

AXIAL PREFERENCES IN SELENANES

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The axial preference of the oxide in thiane 1-oxide (eq. 1, S=O) and of the proton in protonated thiane (eq. 1, S[⊕]-H) has been attributed to attractive interactions between the 1



substituent and the carbons and axial protons at the 3, 5 positions.⁴ For a given 1 substituent, there should be an optimal distance from the 3, 5 atoms that maximizes these attractive forces and hence the proportion of axial isomer. It is not clear that the sulfur system offers the most favorable geometry for the oxide substituent. Lengthening the bonds may make the interactions even more attractive by further descent into the Morse-like potential well, or less attractive if the optimal distance has already been reached. In order to probe the geometric dependence of attractive interactions, we have constructed systems with longer bonds by replacement of sulfur with selenium in these heterocyclic systems. We report an increase in the proportion of axial isomer in selenane 1-oxide (eq. 1, Se=O) over that in the corresponding thiane system, and a clear preference of the methyl group in the Se-methyl-selenonium salt (eq. 1, Se[⊕]-CH₃) for the axial position.

For determination of configuration at the 1 position, we utilize the geminal coupling constant between the protons at the 2 or 6 positions. The magnitude of this coupling is a well-substantiated indicator of configuration at sulfur.^{4, 5} When the substituent is axial (lone

pair equatorial), the coupling constant has a normal value close to 14 Hz. When the substituent is equatorial (lone pair axial), the coupling constant is consistently 2 Hz less. The values for four pertinent sulfur systems are given in Table I. The configuration for the protonated form and both sulfoxides is firmly established.⁴ The configuration of the methylsulfonium salt has not been established by other means, but the value of J_{gem} is consistent with an equatorial orientation. The axial-oxide and the protonated systems, it is noted, have similar geminal couplings. Numerous other sulfoxide and sulfimide systems have been found to follow this pattern.^{4, 6}

We have prepared protonated selenane,^{4a} selenane 1-oxide, and Se-methylselenanium iodide, deuterated in the β position for spectral clarity. The geminal coupling constants for the α protons are given in Table II. Couplings in selenane systems are consistently lower than those in the corresponding thianes because of differences in electronegativity, cp., the parent heterocycles, thiane (13.6 Hz) and selenane (12.3 Hz). The value for protonated selenane has been reported previously; the axial orientation of the 1 proton is guaranteed by the magnitudes of the vicinal coupling constants.^{4a} At -130° , the spectrum of the selenoxide contains AB quartets for both axial (84%) and equatorial (16%) isomers; ring reversal causes spectral averaging above the coalescence temperature (-102° at 90 MHz). Assignment of configuration for the selenoxides parallels that in the sulfoxides.^{4, 5} The axial configuration is assigned to the isomer with a smaller α -proton chemical-shift difference (0.25 vs. 0.80 ppm), the larger coupling constant (Table II), and the higher-field midpoint. The geminal coupling constants for the axial selenoxide and the protonated selenane are essentially identical (13 Hz), and about 3 Hz larger than that for the equatorial selenoxide (10 Hz). The spectrum of the methylselenonium salt contains resonances for a single isomer at -88° . Because coalescence would probably occur below -88° , the observed value of J_{gem} may be a weighted average for two conformations. The quantity, however, remains unchanged from 35 to -88° , so that the presence of two species in equilibrium is unlikely. The geminal coupling constants in the axial and equatorial methylselenonium salts are expected to be quite different, by analogy to the sulfoxides and selenoxides.

The 84% proportion for the axial selenoxide is larger than that for the axial sulfoxide (62%).^{4c} Thus the longer carbon-selenium bonds do enhance the proportion of axial isomer. More startling is the result for the methylselenonium salt. The magnitude of the geminal coupling constant (12.4 Hz) is clearly in the range for the axial isomers, and over 2 Hz larger

Table I

Geminal Coupling Constants at the α -Position in 1-Substituted Thianes (Hz)

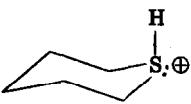
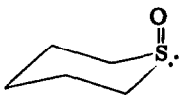
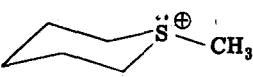
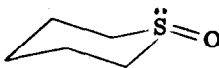

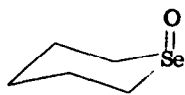
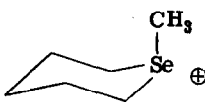
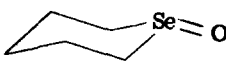
	Axial Group	Equatorial Group
	14.5	
	13.7	
		12.3
		11.7

Table II

Geminal Coupling Constants at the α -Position in 1-Substituted Selenanes (Hz)

	Axial Group	Equatorial Group
	13.0	
	12.9	
	12.4	
		10.0

than the value for the equatorial selenoxide. Even if the observed J_{gem} were a weighted average for two isomers, the equilibrium must lie well on the axial side. In the thiane series, the methyl salt has nearly the same coupling as the equatorial oxide; in the selenane series, as the axial oxide. The axial preference of the methylselenium salt indicates that a gauche interaction in a C-C-Se-C moiety is favored over a trans interaction, contrary to the tenets of hydrocarbon conformational analysis based on the properties of n-butane.⁷

The increase in the proportion of axial isomer for both Se=O and $\text{Se}^{\oplus}\text{-CH}_3$ indicates that lengthening the bonds brings the 1-3 and 1-5 interactions into a still more attractive region of the potential well. Whether the optimal distance has been reached or passed for either the oxide or the methyl substituent cannot be determined without recourse to data from systems with even longer bonds. The conformational equilibrium of eq. 1 has proved to be sensitively controlled by the interplay of atom-atom interactions whose attractive or repulsive nature is strongly dependent on internuclear distances. We have measured the barriers to ring reversal in selenane ($\Delta G^{\ddagger} = 8.2$ kcal/mol), selenane 1-oxide (8.3), selenane 1, 1-dioxide (6.7), and tellurane (7.3), and will report on these quantities in the full treatment of this study.

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