3356 (1963).

(4) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395 (1965). See also H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2045 (1965); M. J. S. Dewar, *Tetrahedron, Suppl.*, No. 8, 75 (1966); W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967).

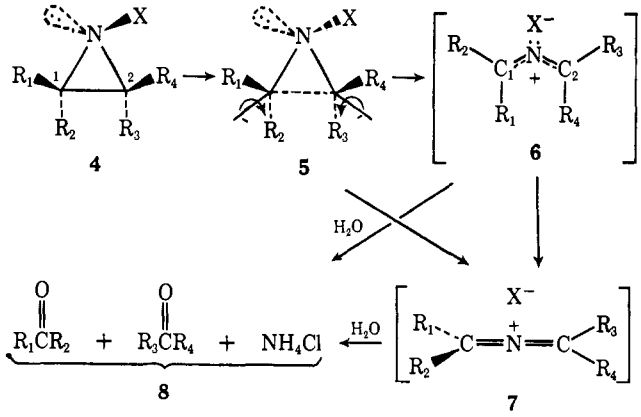
(5) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Amer. Chem. Soc.*, 87, 4006 (1965); C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, 88, 3343 (1966).

(6) P. von R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Paust, *ibid.*, 88, 2868 (1966); U. Schöllkopf, K. Fellenberger, M. Patsch, P. von R. Schleyer, T. Su, and G. W. van Dine, *Tetrahedron Lett.*, 3639 (1967).

(7) For recent summaries of cyclopropyl cation chemistry see U. Schöllkopf, *Angew. Chem. Intern. Ed. Engl.*, 7, 588 (1968); W. E. Parham, *Rec. Chem. Progr.*, 29, 3 (1968); and P. von R. Schleyer, Twentieth National Organic Chemistry Symposium of the American Chemical Society, Burlington, Vt., June 18–22, 1967, Abstracts, pp 7–21.

(8) E. J. Corey and R. F. Atkinson, *J. Org. Chem.*, 29, 3703 (1964).

(9) P. G. Gassman and B. L. Fox, *J. Amer. Chem. Soc.*, 89, 338 (1967); P. G. Gassman, F. Hoyda, and J. Dygos, *ibid.*, 90, 2716 (1968); P. G. Gassman, G. Campbell, and R. Frederick, *ibid.*, 90, 7377 (1968); P. G. Gassman and R. L. Cryberg, *ibid.*, 91, 2047 (1969); and P. G. Gassman and A. Carrasquillo, *Chem. Commun.*, 495 (1969).

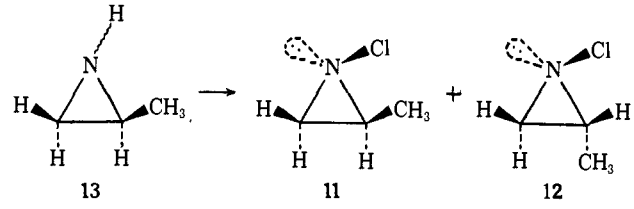


consideration. This transformation would involve no rotation at C_1 and a 90° rotation at C_2, or some combination of these two possibilities (*e.g.*, a 45° rotation at each center) totaling a 90° rotation. The important factor to be stressed in a direct **5** → **7** transformation is that the nonbonding electrons on nitrogen would be involved in the rate-determining step. Symmetry operations indicate that a direct conversion of **5** to **7** would have to involve a conrotatory cleavage instead of a disrotatory cleavage. Thus, on the basis of the rate data given below we can eliminate completely the transformation of **5** into **7** in the rate-determining step.

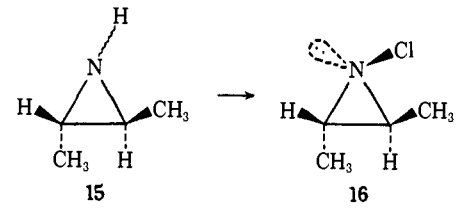
With the above-stated considerations in mind we undertook an investigation of the solvolytic behavior of N-chloroaziridines.[10] Of course, the feasibility of such a study was dependent on the stereochemical stability of the N–Cl moiety. Fortunately, Brois had demonstrated that inversion at nitrogen is a relatively slow process when one of the substituents on nitrogen is chlorine and the nitrogen is part of a three-membered ring.[11]

Synthesis and Spectral Identification. The aziridine and 2-methylaziridine used were commercially available materials. A slight modification of the literature procedure[12] was used to prepare the *cis*- and *trans*-2,3-dimethylaziridines from the corresponding isomeric 2-butenes. 2,2-Dimethylaziridine was synthesized according to the published method.[13]

Using commercial solutions of sodium hypochlorite,[14] aziridine (**9**) was converted into 1-chloroaziridine (**10**).[15] The epimers, *cis*- and *trans*-1-chloro-2-methylaziridine, **11** and **12**, were prepared according to the literature procedure[11] by treating 2-methylaziridine (**13**) with hypochlorite and separation of **11** and **12** by preparative vpc. The preparation of 1-chloro-2,2-dimethylaziridine (**14**) also followed the procedure of Brois.[11]

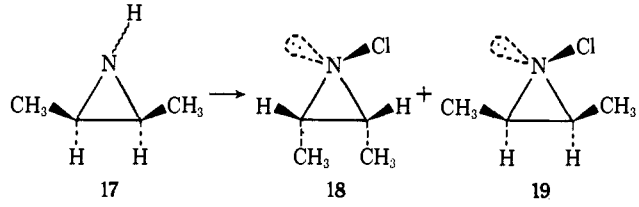


trans-2,3-Dimethylaziridine (**15**) reacted with sodium hypochlorite solution at 0° to give 1-chloro-*cis*,*trans*-



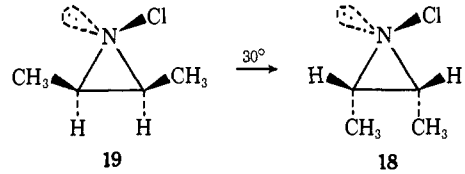
2,3-dimethylaziridine (**16**). Extraction of **16** from the aqueous solution with Freon 11 followed by drying and fractional distillation gave pure **16**. The nmr spectrum of pure **16** in chloroform showed doublets at τ 8.51 (3 H) and 8.77 (3 H) for the two different methyl groups. The absorption at τ 8.51 was assigned to the methyl group which was *cis* to the chlorine and the peak at τ 8.77 was assigned to the methyl *trans* to the chlorine in accord with the assignments of Brois[11] for **11** and **12**.

Treatment of *cis*-2,3-dimethylaziridine (**17**) with sodium hypochlorite at 0° gave a mixture of **18** and **19**. The presence of both **18** and **19** was demonstrated by extraction of the mixture of freshly prepared 1-chloroaziridine into chloroform at 0° and immediate



recording of the nmr spectrum of the solution. Two different methyl peaks were detected at τ 8.68 and 8.81 and the ring protons appeared as a multiplet centered at τ 7.57. Spin decoupling of the methyl protons gave singlets for the ring protons with the singlet for **19** appearing at τ 7.62 and the singlet for **18** appearing at τ 7.51. Irradiation of the ring protons collapsed the different methyl doublets to singlets.

On standing at room temperature **19** completely epimerized to **18**. Ample precedent for this thermally



induced inversion was provided by Felix and Eschenmoser[16] who showed that under very mild conditions ($t_{1/2}$ = 4.5 hr at 29.5°) **20** was rapidly transformed into

(10) For a preliminary report of part of this work see P. G. Gassman and D. K. Dygos, *J. Amer. Chem. Soc.*, **91**, 1543 (1969).

(11) S. J. Brois, *ibid.*, **90**, 506, 508 (1968). See also R. G. Kostyanovsky, Z. E. Samojlova, and I. I. Tchervin, *Tetrahedron Lett.*, 719 (1969).

(12) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

(13) K. N. Campbell, A. H. Sommers, and B. K. Campbell, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley & Sons, Inc., New York, N. Y., 1955, p 148.

(14) Commercial household bleach was used for all the conversions of aziridines to 1-chloroaziridines discussed in this paper. Commercial bleach is *ca.* 0.8 *M* in sodium hypochlorite.

(15) The overall conversions of aziridines into 1-chloroaziridines range from 90 to 100% (determined titrimetrically on the crude N-chloroaziridine).

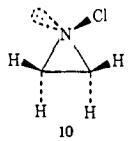
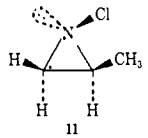
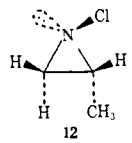
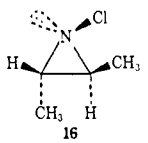
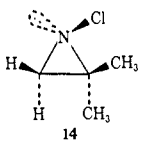
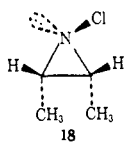
(16) D. Felix and A. Eschenmoser, *Angew. Chem. Intern. Ed. Engl.*, 7, 224 (1968).

Table I. Ultraviolet Maxima for N-Chloroaziridines

Compd	Water λ_{max} (mμ)	Water ε	Methanol λ_{max} (mμ)	Methanol ε
10	247	335		
11	251	377		
12	247	279	254	316
14	247	365	254	365
16	247	320	258	460
18			251	280

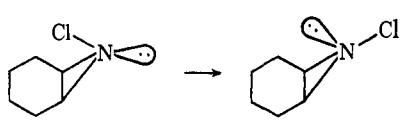
lives except in the case of **11**. Table I lists the ultraviolet absorptions in the N-chloroaziridines studied. Compound **11** presented a special problem because it isomerized to **12** under the solvolytic conditions used. Since **11** and **12** exhibit different extinction coefficients and since the epimerization appears to be slightly catalyzed by the reaction products, the kinetic plot for **11** showed considerable curvature. Although the extinction coefficient for **12** was less than that for **11**,

Table II. Rates of Solvolysis of 1-Chloroaziridines

Compd	Solvent	Temp, °C	Rate (sec^{-1})	k_{rel} at 60° in H_2O[a]
 **10**	Water	60.0 ± 0.1	$(6.5 \pm 1.3) \times 10^{-7}$ [b]	1
 **11**	Water	60.0 ± 0.1	$(9.8 \pm 0.8) \times 10^{-6}$ [c]	1.5×10
		70.0 ± 0.1	$(2.8 \pm 0.1) \times 10^{-5}$	
		80.0 ± 0.1	$(8.3 \pm 0.5) \times 10^{-5}$	
 **12**	Water	50.0 ± 0.1	$(3.57 \pm 0.17) \times 10^{-5}$	
		60.0 ± 0.1	$(1.37 \pm 0.01) \times 10^{-4}$	2.1×10^{2}
		70.0 ± 0.1	$(4.76 \pm 0.05) \times 10^{-4}$	
 **16**	Water	40.0 ± 0.1	$(8.41 \pm 0.31) \times 10^{-5}$	
		50.0 ± 0.1	$(3.13 \pm 0.20) \times 10^{-4}$	
		60.0 ± 0.1	$(9.54 \pm 0.22) \times 10^{-4}$	1.5×10^{3}
	Methanol	60.0 ± 0.1	$(1.26 \pm 0.12) \times 10^{-5}$	
 **14**	Water	40.0 ± 0.1	$(9.79 \pm 0.06) \times 10^{-5}$	
		50.0 ± 0.1	$(3.65 \pm 0.06) \times 10^{-4}$	
		60.0 ± 0.1	$(1.19 \pm 0.03) \times 10^{-3}$	1.8×10^{3}
	Methanol	60.0 ± 0.1	$(3.38 \pm 0.06) \times 10^{-5}$	
 **18**	Methanol[d]	60.0 ± 0.1	$(1.30 \pm 0.03) \times 10^{-3}$	1.5×10^{5}

[a] The relative rate of **18** in water was calculated by multiplying the difference in rates of **16** and **18** in methanol by the relative rate of **16** in water. [b] Kinetic measurements on **10** were complicated by its slow rate and high volatility (bp 70.0–70.5°) at the required solvolysis temperature. [c] All rate constants listed for **11** are extrapolated initial rates. Spectroscopic measurements of the rate of **11** were measured at 210 mμ where the extinction coefficients of **11** and **12** were identical. [d] The rate of solvolysis of **18** in water was too fast to be measured conveniently. Thus it was studied only in methanol.

21. The thermal lability of **19** made it unavailable for further studies.



20 **21**

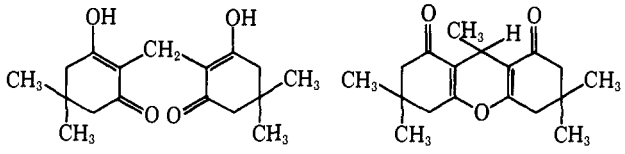
Kinetic and Product Studies. The kinetics of solvolysis of compounds **10, 11, 12, 14, 16,** and **18** were followed spectroscopically by observing the disappearance of the characteristic absorption of the N-chloramines in the 245–260-mμ region of the spectrum. The decrease in intensity of this band was readily followed and showed good pseudo-first-order kinetics for at least two half-

12 solvolyzed considerably faster than **11**, resulting in a rate curve for a constantly increasing rate. The rate of solvolysis of pure **11** could be approximated by extrapolating the rate curve back to the initial rate.[17] Table II lists the rates of hydrolysis and methanolysis of the N-chloroaziridines studied. The dramatic effect of methyl substitution was illustrated by the rate difference of greater than 150,000 between **10** and **18**.

As discussed earlier in this paper a concerted ring cleavage during the solvolysis of the N-chloroaziridines should eventually lead to products which are either

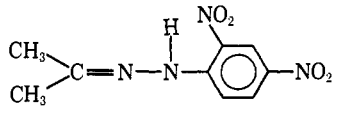
(17) This extrapolation was carried out according to the method of W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, 73, 1958 (1951).

aldehydes or ketones. These carbonyl compounds would result from the hydrolysis of an intermediate such as **6** or **7**. The carbonyl compounds resulting from the solvolysis of **10**, **11**, **12**, **14**, **16**, and **18** should be formaldehyde from **10**, **11**, **12**, and **14**, acetaldehyde from **11**, **12**, **16**, and **18**, and acetone from **14**. The formaldehyde was isolated and identified as its dimedone derivative, formaldehyde bismethone (**22**). Acetaldehyde was isolated and identified as either acetaldehyde bismethone anhydride (**23**) or as its 2,4-dinitrophenylhydrazone, and acetone was isolated and identified as its 2,4-dinitrophenylhydrazone (**24**). Compounds **22** and **23** were readily separated by extracting the mixture with aqueous potassium carbonate since



22

23



24

22 was base soluble while **23** was insoluble in base. The formaldehyde and acetone were separated by reacting the mixture of formaldehyde and acetone with dimedone, followed by distillation of the acetone into 2,4-dinitrophenylhydrazine solution. Table III lists the yields of products. The formaldehyde presented a special problem since it tended to react further under the reaction conditions.[18] Thus at the higher temperatures required for the solvolysis of **10**, **11**, and **12**, much of the formaldehyde was not accounted for as the dimedone derivative. Whether this low material balance was due to a side reaction of the formaldehyde or to some unknown reaction of the formaldehyde precursor is not known.

Table III. Products from the Solvolysis of 1-Chloroaziridines

Compd	Per cent yields 22	23	24
10	10[a]		
11	45	73	
12	43	57	
14	66		82
16		65[a,b]	
18		79[a,b]	

[a] The reported yields are based on 100% of 2 mol of formaldehyde from **10** and 2 mol of acetaldehyde from both **16** and **18**. [b] The acetaldehyde was isolated and identified in this case as its 2,4-dinitrophenylhydrazone, not as **23**.

Discussion of Results

Both the kinetic studies and product studies on the series of aziridines investigated indicate that the heterolytic cleavage of the N–Cl bond was accompanied by a concerted breaking of the C_1–C_2 bond of **4**. The relative inductive and steric effects of the methyl substituents of the N-chloroaziridines were similar to those discussed for the solvolysis of methyl-substituted cyclopropyl tosylates.[5,6] The individual rate differences observed for the substituted N-chloroaziridines studied are best evaluated in terms of the transition states shown in Table IV.

In general the rates were all consistent with a concerted ionization–ring cleavage as prognosticated on the basis of a disrotatory ring opening. In progressing from transition states **25** to **26** two effects are present. In **25** the partial positive charge on carbon is distributed between two incipient primary carbonium ions, whereas in **26** the distribution of the charge is between a developing primary and secondary center. This increased stability of the carbonium ion portion of **26** relative to **25** is probably partially balanced by the inward rotation of the methyl group of **26** which should result in a steric retardation of the concerted ionization. This phenomenon is demonstrated more lucidly by a comparison of **26** and **27** where the stability of the incipient carbonium ions is the same, but where the required disrotatory rotation in **27** is one which would decrease the interaction between the methyl group and the hydrogen. This decrease in the methyl–hydrogen interaction in **27** *vs.* the methyl–hydrogen interaction in **26** accounts for a rate change by a factor of 14.

The solvolysis of **16** is significantly faster than the solvolysis of **12** because as shown by **28** both developing carbonium ion centers are secondary. Steric interactions in **28** are balanced because in the disrotatory ring opening one methyl–hydrogen interaction is increasing while the other methyl–hydrogen interaction is decreasing. In comparing **28** with **29** we see that the steric interactions are for all practical purposes the same. However, the combination of incipient primary and tertiary centers next to nitrogen in **29** is slightly better than the two secondary centers resulting from **28**.

The solvolysis of **18** shows a large rate increase relative to the rates of both **14** and **16**. Although both **28** and **30** involve development of partial positive charge on two incipient secondary centers, the steric interactions in **28** and **30** are very different when considered in terms of a disrotatory ring opening. Transition state **30** should be of much lower energy than **28** due to the relief of the methyl–methyl interaction resulting from the outward rotation of the methyl groups as required by the molecular orbital symmetry considerations for a process involving heterolytic cleavage of the N–Cl bond. Conclusive evidence for the dramatic overall effect of the two methyl groups of **18** was provided by the difference of greater than 150,000 in the rates of solvolysis of **10** and **18**.

In light of the similarities between the solvolysis of cyclopropyl tosylates and N-chloroaziridines a comparison of the relative effects of methyl substitution was desirable. Table V gives the relative rates of solvolysis of substituted cyclopropyl tosylates in acetic acid and N-chloroaziridines in water. In all cases the methyl substituents give a slightly larger rate acceleration for the N-chloroaziridines than for the cyclopropyl tosylates. On the basis of the data available it is not known whether this is a solvent effect or whether the larger rate dependence of the N-chloroaziridines is a

(18) Formaldehyde is known to react with ammonium chloride in the vicinity of 100° [C. S. Marvel and R. L. Jenkins, "Organic Syntheses," Coll. Vol. I, H. Gilman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1932, p 347]. However, under the conditions of our solvolytic studies this did not appear to be a major cause of the loss of formaldehyde.

Table IV

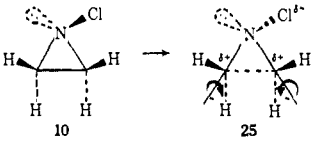
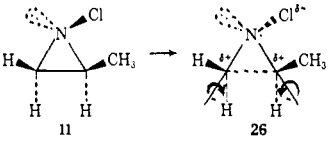
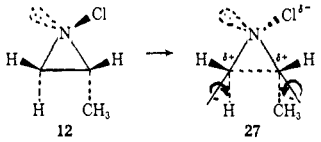
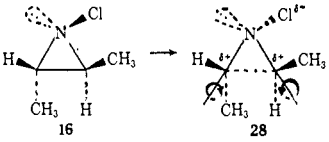
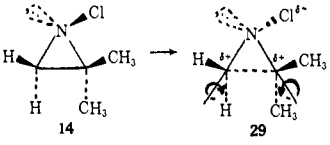
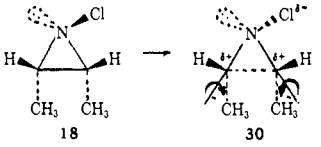
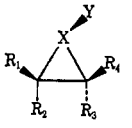
N-Chloroaziridine	Mode of ring opening	Products
 10	25	→ 2HCH + NH_4Cl
 11	26	→ CH_3CH + HCH + NH_4Cl
 12	27	→ CH_3CH + HCH + NH_4Cl
 16	28	→ $2CH_3CH$ + NH_4Cl
 14	29	→ CH_3CCH_3 + HCH + NH_4Cl
 18	30	→ $2CH_3CH$ + NH_4Cl

Table V. Comparison of the Relative Rate Factors for the Solvolysis of Methyl-Substituted 1-Chloroaziridines and 1-Cyclopropyl Tosylates

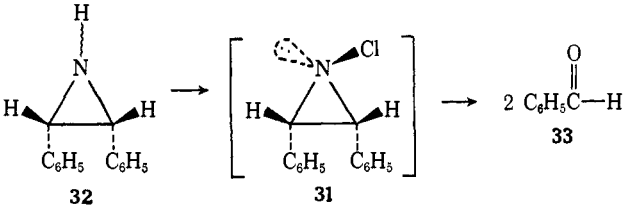


	k_{rel}, 60°, for X = N; Y = Cl[a]	k_{rel}, 100°, for X = CH; Y = OTs[b]
$R_1 = R_2 = R_3 = R_4 = H$	1	1
$R_1 = R_2 = R_3 = H$; $R_4 = CH_3$	15	8[c,d]
$R_1 = R_2 = R_4 = H$; $R_3 = CH_3$	210	70[c,d]
$R_1 = R_3 = H$; $R_2 = R_4 = CH_3$	1,500	490
$R_1 = R_2 = H$; $R_3 = R_4 = CH_3$	1,800	470
$R_1 = R_4 = H$; $R_2 = R_3 = CH_3$	150,000	41,000

[a] Relative rates are for solvolysis in water. [b] Relative rates are for solvolysis in acetic acid.[6] [c] Rates calculated according to the method of Schleyer and Schöllkopf.[6] [d] Subsequent to the submission of this manuscript we were informed by Professor Schleyer that the calculated relative rates of 8 and 70 have now been experimentally measured in his laboratory and are 6 and 138, respectively. We wish to thank P. Schleyer and W. Sliwinski for providing us with their unpublished results.

reflection of greater delocalization of charge than is present in the ionization of the cyclopropyl tosylates. Since nitrenium ions are very unstable by comparison with carbonium ions it might be anticipated that the transition state for the solvolysis of N-chloroaziridines would involve significantly more charge distribution to the adjacent carbon atoms than would be present in the ionization of cyclopropyl tosylates. This hypothesis fits the rate acceleration of 210 (k of **10** *vs.* k of **12**) observed when a single methyl group is substituted *trans* to the leaving group in the N-chloroaziridine system. Clearly, this rate difference is larger than the factor of 70 estimated for the carbocyclic case.[6,19]

In view of the results discussed above it was expected that 1-chloro-*trans*,*trans*-2,3-diphenylaziridine (**31**) should solvolyze at an extremely rapid rate. Numerous attempts to prepare **31** from *cis*-2,3-diphenylaziridine (**32**) failed to yield detectable amounts of **31**. Instead, even under the mildest conditions, only


32 31 33

benzaldehyde (**33**) was isolated (53%). Thus it would appear that **32** was being converted to **31**, but that **31** was so reactive that it was immediately undergoing ionization–ring cleavage to eventually give **33**.

Summary

The solvolytic behavior of N-chloroaziridines was found to be very analogous to the solvolytic behavior of cyclopropyl tosylates. Substituent effects in both

(19) R. A. Sneen, *J. Amer. Chem. Soc.*, 80, 3977, 3982 (1958).

systems were consistent with predictions based on Woodward–Hoffmann molecular orbital symmetry considerations. These findings support the theory that N-chloramines experience heterolytic cleavage of the N–Cl bond under solvolytic conditions to give chlorine anion and a divalent electron-deficient nitrogen species.

Experimental Section

Melting points and boiling points are uncorrected. Nmr spectra were recorded on a Varian Associates Model A60A nuclear magnetic resonance spectrometer. A Cary Model 15 recording ultraviolet spectrophotometer thermostated to ±0.1° was used to follow the kinetics.

Aziridine. Ethylenimine (aziridine) was purchased from the Matheson Coleman and Bell Division of the Matheson Company and used without further purification.

2-Methylaziridine. Propylenimine (2-methylaziridine) was generously provided by the Interchemical Corporation and was used without further purification.

2,2-Dimethylaziridine. The conversion of 2-amino-2-methyl-1-propanol into 2,2-dimethylaziridine was accomplished according to the literature procedure.[13]

***cis*- and *trans*-2,3-Dimethylaziridines.** The *cis*- and *trans*-2,3-dimethylaziridines were prepared from the corresponding 2-butenes by a modification of the five-step sequence of Clark and Helmkamp.[12] The 2-butenes were converted into *cis*- and *trans*-2,3-epoxybutane *via* the chlorohydrin as reported by Wilson and Lucas.[20] The epoxides were opened with ammonia, according to the method of Dickey, Fickett, and Lucas,[21] to give *erythro*- and *threo*-3-amino-2-butanol.

To a solution of 11.5 g of the 3-amino-2-butanol in 70 ml of water was added 12.5 g of concentrated sulfuric acid (98%) in 30 ml of water and the solution was concentrated under reduced pressure. The flask was then connected to a vacuum system (5 mm) and heated to 140°. The reaction gave 20.8 g (95%) of the crude aminobutyl sulfate[22] which was used in the next step without further purification. Recrystallization of the isomeric sulfates from 95% ethanol gave *threo*-3-amino-2-butyl sulfate, mp 269–270° dec, and *erythro*-3-amino-2-butyl sulfate, mp 280.0–281.5° dec. Distillation of the crude sulfate from base gave the pure *cis*- and *trans*-2,3-dimethylaziridines.

1-Chloroaziridine[23] (10). To 4.0 g of ethylenimine was added 240 ml of ice cold Purex (6% sodium hypochlorite content) and the solution was stirred for 1 hr with continued cooling. The 1-chloroaziridine formed was extracted with Freon 11, the extracts were combined, and the solution was dried over anhydrous magnesium sulfate. The solution was filtered, the solvent evaporated, and the residue distilled to give pure **10**, bp 70.0–70.5°.

N-Chlorination of Aziridines. General Procedure. The following general procedure was used for the preparation of the previously described[11] N-chloroaziridines (**11**, **12**, and **14**). To 10 mmol of aziridine was added 15 ml of ice-cold 0.8 *M* (12 mmol) sodium hypochlorite (commercial bleach) with swirling. After 5 min of reaction time the turbid mixture was extracted with four 2.5-ml portions of Freon 11. The combined extracts were dried over anhydrous magnesium sulfate and filtered through glass wool; the solvent was evaporated at temperatures below 30°. The products (**11**, **12**, and **14**) were purified by preparative vpc on a 10 ft × 3/8 in. column of 10% silicone fluid (A. H. Thomas No. 6407-J) on 60–80 Chrom W at 25°. Titration of aliquots of the crude N-chloroaziridines showed 90–100% conversion. The recovery of pure material after preparative vpc was usually *ca.* 50%.

1-Chloro-*cis*,*trans*-2,3-dimethylaziridine (16). A 125-ml Erlenmeyer flask containing 2.50 g (0.035 mol) of *trans*-2,3-dimethylaziridine was cooled in an ice bath and 60 ml of Purex (6% sodium hypochlorite solution), which had also been cooled to 0°, was added to the aziridine. The solution was stirred for 1 hr at 0° and then extracted with four 50-ml portions of Freon 11. The Freon solution was dried over anhydrous magnesium sulfate and filtered; the solvent removed at reduced pressure. The residue after two distillations gave 2.17 g (59%) of **16**, bp 63° (120 mm). The product showed infrared absorptions at 3.30, 3.41, 6.91, 7.29, 9.87, 10.47, and 12.43 μ. The ultraviolet spectrum in methanol had a maximum at 258 mμ (ε 460) and a maximum at 247 mμ (ε 320) in water. The nmr spectrum in chloroform showed two doublets for the two different methyl groups at τ 8.51 (3 H) and 8.77 (3 H). The absorption at τ 8.51 was assigned to the methyl group *cis* to the chlorine by analogy with the work of Brois.[11] A complex multiplet at τ 8.00 was assigned to the two ring protons.

1-Chloro-*trans*,*trans*-2,3-dimethylaziridine (18). A 125-ml Erlenmeyer flask containing 2.50 g of *cis*-2,3-dimethylaziridine was cooled in an ice bath and 65 ml of cold Purex (6% sodium hypochlorite solution) was added. The solution was stirred for 1 hr with continued cooling and then extracted with four 50-ml portions of Freon 11. The Freon solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated under reduced pressure. The residue was distilled to give 1.36 g (37%) of **18**, bp 54–56° (100 mm). The product showed infrared absorptions at 3.27, 6.86, 7.21, 8.81, 9.35, and 12.97 μ. The ultraviolet spectrum in methanol had a maximum at 251 mμ (ε 280). The nmr spectrum in chloroform showed the presence of only **18**. The spectrum consisted of a doublet at τ 8.81 (6 H) which was assigned to the methyl groups and a multiplet centered at τ 7.56 which was assigned to the two ring protons. Spin decoupling of the methyl groups caused the multiplet to collapse to a singlet.

When the experiment was repeated at −10° and the crude reaction mixture was extracted with chloroform at −10°, the nmr of the crude chloroform extract showed the presence of two N-chloroaziridines. The mixture showed methyl absorptions at τ 8.68 and 8.81 due to **19** and **18**, respectively. The ring protons appeared as a multiplet centered at τ 7.57. Irradiation of the methyl protons gave a singlet at τ 7.62 for **19** and a singlet at τ 7.51 for **18**. On warming, the absorptions due to **19** disappeared.

Kinetic Procedure. All kinetic measurements were made spectroscopically in the ultraviolet region of the spectrum. In all cases a Teflon-stoppered 1-cm quartz cell was used in the thermostated cell compartment (±0.1°). The methanol and water solutions ranged from 2.5×10^{-3} to 5.0×10^{-3} *M* in N-chloroaziridine concentration. All solutions appeared to follow Beer's law through at least two half-lives. The kinetic rate constants were calculated by computer.[24]

Product Study. A. 1-Chloroaziridine. A solution of 45 mg of 1-chloroaziridine (**10**) in 100 ml of water was heated for 12 hr at 70°, followed by 1 hr at 80°. Methone (340 mg) was added to the cooled solvolysis mixture and the solution was stirred overnight. The precipitate of formaldehyde bismethone (**22**) was collected by filtration, washed with water, and dried to give 10% of **22**, mp 189–191°, mmp 190–192° (lit.[25] mp 191°).

B. *trans*-1-Chloro-2-methylaziridine. A solution of 167 mg of **12** in 100 ml of water was heated at 80° for 8000 sec. The solution was cooled and 1.0 g of methone and 0.05 ml of N,N-dimethylaniline were added. The reaction mixture was allowed to stand for 12 hr and the precipitated methone derivatives were collected by filtration, washed thoroughly with water, and dried. The dried powder was dissolved in 30 ml of 80% ethanol, 0.05 ml of concentrated hydrochloric acid was added, and the solution was refluxed for 15 min. The solvent was removed on a flash evaporator and the residue was dissolved in ether. The ethereal solution was thoroughly washed with 10% potassium carbonate solution. The ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the solvent removed under reduced pressure. The residue was recrystallized from 80% ethanol to give 384 mg (73%) of **23**, mp 177–178°, mmp 175–177° (lit.[25] mp 175–176°).

The potassium carbonate solution from above was acidified with concentrated hydrochloric acid and the precipitate which formed was collected by filtration, washed with water, and dried to yield 243 mg (45%) of **22**, mp 189–191°, mmp 189–191° (lit.[25] mp 191°).

C. *cis*-1-Chloro-2-methylaziridine (11). The same procedure as used for **12** was used for **11** to give 43% of **22** and 57% of **23**.

D. 1-Chloro-2,2-dimethylaziridine (14). A solution of 243 mg of **14** in 100 ml of water was heated at 70° for 2500 sec. The solution was cooled, 630 mg of methone was added, and the mixture was stirred at room temperature for 48 hr. Sodium hydroxide (0.17 g) was added to dissolve the precipitated **22** and 50 ml of water was distilled from the reaction mixture into a stirred suspension of 456 mg of 2,4-dinitrophenylhydrazine reagent in 50 ml of

(20) C. E. Wilson and H. J. Lucas, *J. Amer. Chem. Soc.*, 58, 2396 (1936).
(21) F. H. Dickey, W. Fickett, and H. J. Lucas, *ibid.*, 74, 944 (1952).
(22) The procedure used is very similar to that recently described: P. G. Gassman and A. Fentiman, *J. Org. Chem.*, 32, 2388 (1967).
(23) A. F. Graefe, U. S. Patent 2,944,051 (1960); *Chem. Abstr.*, 54, 22681a (1960).
(24) We thank the Ohio State University Computer Center for providing us with computer time.
(25) E. C. Horning and M. G. Horning, *J. Org. Chem.*, 11, 95 (1946).

a solution of 1% hydrochloric acid in ethanol. The solvent was removed from the hydrazone solution on a flash evaporator and the residue was chromatographed on alumina to give 429 mg (82%) of acetone 2,4-dinitrophenylhydrazone (**24**), mp 123–125°, mmp 124–126°.

The basic solution was carefully acidified with hydrochloric acid and the precipitated **22** was collected by filtration, washed with water, and dried to yield 425 mg (66%) of pure **22**, mp 191–193°, mmp 190–191°.

E. 1-Chloro-*cis,trans*-2,3-dimethylaziridine (16). In a 50-ml round-bottomed flask equipped with a magnetic stirring bar and a distillation head was placed 25 ml of a 2.62×10^{-2} *M* solution of **16**. The solution was heated to reflux and the acetaldehyde which formed was distilled along with some water into 2,4-dinitrophenylhydrazine reagent. The precipitate which formed was collected by filtration and washed with a small amount of cold ethanol to give 190 mg (65%) of the 2,4-dinitrophenylhydrazone of acetaldehyde, mp 144.0–145.5° (lit.[26] mp 147°).

F. 1-Chloro-*trans,trans*-2,3-dimethylaziridine. (18). The same procedure as used for **16** was used for **18** to give 79% of the 2,4-dinitrophenylhydrazone of acetaldehyde.

(26) C. F. H. Allen, *J. Amer. Chem. Soc.*, 52, 2955 (1930).

***cis*-2,3-Diphenylaziridine (32).** Desoxybenzoin oxime was converted into **32** by lithium aluminum hydride reduction according to the literature procedure.[27]

Reaction of 32 with Sodium Hypochlorite. A solution of 101 mg of **32** in 5 ml of tetrahydrofuran was stirred with 20 ml of 6% sodium hypochlorite solution (Purex) with a vibromix stirrer for 3 hr. The solution was extracted with pentane and the extracts were combined and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent was evaporated under reduced pressure. The residue was dissolved in 10 ml of ethanol and 2,4-dinitrophenylhydrazone reagent was added to give 295 mg (53%) of benzaldehyde 2,4-dinitrophenylhydrazone, mp 237.5–238.0° (lit.[28] 237°).

Acknowledgment. The authors thank the National Cancer Institute of the Public Health Service for Grant No. CA-07110 which supported this work. We also thank Dr. David Dalrymple for stimulating discussions concerning this work.

(27) Patent to Shionogi and Co. Ltd., Netherlands Application 6,515,376; *Chem. Abstr.*, **65**, 15325a (1966); K. Kotera, S. Miyazaki, H. Takahashi, T. Okada, and K. Kitahonoki, *Tetrahedron*, 24, 3681 (1968).

(28) F. L. Roduta and G. Quibilan, *Rev. Filipina Med. Farm.*, 27, 123 (1936); *Chem. Abstr.*, 31, 98[7] (1937).

The Reaction of Highly Strained Polycyclic Molecules with Carbon–Carbon Multiple Bonds[1]

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Abstract: The addition of benzyne to tricyclo[4.1.0.0^{2,7}]heptane and the reaction of dicyanoacetylene with tricyclo[4.1.0.0^{3,7}]heptane have been studied in order to establish the stereochemical factors involved in the unusual addition of carbon–carbon multiple bonds to highly strained carbon–carbon single bonds. It was established that the attacking carbon–carbon multiple bond approaches the backside of the bent σ bond in an end-on manner. The specificity of the reaction is governed by the difference in steric environment of the two ends of the bent bond. The formation of 2-phenyltricyclo[4.1.0.0^{3,7}]heptane from the reaction of benzyne with tricyclo[4.1.0.0^{2,7}]heptane and the production of tricyclo[4.1.0.0^{3,7}]heptyl-5-maleonitrile from the addition of dicyanoacetylene to tricyclo-[4.1.0.0^{3,7}]heptane is discussed in terms of the intermediacy of a diradical species.

The addition of carbon–carbon double bonds to the strained σ bonds of small carbocyclic rings, which was first reported in 1965,[4,5] presented many interesting mechanistic questions. Although this reaction has been applied to a variety of systems,[6–9] it was only recently that the mechanistic details of this addition reaction have been clarified.[10–12] It has been demonstrated that the addition of olefins and acetylenes to bicyclo[2.1.0]pentane (**1**) occurs *via* the formation of a diradical intermediate[5,10,11] and that the approach of the carbon–carbon multiple bond is from the inside of the flap formed by the fused rings of bicyclo[2.1.0]-pentane.[12] The latter facet of the mechanistic picture was illustrated through the addition of maleic anhydride (**2**) to *exo,exo*-2,3-dideuteriobicyclo[2.1.0]pentane (**3**) to give **4** with the original label of **3** in the *exo* position of **4**. The stereochemistry of the deuterium labels of **4** required that the carbon–carbon multiple bond approach **3** from below the flap and invert the flap in the process of reacting.[11] This left, as the major unanswered mechanistic question, the problem of whether the carbon–carbon multiple bond approached the bottom side of **1** in a symmetrical manner as shown in **5**, or whether the approach was end-on as depicted by **6**. In order to demonstrate that a symmetrical ap-

(1) Paper XIII of a series on The Chemistry of Bent σ Bonds. For the preceding papers in this series see (a) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969) and (b) P. G. Gassman, F. J. Williams, and J. Seter, *ibid.*, **90**, 6893 (1968).

(2) Alfred P. Sloan Foundation Research Fellow, 1967–1969.

(3) National Institutes of Health Predoctoral Fellow, 1965–1968.

(4) P. G. Gassman and K. T. Mansfield, *Chem. Commun.*, 391 (1965).

(5) A. Cairncross and E. P. Blanchard, Jr., *J. Amer. Chem. Soc.*, **88**, 496 (1966).

(6) C. D. Smith, *ibid.*, 88, 4273 (1966).

(7) H. J. Reich and D. J. Cram, *ibid.*, **89**, 3078 (1967).

(8) M. R. Rifi, *ibid.*, 89, 4442 (1967).

(9) M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968).

(10) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1524 (1968).

(11) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **90**, 4746 (1968); P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **91**, 1684 (1969).

(12) It has been demonstrated that the approach of nitrogen–nitrogen double bonds also occurs from the inside of the flap of **1**: W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967).