Table I. Fmr Parameters of Some 2,2-Difluoronorbornanes[a]

Substituents	J_{FF}, Hz	Upfield[b] resonance (*endo*)	Downfield[b] resonance (*exo*)	*exo–endo* chemical-shift difference
None	222	2989	4284	1295
1-Methyl	222	2572	3834	1262
exo-3-Methyl	223	2976	3238	262
endo-3-Methyl	226	2353	4386	2033
3,3-Dimethyl	224	2474	3529	1055
endo-5-Methyl	221	2864	4338	1474
endo-6-Methyl	228	3360	4905	1545
7,7-Dimethyl	228	3639	4564	925
anti-7-Methyl	222	3142	4268	1126

[a] All samples were run as dilute solutions in methylene chloride. [b] Chemical shift in Hz downfield from internal C_6F_6.

for norbornyl derivatives that better calculations are clearly necessary before any firm theoretical conclusions can be drawn.

The seventh and eighth entries in Table I show a large *downfield* shift of the fluorine due to a methyl substituent in a 1,3-diaxial or nearly 1,3-diaxial relationship, a phenomenon which has been noted previously for the cyclohexane[4b] and decalin[4a, 7a] systems, but which has probably not been accorded the attention it deserves. Similar but smaller effects have been noted for C-13 and proton nmr parameters for methylcyclohexanes, and the explanation given is one based on steric compression of the atom with the magnetic nucleus in question.[17] The opposite directions of the shifts produced for fluorines eclipsed by vicinal methyls and in 1,3-diaxial relationships to methyls indicate an unexpectedly subtle interaction between methyl and fluorine. It is hoped that further studies will assess the validity of Grant's treatment[17] for systems of this type.

(17) (a) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967); (b) B. V. Cheney, *ibid.*, **90**, 5386 (1968).

Joseph B. Dence, John D. Roberts
Contribution No. 3777
Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109

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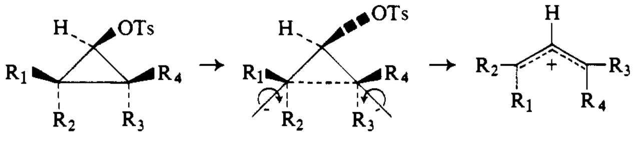
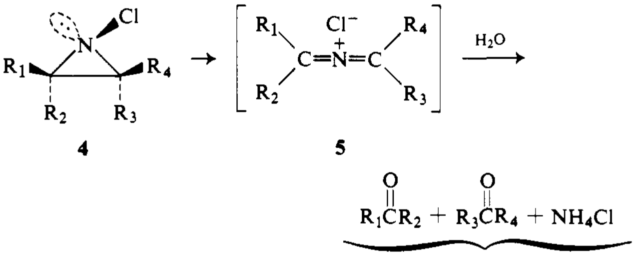
Concerted Carbon–Carbon Bond Cleavage in the Solvolysis of 1-Chloroaziridines[1]

Sir:

Recently the Woodward-Hoffmann symmetry rules[2] have been shown to predict both the products and relative rates for the electrocyclic opening of cyclopropyl cations **1** to allylic cations **2**.[3,4] When the R groups of **3** are hydrogen or methyl a consideration of electronic and steric interactions predicted results which were in agreement with experimental findings.[3,4] We report at this time that similar considerations can be applied, in the case of the three-membered ring, to the nitrogen analog of the carbonium ion, that is, to the nitrenium ion (divalent electron deficient nitrogen). We have found that 1-chloroaziridines (**4**) undergo concerted carbon–carbon bond cleavage under solvolytic conditions, probably to an intermediate such as **5**, followed by hydrolysis under the solvolysis conditions to yield **6**.



3 **1** **2**



4 **5** **6**

cis- and *trans*-2,3-dimethylaziridines were prepared from the corresponding isomeric 2-butenes utilizing a slight modification of the literature procedure.[5] *trans*-2,3-Dimethylaziridine (**7**) was converted into 1-chloro-*cis*,-*trans*-2,3-dimethylaziridine (**8**)[6] by stirring with 6% aqueous sodium hypochlorite at 0°. Extraction of **8** with Freon 11 followed by drying and fractional distillation at reduced pressure gave pure **8**. When *cis*-2,3-dimethylaziridine (**9**) was allowed to react under similar conditions a mixture of **10** and **11** was obtained at 0°.[8]

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(1) Paper VI in a series on the chemistry of nitrenium ions. For the previous paper in this series see P. G. Gassman, G. Campbell, and R. Frederick, *J. Am. Chem. Soc.*, **90**, 7377 (1968).

(2) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965). See also H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

(3) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965).

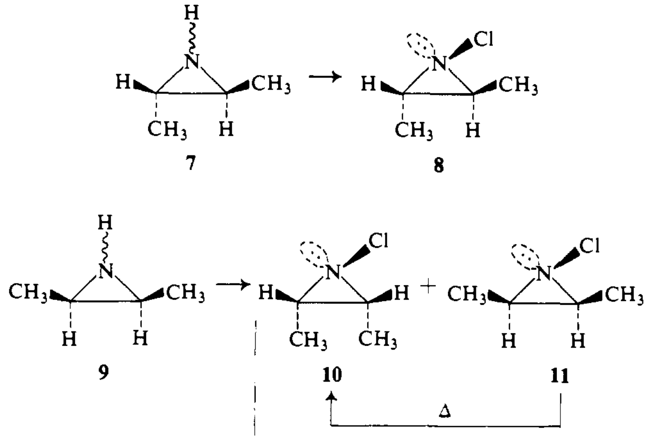
(4) P. von R. Schleyer, G. W. Van Dine, U. Schollkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

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

(6) Compound **8** showed an ultraviolet spectrum in methanol with λ_{max} 258 mμ (ε 460) and in water with λ_{max} mμ 247 (ε 320). The nmr spectrum 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 while the peak at τ 8.77 was assigned to the methyl *trans* to the chlorine. These assignments were based on the work of Brois[7] on the monomethyl-N-haloaziridines.

(7) S. J. Brois, *J. Am. Chem. Soc.*, **90**, 506, 508 (1968).

(8) Extraction of the mixture of 1-chloro-2,3-dimethylaziridines (**10** and **11**) into chloroform and immediate recording of the nmr spectrum showed the presence of two isomers. The methyl absorptions occurred 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 **11** appearing at τ 7.62 and the singlet for **10** appearing at τ 7.51. Irradiation of the ring protons collapsed the doublets of the methyl protons to singlets.



On standing at room temperature **11** completely isomerized to **10**.[9]

By analogy with our previous work on the thermal and silver ion catalyzed heterolytic cleavage of the N-Cl bond of a variety of N-chloramines,[10] we anticipated that simple 1-chloroaziridines should undergo solvolysis with heterolytic cleavage of the N-Cl bond to give chloride anion and the nitrogen analog of the cyclopropyl–allyl cation. In order to confirm our predictions we studied the solvolyses of **12**, **8**, and **10**. *We found that these 1-chloroaziridines solvolyzed with relative rates of* 1, 1.49 × 10^3, *and* 1.55 × 10^5, *respectively*, in the absence of silver ion.[11]

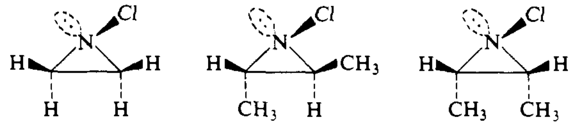
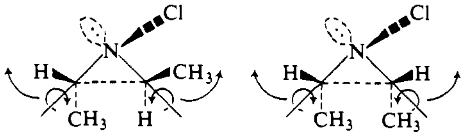


Table I. Rates of Solvolysis of 1-Chloroaziridines at 60°

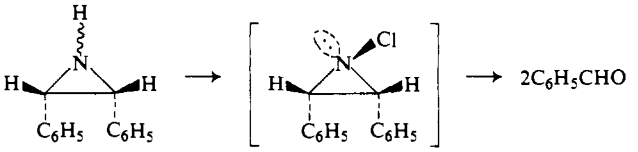
Compound	Solvent	Rate, sec^{-1}
12	Water	$(6.5 \pm 1.3) \times 10^{-7}$
8	Water	$(9.6 \pm 0.3) \times 10^{-4}$
	Methanol	$(1.2 \pm 0.2) \times 10^{-5}$
10	Methanol	$(1.3 \pm 0.1) \times 10^{-3}$

The rate constants are listed in Table I. Several features of the solvolysis indicated that heterolytic cleavage of the N-Cl bond was occurring. In particular the increase in rate by a factor of 76 in going from methanol to water demonstrated the polar nature of the transition state. In addition the greatly increased rates due to methyl substitution demonstrated that considerable charge was being developed on the carbons adjacent to nitrogen in the transition state. All of these features are consistent with a Woodward–Hoffmann type of concerted carbon–carbon bond cleavage in the transition state. On these grounds the rate increase by a factor of 104 in going from **8** to **10** was expected because of the greater relief of steric strain in transition state **13** than in transition state **14**. Since this type of carbon–carbon bond cleavage should involve a disrotatory process, the rotation shown in **13** would relieve the methyl–methyl interaction while the hydrogen–hydrogen interaction would increase. This can be compared to **14** where a methyl–hydrogen interaction is being decreased on one side of the ring and increased on the other side of the ring. Energywise, **13** should be preferred. Kinetically, this difference is demonstrated by **10** solvolyzing 104 times faster than **8**.[12]



Product studies were carried out for both the thermal and silver ion catalyzed solvolyses of **8** and **10**. In the presence of silver ion in water 1 equiv of **8** gave 61% of 2 equiv of acetaldehyde (isolated as its 2,4-dinitrophenylhydrazone) and 99% of the theoretical amount of silver chloride. In the absence of silver ion 65% of the theoretical amount of acetaldehyde was obtained. In the same manner the solvolysis of **10** in water gave 79 and 70% of the theoretical amount of acetaldehyde in the non-silver ion catalyzed reaction and silver ion catalyzed reaction, respectively.

On the basis of the results discussed above it was anticipated that 1-chloro-*trans,trans*-2,3-diphenylaziridine (**15**) should be extremely reactive. In fact **15** was so reactive that it could not be detected. When *cis*-2,3-diphenylaziridine[13] (**16**) was treated with hypohalite under the mildest conditions which we were able to use, the only isolable product was benzaldehyde (53% of theoretical). We believe that the benzaldehyde was formed *via* the intermediacy of **15**.



We are currently investigating several aspects of the solvolysis of 1-chloroaziridines.

Acknowledgment. The authors wish to thank the National Cancer Institute of the Public Health Service for Grant CA-07110 which supported this work.

(9) The rapid thermal isomerization of **11** to **10** has ample precedent in the literature. See D. Felix and A. Eschenmoser, *Angew. Chem. Intern. Ed. Engl.*, **7**, 224 (1968).

(10) (a) P. G. Gassman and B. L. Fox, *J. Am. Chem. Soc.*, **89**, 338 (1967); (b) P. G. Gassman and R. L. Cryberg, *ibid.*, **90**, 1355 (1968); (c) P. G. Gassman, F. Hoyda, and J. Dygos, *ibid.*, **90**, 2716 (1968).

(11) Kinetic measurements were made by following the disappearance of the N-Cl bond in the ultraviolet region of the spectrum. A Cary Model 15 recording ultraviolet spectrophotometer thermostated to ±0.1° was used to follow the kinetics. The equilibration time of the sample resulted in larger than desired variation between individual runs. Kinetic measurements on **12** were particularly difficult due to its very slow rate and high volatility (bp 70.0–70.5°) at the required solvolysis temperature.

(12) This rate difference does not reflect the actual difference in transition-state energies since **10** probably has a higher ground-state energy than **8** because the methyl-methyl interaction in the ground state of **10** is probably greater than the methyl-chlorine interaction in the ground state of **8**.

(13) Patent to Shionogi and Co., Ltd., Netherlands Application 6,515,376; *Chem. Asbtr.*, **65**, 15325*a* (1966).

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

Paul G. Gassman,[14] Dorothy K. Dygos
Department of Chemistry
The Ohio State University, Columbus, Ohio 43210

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