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AZIRIDINES VII. PROTON COUPLING CONSTANTS IN STYRENIMINES

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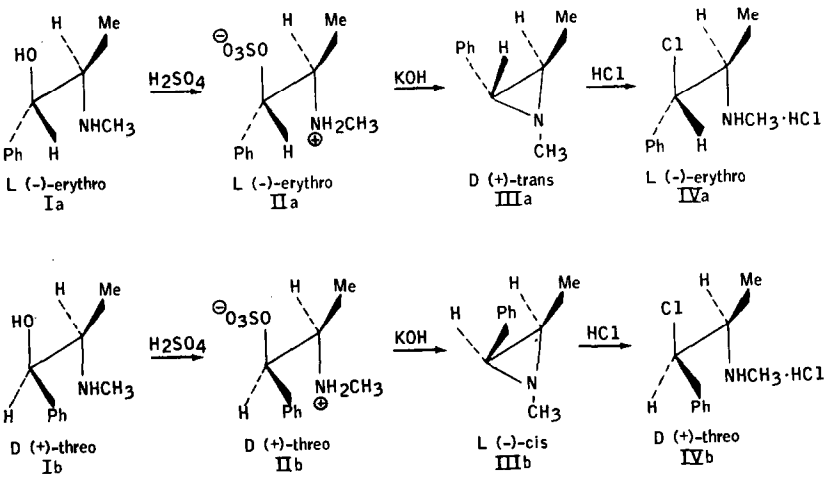
In a recent paper[1] we proposed that cis coupling was larger than trans coupling between ring protons in styrenimines by analogy with nmr parameters reported[2] for simple epoxides. Moreover, Karplus' theoretical work on the dependence of vicinal coupling constants on dihedral angle[3] also lends qualitative support to this same assignment.

To date, no unambiguous measurements of the cis and trans proton coupling constants in aziridines have been reported. In the present communication, the analysis of configurationally pure styrenimines was undertaken to obtain these values. In addition, our studies on substituted styrenimines revealed a remarkable variation of coupling constants with the position of the electronegative substituent on the aziridine ring.

The styrenimines studied were obtained via a new stereospecific synthesis we recently described[4]. Contrary to earlier reports[5], the sulfation of naturally occurring L(-)ephedrine and D(+)-pseudoephedrine with sulfuric acid gives sulfate esters (II) which readily cyclize in high yields to optically active aziridines (III) under basic conditions. Conversion of IIIa and IIIb to the known[5b,5c,6] chloroamine hydrochlorides IVa and IVb respectively, firmly established the optical purity of the arylaziridines.



The application of this procedure to norephedrine (Va) and pseudo-norephedrine (Vb) gave excellent yields of the configurationally pure aziridines VIa and VIb shown in Figure 4. The proton spectra of the freshly distilled styrenimines, IIIa, IIIb, VIa and VIb were recorded as neat liquids (TMS as internal reference) at room temperature on a Varian A60 spectrometer. These spectra are illustrated in Figures 1, 3 and 4. Since IIIa appeared to be a mixture of invertomers at ambient temperature, the ring proton signals were not well defined (see Figure 1). Excellent resolution of the ring protons was realized at temperatures of 100° or higher thus allowing an accurate determination of the vicinal coupling constant for the trans isomer IIIa (Figure 2).

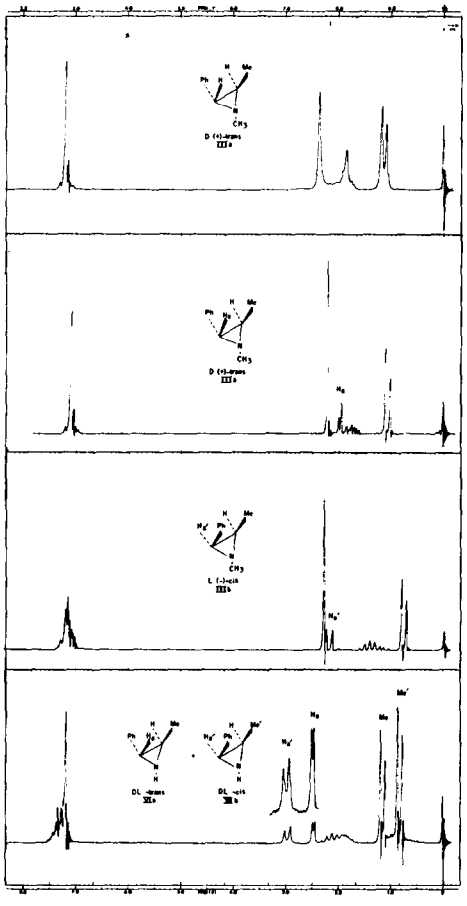


Figure 1. Proton spectrum of neat IIIa at room temperature. Phenyl resonance signal attenuated 2x.

Figure 2. Proton spectrum of neat IIIa at 150°C (internal HMDS).

Figure 3. NMR spectrum of neat IIIb at room temperature.

Figure 4. NMR spectrum of neat VIa and VIb at room temperature. Phenyl resonance signals attenuated 2x.

The coupling constants for these isomerically homogeneous aziridines (determined at a sweep width of 100 cps) are depicted in Table I.

TABLE I

Vicinal Coupling Constants for Styrenimines

Aziridine	$J_{vicinal}$ (cps)
IIIa (trans)	2.8
IIIb (cis)	6.6
VIa (trans)	2.8
VIb (cis)	6.6

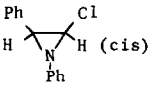
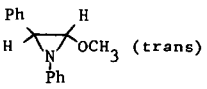
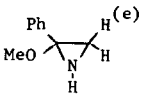
In accord with expectations, our data provide unequivocal evidence for the validity of the premise that the cis protons are more strongly coupled than the trans protons in the aziridine ring[7]. Moreover, our analysis of a wide spectrum of N-alkyl, N-aralkyl, N-aroyl, N-carbamyl, N-carboalkoxy, N-halo, N-arylsulfonyl, and N-alkanesulfonyl styrenimines, 2-vinylaziridines and 2-carboalkoxyaziridines suggests that the stereospecificity of vicinal coupling, i.e., $J_{cis} > J_{trans}$ will prevail regardless of the nature of the substituents on the aziridine ring. Accordingly, this relationship provides an invaluable aid in making configurational assignments.

In harmony with the observed dependence of J on substituent electronegativity in epoxides and cyclopropanes[8], we have also found variations in the proton coupling constants with the nature of the substituent on the ring. The possibility that a clear-cut dependence of J on substituent electronegativity (SE) exists is currently being assessed in a systematic study of 1- and 2-substituted styrenimines.

Germane to the mechanism of proton coupling in three-membered rings is the striking variation in J with the position of the electronegative substituent on the aziridine ring. A comparison of the J values of styrenimine and its N- and C-chloro and methoxy analogs cited in Table II clearly illustrates this unusual "positional effect".

TABLE II

J_{cis}, J_{trans} and J_{gem} Values for Styrenimines[a]

Aziridine	J_{cis}	J_{trans}	J_{gem}
	6.1	3.3	0.9
	8.5[b]	6.3[b]	3.3
	5.0[c]		
		2.0[c,d]	
			0[f]

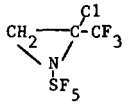
(a) The J_{cis} and J_{trans} values predicted by the Karplus equation (3) are 8.2 and 5.9 cps, respectively. The J_{gem} value predicted by Gutowsky et al (2b) is 5.1 cps.

(b) The J_{cis} and J_{trans} assignments were confirmed by N-chlorination of VIa and VIb with t-butylhypochlorite. The J_{vic} values for the N-chloro analogs of VIa and VIb were 5.9 and 8.6 cps, respectively.

(c) Value reported by J. A. Deyrup and R. B. Greenwald, J. Am. Chem. Soc. 87, 4538 (1965).

(d) Since the results of Williamson and co-workers[8] predict that the methoxy and chloro groups will have about the same effect on J, the trans isomer of 3-chloro-1,2-diphenylaziridine should have a coupling constant of approximately 2 cps.

(e) Prepared via the sodium methoxide-catalyzed addition of methanol to 2-phenylazirine as described by R. F. Purcell, Chem. and Ind. 1396 (1963). A sample of 2-phenylazirine was kindly provided by Dr. C. Smolinsky.

(f) As in (d), it is assumed that the methoxy and chloro substituents affect J similarly. Recently, A. L. Logothetis, J. Org. Chem. 29, 3049 (1964) found that J_{gem} in  was also zero.

Clearly, C-substituents of increasing electronegativity tend to decrease the vicinal and geminal couplings in the aziridine ring. On the other hand, N-substituents of increasing electronegativity appear to increase these couplings[9].

The data in Table II reveal that only the vicinal couplings for aziridines with electronegative N-substituents, e.g., N-chlorostyrenimines, show good agreement with Karplus' calculations. In general, a conspicuous lack of quantitative agreement exists between the predicted and experimental vicinal and geminal couplings in aziridines.

It appears that substituent electronegativity[10] and substituent position play important roles in determining the magnitude and perhaps the relative signs[11] of geminal and vicinal proton-proton couplings in aziridines. It is quite likely that substituent perturbations affect these couplings through a combination of mechanisms which at present cannot be explained.

A complete account of the present communication will be published elsewhere.

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