Carbon-13 Nuclear Magnetic Resonance Studies of Some Organoselenium Compounds containing Carbon–Selenium Double Bonds

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Carbon-13 n.m.r. spectra were obtained for eight compounds having C=Se double bonds. These comprised five selenoketones, 2,2,4,4-tetramethylpentane-2-selone (1-Se), 1-thia-3,3,5,5-tetramethylcyclohexane-4-selone (2-Se), 1,1,3,3-tetramethylindane-2-selone (3-Se), 2,2,5,5-tetramethylcyclopent-3-ene-1-selone (4-Se), and selenofenchone (5-Se), one selenoester, ethyl selenobenzoate (6-Se), and two selenoamides, *NN*-dimethylselenobenzamide (7-Se) and *NN*-dimethyl-2,2-dimethylselenopropanamide (8-Se). Coupling constants, $^1J(^{13}C-^{77}Se)$, were measured for (1) and (3)—(7). A comparison was made among the chemical shifts of (1)—(8), their oxygen analogues, and the sulphur analogues of (1), (5), and (7). The selenocarbonyl carbon atoms were shifted 34—72 p.p.m. downfield and the α-carbon atoms 10—19 p.p.m. downfield from their oxygen analogues. The differences, $\delta\Delta_{Se,O}$, for the remaining carbons are only a few p.p.m. Values of $^1J(^{13}C-^{77}Se)$ were 209—221 Hz, much larger than any previously observed $^{13}C-^{77}Se$ coupling constants.

FEW compounds having selenium–carbon double bonds are known; most examples are of selenoamides.[1] We have prepared five selenoketones (selones), two selenoamides, and a selenoester and recorded their ^{13}C n.m.r. spectra.[2] The results are reported below and discussed in comparison with their carbonyl, and in three cases, thiocarbonyl analogues.

RESULTS

Values of $\delta(^{13}C)$ for the selenocarbonyl, thiocarbonyl, and carbonyl compounds are given in the Table together with the values for $^1J(^{13}C-^{77}Se)$. Assignments of the resonances to the various carbon atoms are straightforward in most cases. The $^{13}C=X$ carbons always appear quite far downfield so their assignments pose no problems. The remaining $\delta(^{13}C)$ values for (1-Se), (1-O), (2-Se), (2-O), (4-Se), (4-O), (8-Se), and (8-O) are also readily assigned by consideration of chemical shifts, low peak intensities for the quaternary carbons, and partially or fully coupled spectra. Spectra of compounds (1-S), (5-S), (5-O), (7-Se), (7-S), and (7-O) were previously analysed by others. Shifts for compound (5-Se) may be assigned by comparison to the shifts observed for (5-S) and (5-O).

^{77}Se with a spin of 1/2 has a natural abundance of 7.6%, so it was possible to observe the $^{13}C-^{77}Se$ coupling from the ^{77}Se satellites in the ^{13}C spectra. In (1-Se)—(8-Se), the carbon atoms directly bonded to Se are non-protonated, so it was not possible to determine the signs of $^1J(^{13}C-^{77}Se)$, although in most other compounds they were shown to be negative. Absolute values of $^1J(^{13}C-^{77}Se)$ (Table) range from 209.4 for (7-Se) to 220.8 Hz for (5-Se).

DISCUSSION

$\delta(^{13}C)$ values for the selenocarbonyl, thiocarbonyl, and carbonyl compounds are given in the Table. The selone carbonyl carbons occur at δ 287—295 p.p.m., the thione carbonyl carbons at δ 278—280 p.p.m., and the ketone carbonyl carbons at δ 216—226 p.p.m. The selenoester and two selenoamide carbonyls resonate at δ 204—220 p.p.m., the one thioamide at δ 201 p.p.m., and the ester and two amides at δ 166—177 p.p.m. Chemical shifts for selenocarbonyl and carbonyl carbons together with values for four compounds taken from ref. 4*a* gave the relationship $\delta(^{13}C=Se) = 1.66\ \delta(^{13}C=O) - 75.60$ with a correlation coefficient *r* 0.9785. Kalinowski and Kessler [3] and Lawesson *et al.*[4] previously derived similar linear relationships between some thiocarbonyl and carbonyl compounds. The former obtained $\delta(^{13}C=S) = 1.45\ \delta(^{13}C=O) - 46.5$; the latter obtained $\delta(^{13}C=S) = 1.57\ \delta(^{13}C=O) - 71.45$. All three relationships are roughly parallel but the correlation coefficient for the selenocarbonyl case (*r* 0.979) is not nearly as good as those for the two thiocarbonyl cases (*r* 0.997 [3a] and 0.995 [4a]). One possible explanation for a departure from a linear relationship was offered by Rae,[5] who observed that the correlation of the $\delta(^{13}C)$ values of thiolactams and lactams using the equation of Kalinowski and Kessler is poorer for smaller ring compounds where some angular strain is present. Substantial angular strain exists in (3)—(5) and probably also in (1). However, it is the ester and amides which deviate most from our linear relationship and not the selones.

The major contribution to $\delta(^{13}C=Se)$ is from the paramagnetic screening term, σ_p [equation (1) where ϱ_{AA}

$$\sigma_p = -K/\Delta E\ \langle r^{-3}\rangle\ [\varrho_{AA} + \sum_{B} \varrho_{AB}] \qquad (1)$$

and ϱ_{AB} are charge density and bond order terms, ΔE is the mean excitation energy, and $\langle r^{-3}\rangle$ the expectation value [6] for *r* in a 2*p* orbital on the atom in question]. Presumably, the magnitude of ΔE is the predominant factor affecting the chemical shifts. All the selenocarbonyl compounds are highly coloured in contrast to the colourless carbonyl compounds. The $\lambda_{max.}$ values of the lowest electronic transitions of the selenocarbonyl compounds are substantially larger (lower energy) than those of the oxygen compounds.[7] They exhibit the typical behaviour of $n \longrightarrow \pi^*$ transitions because a shift to shorter wavelengths occurs on going from cyclohexane to the more polar solvent ethanol. The $\lambda_{max.}$ values of the selenoamides (7-Se) and (8-Se) and the selenoester

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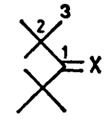
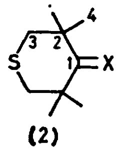
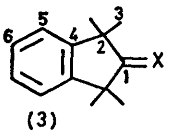
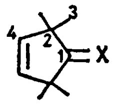
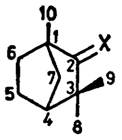
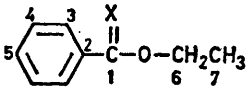
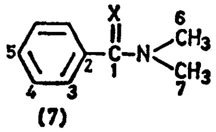
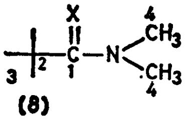
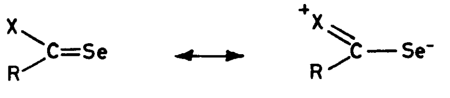
δ(^{13}C) (p.p.m. from tetramethylsilane) of selenocarbonyl and corresponding thiocarbonyl and carbonyl compounds and $^1J(^{13}C-^{77}Se)$/Hz

	Carbon	X = Se	$^1J(^{13}C-^{77}Se)$/Hz	X = S	X = O	
 (1)	1	291.4[a]	213.6	278.4[b]	218.6[b]	
	2	60.1		53.7	45.7	
	3	32.7		33.0	28.5	
 (2)	1	287.0			216.6	
	2	60.1			46.2	
	3	39.5			42.8	
	4	33.2			27.1	
 (3)	1	294.0	215.1		226.0	
	2	67.3			48.9	
	3	31.3			26.7	
	4	147.4			145.8	
	5	123.4			123.0	
	6	127.7			127.7	
 (4)	1	294.9	216.0		226.0	
	2	68.7			49.6	
	3	29.4			25.1	
	4	136.6			136.7	
 (5)	1	72.6	220.8	66.3[b]	53.7[c]	53.6[d]
	2	292.5[a]		280.25	219.3	218.9
	3	63.3		57.7	46.9	46.9
	4	47.3		47.0	45.5	45.3
	5	27.6			25.1	25.1
	6	32.9			31.8	31.8
	7	42.6			41.6	41.6
	8	26.5		28.65	23.5	23.4
	9	25.0		26.5	21.9	21.7
	10	20.8		19.2	14.8	14.8
 (6)	1	222.4	211.1		166.3	
	2	143.1			130.9	
	3	129.0			129.7	
	4	128.4			128.4	
	5	132.6			132.8	
	6	73.0			60.8	
	7	13.9			14.4	
 (7)	1	204.7[e]	209.4	201.0[f]	171.4[e]	
	2	145.8		143.4	135.5	
	3	127.7		128.7	128.2	
	4	124.3		125.7	126.9	
	5	128.0		128.5	129.4	
	6	47.0		43.1	35.2	
	7	45.5		44.1	39.6	
 (8)	1	218.4			177.0	
	2	52.4			38.5	
	3	31.7			28.2	
	4	45.6			38.1	

[a] Olah *et al.* report δ 291.4 p.p.m. for C(1) of (1) and δ 291.7 p.p.m. for C(2) of (5), G. A. Olah, T. Nakajima, and G. K. Surya, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 811. [b] C. G. Andrieu, D. Debruyne, and D. Paquier, *Org. Magn. Reson.*, 1978, **11**, 528. [c] E. Lippmaa, T. Pehk, J. Paasvirta, N. Belikova, and A. Plate, *Org. Magn. Reson.*, 1970, **2**, 581. In CS_2. Converted by δ(Me_4Si) = 192.3 − δ(CS_2). [d] E. Wenkert, A. O. Clouse, D. W. Cochran, and D. Doddrell, *Chem. Commun.*, 1969, 1433. [e] Our values and those in ref. 5 agree within experimental error except for the values of C(2) of (7-O) where ref. 5 gives δ 132.3 p.p.m. C. W. Fong, S. F. Lincoln, and E. H. Williams, *Aust. J. Chem.*, 1978, **31**, 2615 gives δ 135.5 p.p.m. The latter two references give reverse assignments to C(3) and C(4) of (7-O). [f] Values from ref. 5. [g] Assignments to C(5) and C(6) of (3) and C(2) and C(3) of (6) and (7) were not established with certainty in our work. The numbering system used for (1)—(8) is arbitrary and does not correspond to the I.U.P.A.C. system used in this paper.

(6-Se) occur at shorter wavelengths than those of the selones (1-Se)—(5-Se) and is reflected in the upfield shifts of $\delta(^{13}C)$ of (6-Se)—(8-Se) compared with (1-Se)—(5-Se) by *ca.* 70 p.p.m. However, $\delta(^{13}C{=}Se)$ does not correlate in a simple way with $\lambda_{max}^{n\rightarrow\pi^*}$, which frequently can be used to approximate ΔE^{-1}. Lack of a straightforward relationship between $\delta(^{13}C{=}Se)$ and $\lambda_{max}^{n\rightarrow\pi^*}$ is in sharp contrast to the good linear relationship between $\delta(^{77}Se)$ and $\lambda_{max}^{n\rightarrow\pi^*}$ for the same series of compounds.[7] This difference is probably due to a larger contribution from the σ_d term to ^{13}C chemical shifts than to ^{77}Se chemical shifts. As for amides and esters, the usual interpretation for the upfield shift of $\delta(^{13}C)$ of the selenoamides and the selenoester from those of the selones is the contribution from the mesomeric form B which is not important in selones and which neutralizes positive charge on the carbonyl carbon.[8] This may account in part for the 70—80 p.p.m. difference between the selones and the selenoamides and selenoester.



(A) (B)

An indication of the degree of mesomerism is the two ^{13}C resonances for the *N*-methyl groups of *NN*-dimethylselenobenzamide (7-Se) at 35 °C; the corresponding *NN*-dimethylbenzamide (7-O) gives two distinct signals only at reduced temperature (8 °C).[5] The nonequivalence of the two methyl groups is due to the high rotational barrier of the C–N bond caused by significant partial double bond character [mesomeric form (B)]. Assignment of the low-field methyl ^{13}C resonance to the *N*-methyl *syn* to selenium in (7-Se) was made by Rae;[5] the *syn*-*N*-methyl is at 1.5 p.p.m. lower field than the *anti*-*N*-methyl. In contrast, (8-Se) gives only a single *N*-methyl ^{13}C resonance at normal probe temperatures because of a lower rotational barrier presumably sterically induced by the bulky t-butyl group.[9a] In agreement with this idea, the rotational barrier for *NN*-dimethylselenoacetamide was found to be higher than that of (7-Se).[9b] The barriers appear to decrease in the order selenoacetamide > selenobenzamide > selenopivalamide.

Among the selones (1-Se)—(5-Se) and the selenoamides and -ester (6-Se)—(8-Se) an increase in the shielding of ^{13}C of the selenocarbonyl carbon is accompanied by a deshielding of the ^{77}Se.[7] However, the relation is not simple: for (1)—(5), $\delta(^{77}Se) = 1\,905 \pm 182$ and $\delta(^{13}C) = 292.0 \pm 2.2$ whereas for (6) and (7), $\delta(^{77}Se) = 763 \pm 102$ and $\delta(^{13}C) = 215.2 \pm 7.0$. This behaviour is analogous to the relationship between $\delta(^{17}O)$ and $\delta(^{13}C{=}O)$ of ketones.[10]

The other significantly affected $\delta(^{13}C)$ in the selenium compounds is that of the carbon α to the carbonyl carbon. All these carbon atoms are non-protonated. $\delta(^{13}C)$ Values of the α-carbon are 14—20 p.p.m. downfield from the corresponding oxygen compounds for selones (1-Se)—(5-Se) and 10—14 p.p.m. downfield for the selenoamides (7-Se) and (8-Se) and the selenoester (6-Se). Rae[5] reported similar values of $\Delta\delta_{Se,O}$ for the selenocarbonyl compounds he investigated. Carbon atoms two bonds away from the selenocarbonyl carbon generally exhibit downfield shifts of 3—4 p.p.m. in the selones compared to the ketones. An exception is (2) where $\Delta\delta_{Se,O}$ for C(3) is −3.3 p.p.m. For the acyl compounds, RC(Se)XR′, $\delta(^{13}C)$ of the carbon atoms bonded to heteroatom X two bonds away from C=Se are also shifted downfield. For the methylene carbon of (6), $\Delta\delta_{Se,O}$ is 12.2 p.p.m., and for the *NN*-dimethylamides (7) and (8), the $\Delta\delta_{Se,O}$ values are 8 ± 1 p.p.m.

The aromatic carbons in (6-Se) and (7-Se), except for the carbon α to C=Se as discussed above, are relatively unaffected by the substitution of O by Se although $\Delta\delta_{Se,O}$ for C(5) of (7) may be evidence for the greater electron-withdrawing ability of the C=O group compared to C=Se.[11] But $\Delta\delta_{Se,O}$ for C(5) of (7) is practically zero.

^{12}C–^{77}Se *Spin–Spin Coupling Constants*.—^{13}C–^{77}Se Spin–spin coupling constants are interesting because they are sensitive to the electronic states of the carbon and selenium atoms involved.[12] The sign of $^{1}J(^{13}C–^{77}Se)$ has been shown to be negative by double resonance techniques.[12–14] In (1-Se)—(8-Se) the carbon atoms directly bonded to Se are non-protonated, so it was not possible to determine the signs of $^{1}J(^{13}C–^{77}Se)$. However, from the trend of their change in magnitude, there is no doubt that they are all negative. The magnitudes of most of the reported $^{1}J(^{13}C–^{77}Se)$ values are 50—75 Hz between sp^3-carbon and selenium, and 110—140 Hz between sp^2-carbon and selenium.[12,15–18] For many molecules in the latter category, varying degrees of partial C–Se double bond character are expected. The present group of molecules is the first series studied which possess a true carbon–selenium double bond. Absolute values of $^{1}J(^{13}C–^{77}Se)$ for these molecules (Table) vary from 209.4 for (7-Se) to 220.8 Hz for (5-Se). These values are much higher than sp^2-carbon–selenium coupling constants of carbon–selenium single bonds. No $^{2}J(^{13}C–^{77}Se)$ were observed. The assumed negative sign of $^{1}J(^{13}C–^{77}Se)$ would imply that the mean electronic excitation energy approximation is invalid and the relationship (2) should be used.[12,19]

$$^{1}J(^{13}C–^{77}Se) \propto \gamma_{Se}\gamma_{C}\psi_{Se}^{2}(0)\psi_{C}^{2}(0)\pi_{SeC} \qquad (2)$$

$\psi^2(0)$ is the valence *s*-electron density at the nucleus, and π_{SeC} is the mutual polarizability of the *s*-orbitals contributing to the C–Se bond. Among the selones (1-Se)—(5-Se), the magnitude of $^{1}J(^{13}C–^{77}Se)$ increases even though $\delta(^{77}Se)$ shifts upfield. The C–C(Se)–C angle decreases on going from (1-Se) to (5-Se) because of ring formation.[7] Such a change in angle will increase the *s* character of the carbon orbital involved in C–Se σ bonding[20] which is turn will increase the magnitude of $^{1}J(^{13}C–^{77}Se)$. The increase in $^{1}J(^{13}C–^{77}Se)$ is parallel to the increase in the C=O stretching frequency of the corresponding carbonyl compounds because an increase in σ bonding increases the overall bond strength.[21,*] This is probably accompanied by an increase in the extent of C–Se π-bonding[7] which decreases $\lambda_{max}^{n\rightarrow\pi^*}$ and shifts $\delta(^{77}Se)$ upfield in going from (1) to (5).

Although the $^1J(^{13}C-^{77}Se)$ values for selenoester (6-Se) and the selenoamide (7-Se) are comparable in magnitude to those of the selones (1-Se)—(5-Se), the large changes in structure and electronegativity of the substituent groups in going from (1-Se)—(5-Se) to (6-Se) + (7-Se) make any comparison difficult between these two categories of selenocarbonyl compounds. Factors influencing $^1J(^{13}C-^{77}Se)$ of selenoesters and selenoamides must await further study of such compounds.

EXPERIMENTAL

The selenoketones, selenoamides, and selenoester were synthesized according to published procedures.[2] All spectra were obtained in deuteriochloroform solution in 10 mm tubes with chemical shifts measured from $CDCl_3$ taken as 77.0 p.p.m., relative to Me_4Si. Spectra were taken on a Bruker HX-270 spectrometer operating at 67.89 MHz and on a JEOL FX-90Q spectrometer operating at 22.5 MHz. In both cases, quadrature detection and 8 K or 16 K points were used. Due to the long spin–lattice relaxation times of the nonprotonated carbons, a *ca.* 12 μs pulse-width, which corresponds to a *ca.* 40° nutation angle, and 3—5 s delays were generally used. Most spectra were taken with proton noise decoupling. In some cases, proton-coupled spectra were taken to confirm peak assignments. $^1J(^{13}C-^{77}Se)$ Values were obtained from the ^{77}Se satellites of the ^{13}C spectra with ^1H noise decoupling.

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REFERENCES

[1] P. D. Magnus, in 'Comprehensive Organic Chemistry,' ed. D. N. Jones, Pergamon, Oxford, 1979, vol. 3, p. 520.

[2] (*a*) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, 1976, 2079; (*b*) F. S. Guziec, Jr., and C. J. Murphy, *J. Org. Chem.*, 1980, **45**, 2890; (*c*) E. R. Cullen, F. S. Guziec, Jr., M. I. Hollander, and C. J. Murphy, *Tetrahedron Lett.*, in the press.

[3] (*a*) H.-O. Kalinowski and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 90; (*b*) H.-O. Kalinowski and H. Kessler, *Org. Magn. Reson.*, 1974, **6**, 305.

[4] (*a*) B. S. Pedersen, S. Scheibye, N. H. Nilsson, and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, 1978, **87**, 233; (*b*) S. Scheibye, B. S. Pedersen, and S.-O. Lawesson, *ibid.*, p. 229.

[5] I. D. Rae, *Aust. J. Chem.*, 1979, **32**, 567.

[6] (*a*) J. A. Pople, *Mol. Phys.*, 1963, **7**, 201; (*b*) M. Karplus and J. A. Pople, *J. Chem. Phys.*, 1963, **38**, 2803.

[7] T. C. Wong, F. S. Guziec, Jr., C. J. Murphy, E. R. Cullen, and K. K. Andersen, *J. Am. Chem. Soc.*, 1981, **103**, 7055.

[8] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 280.

[9] (*a*) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, 1970, **70**, 517; (*b*) U. Svanholm, in 'Organic Selenium Compounds: Their Chemistry and Biology,' eds. D. Klayman and W. H. H. Gunther, Wiley, New York, 1973, p. 916.

[10] C. Delseth and J.-P. Kintzinger, *Helv. Chim. Acta*, 1976, **59**, 466.

[11] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 196.

[12] W. McFarlane, D. S. Rycroft, and C. J. Turner, *Bull. Soc. Chim. Belg.*, 1977, **86**, 457.

[13] H. Dreeskamp and G. Pfisterer, *Mol. Phys.*, 1968, **14**, 295.

[14] W. McFarlane, *Mol. Phys.*, 1967, **12**, 243.

[15] H. C. E. McFarlane and W. McFarlane, in 'NMR and the Periodic Table,' eds. R. K. Harris and B. E. Mann, Academic Press, New York, 1978, p. 402.

[16] M. Garreau, G. J. Martin, M. L. Martin, J. Morel, and C. Paulmier, *Org. Magn. Reson.*, 1974, **6**, 648.

[17] T. C. Wong and E. M. Engler, *J. Mol. Struct.*, 1980, **67**, 279.

[18] J. R. Bartels-Keith, M. T. Burgess, and J. M. Stevenson, *J. Org. Chem.*, 1977, **42**, 3725.

[19] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[20] C. A. Coulson and W. E. Moffit, *Philos. Mag.*, 1949, **40**, 1.

[21] S. Bank, W. D. Closson, and L. T. Hodgins, *Tetrahedron*, 1968, **24**, 381.

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[*] The C=O stretching frequencies of ketones (1–O)—(5–O) are 1 690, 1 690, 1 738, 1 743, and 1 745 cm^{-1}, respectively. These numbers vary depending on the literature source, but are probably accurate to ±5 cm^{-1}.