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The elucidation of the stereochemistry of vinylic selenides can be simplified by the application of <sup>77</sup>Se NMR, using in difficult cases a deuterated selenophenyl group to eliminate aromatic protons/<sup>77</sup>Se coupling.

Keywords: <sup>77</sup>Se NMR, vinylic selenides, acetylenic selenides.

## INTRODUCTION

The application of <sup>77</sup>Se NMR to the elucidation of the stereochemistry of alkenylic selenides was proposed six years ago by Johansen *et al.*<sup>1</sup>; they showed that the correct structure can be deduced from the observed olefinic protons/<sup>77</sup>Se coupling constants. This information can be obtained from proton-coupled <sup>77</sup>Se spectra, when the spectra are amenable to first order analysis.

However, since probably the most popular selenium-bearing moiety in organic chemistry is the selenophenyl group, which protons also couple to <sup>77</sup>Se, with  $J(^{77}\text{Se}, \text{H } \textit{ortho}) \cong 4\text{Hz}$  and  $J(^{77}\text{Se}, \text{H } \textit{meta}) \cong 1\text{ Hz}$ , we felt that the selective removal of these (stereochemically meaningless) aromatic protons/<sup>77</sup>Se coupling constants could be useful, specially in difficult cases.

In order to test this idea we synthesized some vinylic pentadeuterophenyl-selenides. As  $J(^2\text{H}, ^{77}\text{Se}) = (\gamma^2\text{H}/\gamma^1\text{H}) \cdot J(^1\text{H}, ^{77}\text{Se})$  and  $(\gamma^2\text{H}/\gamma^1\text{H}) = 0.1535$ , this should virtually eliminate the aromatic protons/<sup>77</sup>Se couplings.

## RESULTS AND DISCUSSION

That the use of the pentadeutero-selenophenyl group as selenium-bearing moiety actually simplifies the spectra can be seen when one compares the spectra of the isomeric mixture of 2-selenophenylstyrenes (70% *cis*, Figure 1) to that of their deuterio-isotopomers (80% *trans*, Figure 2). For instance, the multiplet (at  $\delta$  394.8) due to the *trans*-isomer (in Figure 1) is rather difficult to interpret from the point of view of first-order analysis, unless one assumes the existence of a hidden line. If so, then the signal is a doublet of doublet triplets, due to the coupling with the *gem*, *cis* and *ortho* protons, respectively, the *meta* protons having a coupling too small to be observed at this resolution. However, the deuterio-*trans*-isomer (in Figure 2) gives rise to the expected doublet of doublets (at  $\delta$  394.0). These spectra also show that the isotopic shifts are very small ( $\Delta\delta$  1.6 for the *cis*- and  $\Delta\delta$  0.8 for the *trans*-isomers).

It must be pointed out that while the chemical shifts of

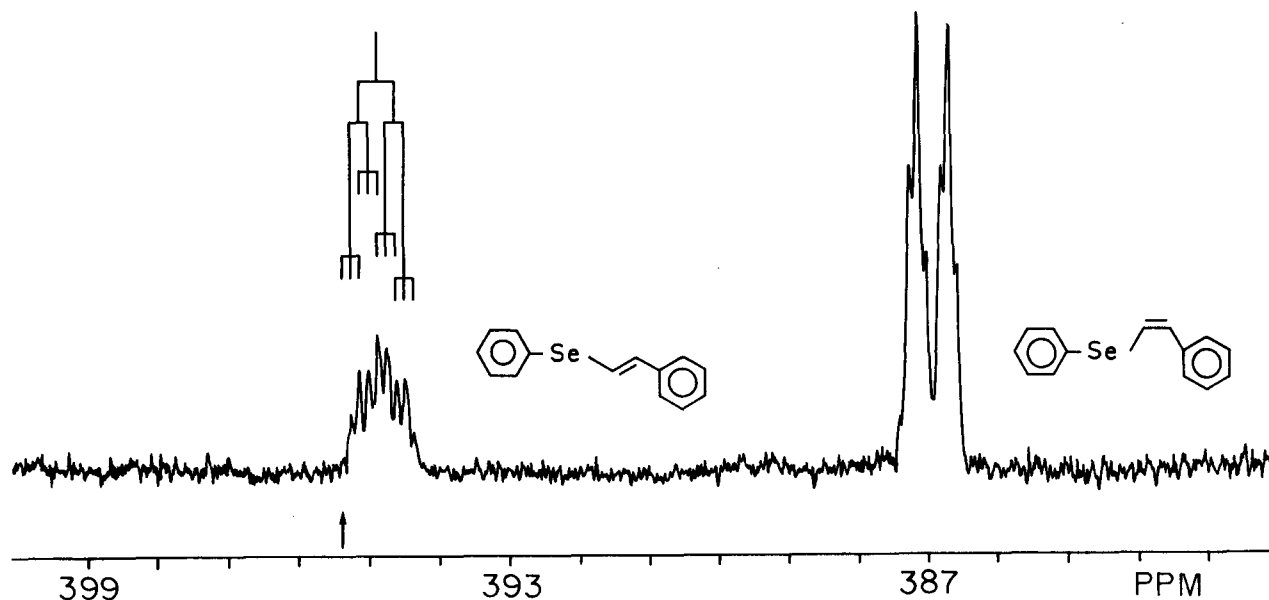


Figure 1. 38.14 MHz <sup>77</sup>Se NMR of 2-selenophenylstyrenes (70% *cis*). The signal corresponding to the *trans*-isomer shows its 1<sup>st</sup> order analysis (above) and an arrow pointing at the hidden line.

**Table.**  $^{77}\text{Se}$  NMR data of deuterated selenium compounds.

Compound	$\delta$ $^{77}\text{Se}$	$J_{\text{gem}}$ (Hz)	$J_{\text{cis}}$ (Hz)	$J_{\text{trans}}^*$ (Hz)
	471.1	-	-	-
	469.4	-	-	-
	279.4	-	-	-
	281.5	-	-	-
	274.4	-	-	-
	275.4	-	-	-
	394.0	15.9	9.9	-
	399.0	16.8	9.4	-
	370.4	15.1	10.5	-
	379.7	18.4	9.4	-
	385.4	15.1	-	2.5
	387.2	16.8	-	1.0

\* Coupling constants evaluated from the ratios of the mean width-at-half-height of the multiplet lines (in the proton coupled spectra) to that of the lines in the corresponding proton "NOISE" decoupled spectra.

organic selenium compounds have usually a very small dependence on temperature<sup>2</sup>, this is not the case for diphenyl diselenide<sup>2,3,6</sup>. Notwithstanding, it can be used as a standard<sup>3</sup> due to the ease of handling, the availability and the insensitivity of its chemical shift to concentration. To do so, we always used the same solution, in a sealed tube, as the standard. This solution was calibrated against *cis*-2-selenophenylstyrene<sup>1</sup> ( $\delta$  387.0 vs.  $\text{H}_3\text{CSeCH}_3$ ) and 2-selenophenyl-1-phenyl-acetylene<sup>4</sup> ( $\delta$  280.0 vs.  $\text{H}_3\text{CSeCH}_3$ ) and has an apparent chemical shift of  $\delta$  471.1, in our experimental conditions.

The results we obtained with all the deuterated-selenophenyl ethylenes and acetylenes are presented in the Table, and confirm the coupling constant ranges determined by Johansen *et al.*<sup>1</sup> (using all-protic selenium substituted alkenes).

#### EXPERIMENTAL

The  $^{77}\text{Se}$  NMR spectra were recorded at 38.14MHz (Bruker AC-200-F with multinuclear 10mm VSP probehead), in 10mm tubes containing 400mg sample/3mL  $\text{CDCl}_3$  solution and a

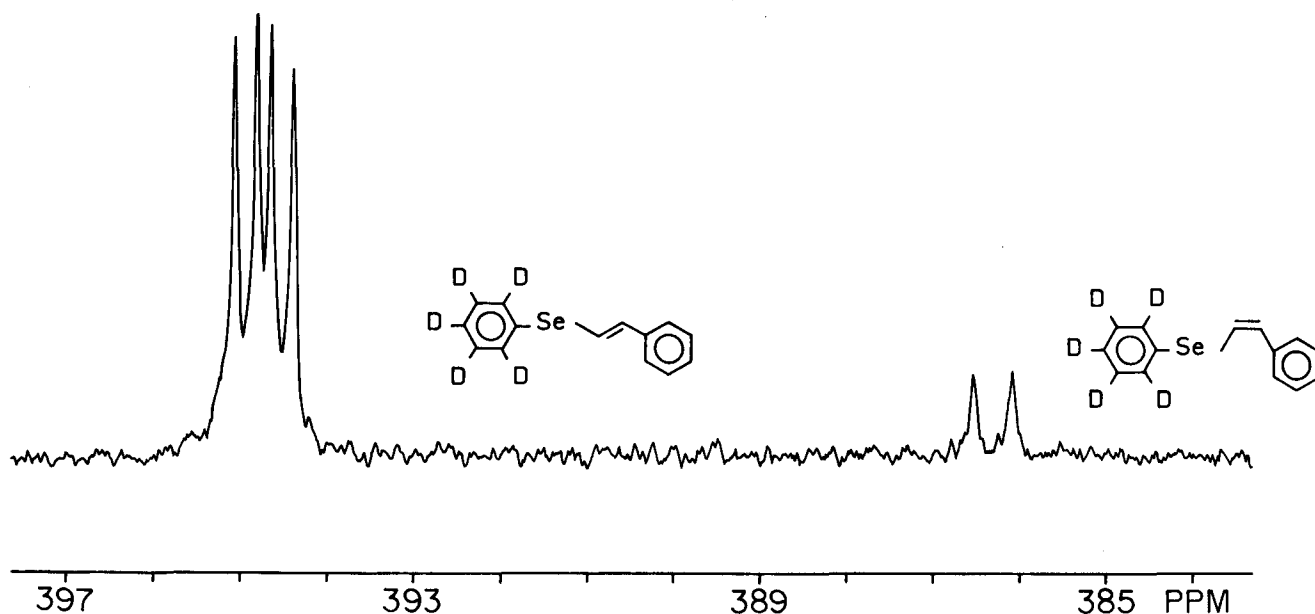


Figure 2. 38.14 MHz  $^{77}\text{Se}$  NMR of 2-seleno(pentadeutero)phenylstyrenes (80% trans).

sealed 5mm tube containing, as the standard, 0.5mL of a 1.06 mol.L $^{-1}$   $\text{CDCl}_3$  solution of diphenyl-diselenide, in a co-axial arrangement.

The  $J(^{77}\text{Se},^1\text{H})$  were obtained from fully  $^1\text{H}$  coupled  $^{77}\text{Se}$  spectra, while the  $\delta$   $^{77}\text{Se}$  were determined using  $^1\text{H}$  noise broadband decoupling. Pulse widths were 5.0 $\mu\text{s}$  (32 $^\circ$ ), the repetition rates were 1-5s and the digital resolution was 0.5Hz per data point. The reproducibility of the  $^{77}\text{Se}$  chemical shifts was  $\delta$  0.2 at room temperature, which was kept constant at 20 $^\circ\text{C}$ .

The infrared spectra were recorded with a Nicolett 510 FT-IR as KBr pellets or as liquid films (on NaCl plates). The mass spectra were recorded in a Finnigan ITD-800 spectrometer.  $^1\text{H}$  NMR spectra were obtained at 200MHz, in the same Bruker AC-200-F.

All compounds were prepared by literature<sup>5,6</sup> procedures and were consistent with the  $^1\text{H}$  NMR, infrared and mass spectral data. The stereochemistry of vinylic selenides was determined by  $^1\text{H}$  NMR spectral analysis.

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