$$-\frac{\mathrm{d}A}{\mathrm{d}t} = k_3AB \tag{2}$$

$$A_0 = A + C \tag{3}$$

$$K = \frac{k_1}{k_2} = \frac{BC}{A} \tag{4}$$

$$A_0\left(\frac{1}{A} - \frac{1}{A_0}\right) + \ln\frac{A}{A_0} = \frac{k_1k_3}{k_2}t \tag{5}$$

The experimental data fit the equation satisfactorily (Table I, columns 3, 4). The rate enhancement observed when going to lower concentrations, $A_0$, was shown to be due to a "salt effect";[14] adding lithium perchlorate to a run starting with $A_0 = 0.02\ M$ to bring the total lithium concentration to 0.18 $M$ ($A_0/(\mathrm{LiClO_4}) = {}^1/_7$) reduces the value of $k_1k_3/k_2$ to that of the 0.18 $M$ run (Table I, column 5).

Adding lithium thiophenolate (C) must decrease the rate by shifting equilibrium 1a to the left side ("common ion effect"). As demonstrated for $A_0 = 0.06$ and $C_0 = 0.05\ M$ by curve II in Figure 1, this is the case. If, as anticipated, no rate-determining species other than A, B, and C are present or accumulate during the reaction, this run must correspond to an approximately half-reacted run having started with $A_0 = 0.11\ M$ and with no $C_0$ added. In fact, II falls exactly on I if plotting is started at 50% (Figure 1, I, crosses). This is also verified mathematically by using eq 5, modified for this situation to $(A_0 + C_0)\cdot[(1/A) - (1/A_0)] + \ln(A/A_0) = (k_1k_3/k_2)t$ (Table I, column 6).

The results described here are the first example of a kinetic measurement of carbenoid decomposition.[10] The unusual kinetic behavior found is described by a simple equation, in accordance with the existence of a free methylene[15] formed by α elimination in THF solution and with the reaction of this carbene with its carbenoid precursor to form the "dimer." Previously, this mode of dimer formation has been postulated to be most likely.[4,16] Further measurements with the aim of determining the equilibrium constant $K$ are in progress.

(14) Or the dissociation of A to $(\mathrm{C_6H_5S})_3\mathrm{C^-}$ and $\mathrm{Li^+}$ prior to formation of the carbene.

(15) Calling a spade a spade, we would rather name it "carbon monoxide bis(phenylthio)acetal," according to its low electrophilic carbene reactivity.[1]

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## Nuclear Magnetic Resonance Spectroscopy. Studies of Fluorine-19 Chemical Shifts in Norbornane Derivatives[1]

*Sir:*

The use of fluorine-19 nuclear magnetic resonance (fmr) spectroscopy for investigation of conformational analysis has achieved considerable popularity in recent years.[2-7] However, little attention has been paid to a detailed structural interpretation of the wide variation in the fluorine chemical shifts which are observed, although it has been pointed out that chemical-shift differences in a related series of fluorides may reflect conformational subtleties.[8,9]

We have initiated research on substituent effects on fluorine shielding in relatively rigid systems, taking as a starting point norbornyl compounds, which have proven to be so interesting and useful in studies of other kinds. We present here some preliminary results on fmr chemical shifts in variously methylated 2,2-difluoronorbornanes.

Nine 2,2-difluoronorbornanes were prepared by treatment of the corresponding ketones with sulfur tetrafluoride,[10,11] and their fluorine shifts were obtained at 56.4 MHz with a Varian A56/60 spectrometer (see Table I). The spectra were basically of the AB type with varying amounts of resolvable fine structure caused by proton–fluorine coupling. The broadness of the signals often made it impossible to determine the coupling constants and chemical shifts to better than 5–10 Hz.

The work of Anet[12] plus the demonstration by Williamson[13] that a Karplus-type curve is a good description of vicinal proton–fluorine coupling permitted in each case the reasonable assignment of the upfield resonances as being due to the *endo* fluorines. The data clearly show the extreme sensitivity of fluorine shielding to the molecular environment in closely related compounds. Examination of the data for the first four entries in Table I reveals an important vicinal orientation effect on fluorine shielding. A large upfield shift occurs at a methyl–fluorine dihedral angle of 0°; the effect is much smaller at 60° and essentially absent at 120°. The data for *trans*-decalin derivatives indicate that a large upfield shift should also occur at a dihedral angle of 180°.[14] Approximate molecular orbital calculations employing extended Hückel wave functions[15] and the magnetic shielding formalism of Pople[16] provide some quantitative support for the effect of a vicinal methyl group on fluorine shielding as a function of dihedral angle.[14] The computed effects are, however, so much smaller than those actually observed

(1) Supported by the National Science Foundation.

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(11) Satisfactory elementary analyses have been obtained for new compounds.

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**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.

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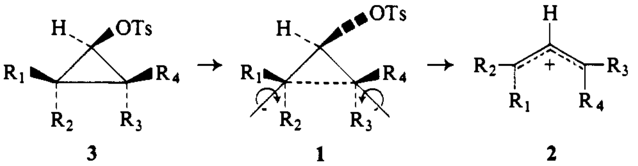
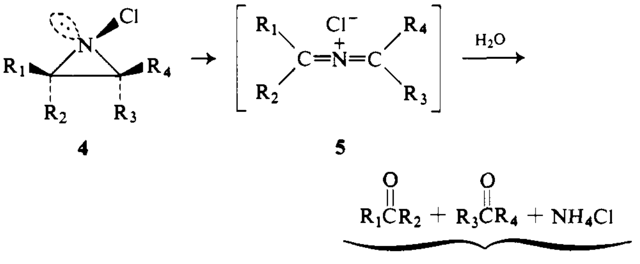
## Concerted Carbon–Carbon Bond Cleavage in the Solvolysis of 1-Chloroaziridines[1]

*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).

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(6) Compound **8** showed an ultraviolet spectrum in methanol with $\lambda_{max}$ 258 mμ (ε 460) and in water with $\lambda_{max}$ 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.