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### REINTERPRETATION OF EARLIER SELENIUM-77 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA OF SUBSTITUTED VINYLIC SELENIDES IN THE LIGHT OF THE $\gamma$ -cis EFFECT AND A COMMENT ON ITS UBIQUITOUS NATURE

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# REINTERPRETATION OF EARLIER SELENIUM-77 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA OF SUBSTITUTED VINYLIC SELENIDES IN THE LIGHT OF THE $\gamma$ -cis EFFECT AND A COMMENT ON ITS UBIQUITOUS NATURE

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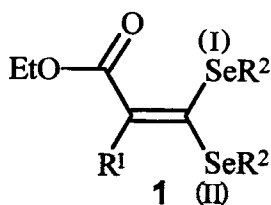
The generality of the  $\gamma$ -cis effect is discussed in connection with various nuclei and shieldings due to this effect are used as a criterion for the reassignment of earlier  $^{77}\text{Se}$  NMR data of E and Z isomers of substituted vinylic selenides. The application of the observed  $\gamma$ -cis effect to gauge the stereochemistry of olefins bearing phosphorus-, tin- and lead-containing substituents is suggested.

**Key words:**  $^{77}\text{Se}$  NMR, E/Z isomers,  $\gamma$ -cis effect, Multinuclear Magnetic Resonance, vinylic selenides.

In early 1993, Robinson *et al.*<sup>1</sup> published  $^{77}\text{Se}$  NMR data for two series of regioisomers of seventeen ethyl- $\alpha$ -(phenylseleno)cinnamates: the "series 1" isomers presented  $\delta\pi_{\text{Se}} = 326.8\text{--}367.5$  ppm and  $^3J_{\pi_{\text{Se}}\text{--}^1\text{H}} = 6\text{--}8$  Hz (olefinic proton), while, for the "series 2,"  $\delta\pi_{\text{Se}} = 472.7\text{--}485.4$  ppm and  $^3J_{\pi_{\text{Se}}\text{--}^1\text{H}} = 4\text{--}5$  Hz (olefinic proton). Thus, the authors considered that "series 1" should be the E-isomers and "series 2," the Z-isomers, based solely on the measured coupling constants, according to the work of Johannsen *et al.*<sup>2</sup>

However, subsequent results by Fäcke *et al.*,<sup>3</sup> and by ourselves,<sup>4</sup> on other vinylic selenides, have shown that the use of  $^3J_{\pi_{\text{Se}}\text{--}^1\text{H}}$  (olefinic proton) to gauge the stereochemistry of these compounds can be misleading. There are, now, various known examples<sup>3,4</sup> of pairs of isomers presenting a larger value of  $^3J_{\pi_{\text{Se}}\text{--}^1\text{H}}$  for the *trans*-, rather than for the *cis*-olefinic proton, in contrast to the results of Johannsen *et al.*<sup>2</sup>

We have proposed to use the fact that the Z-isomers always present  $^{77}\text{Se}$  NMR absorptions shielded in regard to the E-isomers (due to the  $\gamma$ -cis effect) as a more reliable criterion for regioisomer assignment than the one based on the coupling constants, proposed by Johannsen *et al.*<sup>2</sup> Hence, as the "series 1" presents NMR signals shielded by 117.9–145.9 ppm, as compared to "series 2," we suggest that the former should be reassigned to the Z-isomers and the latter, to the E-isomers, reversing the previously reported<sup>1</sup> assignments.



It must be pointed out that, at present, there is no exception to the observation of  $\gamma$ -*cis* effect induced shieldings, both in the case of tetra- and tri-substituted ethylenes (including ethyl esters) bearing at least one selenium substituent, as one can ascertain from the literature data.<sup>3-6</sup> On the other hand, disubstituted ethylenes present the only reported anomalous case, to the best of our knowledge: two pairs of regioisomeric ethyl- $\beta$ -(organoselenium)acrylates fail to present the expected  $\gamma$ -*cis* effect induced shieldings in the  $^{77}\text{Se}$  spectra of their *Z*-isomers<sup>2,4</sup> (presumably due to differences in preferred rotamers). This notwithstanding, they do conform to the criterion of Johannsen *et al.*<sup>2</sup> So, for disubstituted olefins, whenever possible, one should use the well established values of  $^3J_{\text{H-H}}$  to confirm the stereochemical assignments.

Next we wish to consider the problem of some ketene(diseleno)ketals (**1**), whose unassigned  $^{77}\text{Se}$  NMR data were also reported in the same pioneer work of Johannsen *et al.*<sup>2</sup> Assuming that the  $\gamma$ -*cis* effect induced shieldings are characteristic of each individual substituent, on comparing the data for the compound pairs **1b/1e** and **1c/1f** we suggest the assignments presented in Table I. For the pair **1a/1d**, however, we offer no assignments, as the presence of angular strain<sup>7</sup> due to the five-membered ring invalidates our initial assumption. Compound **1g** was included in Table I for comparison purposes only, as its  $^{77}\text{Se}$  NMR data had already been assigned by Johannsen *et al.*<sup>2</sup>; it serves to illustrate the point that, in the absence of perturbing effects (such as ring tension), the carboxyethyl group induces a shielding of ca. 100 ppm: thence we calculate shieldings due to the acetyl and cyano groups to be ca. 45 ppm (from **1b/1c**) and ca. 14 ppm (from **1e**), respectively, in agreement with the expected bulk of each substituent (all rotamers being accounted for). The 615 ppm shielding observed in compound **1f**, however, taken at face

TABLE I  
 $^{77}\text{Se}$  chemical shifts<sup>a</sup> of ketene(diseleno)ketals **1**<sup>2</sup>

compd.	R <sup>1</sup>	R <sup>2</sup>	$\delta\pi\text{Se (I)}$ / ppm	$\delta\pi\text{Se (II)}$ / ppm
<b>1a</b>	-COMe	-CH <sub>2</sub> CH <sub>2</sub> -	606 or 639 <sup>b</sup>	
<b>1b</b>	-COMe	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	399	455
<b>1c</b>	-COMe	-CH <sub>2</sub> Ph   -CH <sub>2</sub> Ph	462	515
<b>1d</b>	-CN	-CH <sub>2</sub> CH <sub>2</sub> -	593 or 615 <sup>b</sup>	
<b>1e</b>	-CN	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	401	487
<b>1f</b>	-CN	-CH <sub>2</sub> Ph   -CH <sub>2</sub> Ph	462	615
<b>1g</b>	-H	-CH <sub>2</sub> Ph   -CH <sub>2</sub> Ph	417 <sup>c</sup>	514 <sup>c</sup>

<sup>a</sup> At 17.04 MHz, in CDCl<sub>3</sub>, Me<sub>2</sub>Se = 0 ppm; <sup>b</sup> Not assigned; <sup>c</sup> Assignments from ref.<sup>2</sup>.

value, would seem to indicate a deshielding  $\gamma$ -cis effect, contradicting that observed in **1e**: this puzzling datum, as well as the present impossibility to provide even tentative assignments for the data due to compounds **1a/1d** are a sure indication that this problem still merits further investigation.

In conclusion, we would like to address the question of the ubiquity of the  $\gamma$ -cis effect: the relatively additive effects due to alkyl and aryl substituents on the chemical shifts in  $^{13}\text{C}$  NMR were observed quite early, during the development of this technique as a tool for structural investigation. Particularly, the shieldings due to  $\gamma$  substituents proved to be a very characteristic effect and various theories<sup>7,15</sup> regarding its origins have been put forward, although usually dealing with the  $\gamma$ -gauche, rather than the  $\gamma$ -cis effect. During the investigation of other nuclei, various authors observed upfield shifts due to Z-substituents (Table II), in some cases a quite large shielding, and either attributed this to the  $\gamma$  effect or did not comment upon it. To our knowledge, we were the first to point out that this fact could be used as a probe to distinguish between isomers.<sup>4</sup> More recently we put forward the idea that softer nuclei should exhibit greater sensitivity to the  $\gamma$  effect.<sup>13</sup> The data presented in Table II provides support for this idea, although the examples selected, while the simplest we could find, are far from ideal. Certainly, various other effects, besides the  $\gamma$ -cis, should be considered if we wish to explain the fine variations presented in that table (for instance, intersubstituent strain around the silicon atom may be responsible for the surprisingly small effect observed for compounds **2f**<sup>11</sup>). Nonetheless, these data permit us to suggest that it is possible to use the  $\gamma$ -cis effect to gauge the stereochemistry not only of vinylic selenides and tellurides, but also of olefins containing other heteroatom bearing substituents, especially phosphorus, tin and lead. It may also be of help in the investigation of

TABLE II  
Chemical shifts<sup>a</sup> ( $\delta_{\gamma}$ ) and  $\gamma$ -cis Shieldings<sup>b</sup> ( $\Delta\delta_{\gamma}$ ) of  $\text{RCH}=\text{CHY}$  regioisomer pairs (E/Z)

compd.	obsrvd. nucleus	R	Y	$\delta_{\gamma}$ / ppm		$\Delta\delta_{\gamma}$ / ppm	ref.
				E	Z		
<b>2a</b>	$^{19}\text{F}$	Me	F	-129.6	-131.5	1.9	8
<b>2b</b>	$^{17}\text{O}$	Me	OMe	44	35	9	9
<b>2c</b>	$^{15}\text{N}$	Et(C=O)	NHMe	296.0	286.4	9.6	10
<b>2d</b>	$^{13}\text{C}$	Me	Me	17.6	12.1	5.5	11
<b>2e</b>	$^{31}\text{P}$	Me	PPh <sub>2</sub>	-14.2	-32.7	18.5	12
<b>2f</b>	$^{29}\text{Si}$	Me	SiMe <sub>3</sub>	-10.6	-8.4	2.2	11
<b>2g</b>	$^{77}\text{Se}$	Bu <sup>n</sup>	SePh	374.9	331.9	43.0	4
<b>2h</b>	$^{125}\text{Te}$	Bu <sup>n</sup>	TeC <sub>6</sub> H <sub>4</sub> OMe	633.6	552.5	81.1	13
<b>2i</b>	$^{119}\text{Sn}$	Me	SnMe <sub>3</sub>	-42	-58	16	14
<b>2j</b>	$^{207}\text{Pb}$	Me	PbMe <sub>3</sub>	-69	-110	41	11

<sup>a</sup>Chemical shifts<sup>a</sup> signals normalized: a minus sign indicates absorption at lower frequencies than that of the standard compound ( $\delta_{\gamma}=0$ ) for a given nucleus<sup>16</sup>;

<sup>b</sup> $\Delta\delta_{\gamma}=\delta_{\gamma}(\text{E})-\delta_{\gamma}(\text{Z})$ .

the regioisomers of eneamines, as it permits the direct assignment and analysis of reaction mixtures. More data are available in the references cited in Table II for each of the nuclei represented in that table.

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