Stereochemical Dependence of Geminal Selenium–Carbon Coupling Constants

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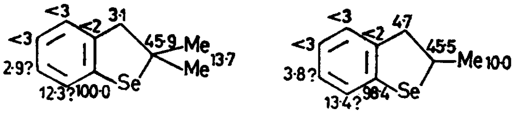
Summary Geminal ^{13}C–^{77}Se and vicinal ^{1}H–^{77}Se n.m.r. couplings are stereospecific in a selenide, selenoxide, selenonium salt, and selenonium ylide; coupling is largest to the nuclei nearest the selenium lone pair(s).

OUR interest in organoselenium stereochemistry[1] as well as in the application of organoselenium reagents in organic chemistry[2] has prompted us to measure n.m.r. properties of a variety of selenium-containing compounds. In the course of these studies we observed a pronounced stereochemical dependence of ^2J (^{13}C–^{77}Se) and ^3J (H–Se) in several conformationally rigid systems.[3]

Selenium–carbon couplings in two dihydrobenzoselenophen derivatives (**1**) and (**2**) are shown in the Figure.† The geminal couplings to selenium vary substantially: coupling is large to the CH_3 and one *ortho* carbon atom, but small to the CH_2 and the other *ortho* carbon atom.



(**1**) (**2**)

FIGURE. J (Se–C) coupling constants (in Hz) for (**1**) and (**2**).

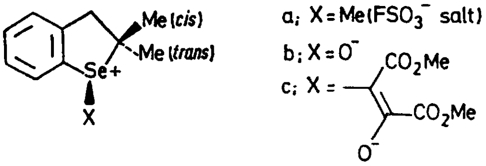
More striking examples are provided by the selenonium salt (**3a**), the selenoxide (**3b**) and the ylide (**3c**) (Table). All compounds are pyramidal at selenium and configurationally stable on the n.m.r. time-scale, as shown by the observation of diastereotopic ^1H and ^{13}C signals. Assignments for (**3a**) were established for the ^1H resonances by homonuclear NOE–INDOR experiments,[4] and correlation of ^1H and ^{13}C resonances by single-frequency off-resonance decoupling, $^{13}C\{H\}$. Assignments for (**3b**) were made on the basis of the larger europium complex-induced shifts for the proton and carbon *cis*-methyl resonance.[5] In all three compounds the ^{13}C assignments were compatible with an upfield steric γ-shift[6] for the Me group *cis* to the substituent on selenium. In each case the three geminal C–Se couplings follow the same pattern: one methyl carbon atom (the one eclipsed relative to the lone pair) is substantially more strongly coupled than the other two. The selenides (**1**) and (**2**) also fit this pattern. Three-bond proton–selenium couplings follow the trend set by the carbon couplings, although stereochemical dependence is less pronounced.

TABLE. ^1H and ^{13}C N.m.r. data† for (**3a**—**c**)

	(**3a**)[a]				(**3b**)[b]				(**3c**)[c]			
	δ_H	δ_C	^3J(H–Se)	^2J(C–Se)	δ_H	δ_C	^3J(H–Se)	^2J(C–Se)	δ_H	δ_C	^3J(H–Se)	^2J(C–Se)
cis-Me	1·93	24·0	10·5	<6	1·65	21·5	9·5	8·4	1·62	24·6	12·0	13·7
trans-Me	1·80	26·9	23·0	25·7	1·26	23·6	19·0	26·9	1·71	28·3	24·0	34·7
CH_2	3·53[d] 3·87	46·6		<5	3·13[d] 3·71	47·9		<5	3·17[d] 4·04	52·2		<8

[a] In CD_2Cl_2 solution at 25 °C. [b] In $CDCl_3$ solution at −15 °C. [c] In $CDCl_3$ solution at 25 °C. [d] J_{gem} 16—17 Hz.

We feel that these regularities, if found to be general, may be an important aid for determining structures and conformations of organoselenium compounds, and, by analogy, for organosulphur compounds for which such n.m.r. information is not available.



(**3**)

Several reports of stereospecific ^2J (^{13}C–^{31}P) for phospholens,[7] phosphetans,[8] and acyclic phosphines[9] have appeared. These couplings show remarkably similar magnitude and stereochemistry to those reported above for 3-co-ordinate selenium.

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† Signs of coupling constants were not determined.

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