Preparation of Unsymmetrical Alkyl Methyl and Alkyl Phenyl Diselenides and Determination of Their Selenium-77 Chemical Shifts and ^{77}Se–^{77}Se Spin–Spin Coupling Constants[1]

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Fifteen unsymmetrical alkyl methyl and alkyl phenyl diselenides were prepared by reacting (1) symmetrical dialkyl diselenides with benzeneselenol, (2) benzeneselenenyl chloride with an alkaneselenol, (3) dimethyl diselenide with an alkaneselenol, (4) lithium alkylselenenylselenolate with an alkyl iodide, and (5) alkaneselenenyl halide with sodium alkaneselenolate. The easily prepared unsymmetrical diselenides are thermally labile species undergoing disproportionation to the symmetrical diselenides upon distillation with the single exception of ethyl methyl diselenide that distills as a mixture, thermally stable enough to fully characterize with GC/mass spectroscopy. Phenyl isopropyl diselenide, the only compound to display evidence of dynamical chemical exchange in the NMR spectra (^{13}C and ^{77}Se), was investigated by a ^{77}Se DANTE selective magnetization transfer experiment. Chemical exchange was suggested to occur via scission of selenium–selenium bonds and not carbon–selenium bonds and was found to stop (or slow extensively) upon subsequent aqueous workup. The ^{77}Se chemical shifts, spanning a range of 406 ppm, were found to correlate well with the number of α minus β protons, suggesting additivity of the ^{77}Se chemical shifts similar to that of ^{13}C chemical shifts. β and γ ^{77}Se chemical shift additivity parameters were determined for α-methyl substitution in alkyl methyl diselenides. Correction factors for branching at the remote selenium were found necessary to compute the ^{77}Se chemical shifts in contrast with ^{13}C chemical shifts that only require correction factors for adjacent branching. The one-bond ^{77}Se–^{77}Se spin–spin coupling constant $^1J_{\mathrm{SeSe}}$ varies in magnitude from 36.3 Hz for *n*-butyl methyl diselenide to ±2.7 Hz for *tert*-butyl methyl diselenide. A linear correlation of $^1J_{\mathrm{SeSe}}$ with the sum of the α minus β protons for both substituents tentatively suggests that a change in sign of the coupling constant may occur for *tert*-butyl methyl diselenide and with phenyl isopropyl and *tert*-butyl phenyl diselenide. A new preparation of di-*tert*-butyl selenide and di-*tert*-butyl diselenide is described along with their characterization.

Introduction

The rich and diverse nature of the chemistry of the chalcogens, group 6A of the periodic table, is well-known,[3] spanning a range in chemical variation from the non-metal oxygen to the radioactive metal polonium. Nuclear magnetic resonance (NMR) spectroscopy, a technique which has helped tremendously to characterize the chemistry of many other elements, has been slower in development in group 6A.[4] This has been due, in part, to the fact that the only magnetically active nuclei of the first two elements of this group are quadrupolar in nature and have low natural abundances. Oxygen-17 with $I = {}^5/_2$, natural abundance of 0.037%, and a negative gyromagnetic ratio has a receptivity of only ca. 6×10^{-2} relative to ^{13}C at constant field while ^{33}S with $I = {}^3/_2$ and a natural abundance of 0.76% is slightly less receptive than ^{17}O (ca. 1×10^{-3} relative to ^{13}C at constant field).[5] The existence of suitable spin $-{}^1/_2$ isotopes of selenium (^{77}Se) and tellurium (^{125}Te, ^{123}Te) has spurred many more NMR investigations of these two elements with study of the ^{77}Se NMR parameters being the most extensively developed.[4] The large chemical shift range (~3000 ppm) of the ^{77}Se resonance coupled with an adequate natural abundance (7.5%) and relative receptivity (2.98 with respect to ^{13}C at constant field)[5] combine to make ^{77}Se NMR spectroscopy an extremely versatile probe of the chemical and physical properties of selenium-containing compounds in solution.

One of the least studied of the ^{77}Se NMR parameters is scalar coupling of the ^{77}Se nucleus to other nuclei with only a few scattered reports for the value of homonuclear ^{77}Se coupling constants having appeared since McFarlane's determination[6] of the sign and magnitude of the one-bond ^{77}Se–^{77}Se coupling constant ($^1J_{\mathrm{SeSe}}$) in methyl phenyl diselenide (+22 ± 4 Hz). For example, of the inorganic Se-containing polyatomic cations,[7] the square-planar compound $\mathrm{TeSe_3}^{2+}$ has the largest reported $^1J_{\mathrm{SeSe}}$ of 188 Hz,[7a] while much smaller $^1J_{\mathrm{SeSe}}$ values have been reported for *o*-nitrophenyl phenyl diselenide (15.0 Hz)[8] and 2-nitro-3-thienyl phenyl diselenide (13.7 Hz).[8] The smallest $^1J_{\mathrm{SeSe}}$ value reported to date is 10.4 and 11.5 Hz for two purported rotamers[9] of perfluoromethyl methyl diselenide. While Granger and co-workers reported[8] that $^3J_{\mathrm{SeSe}}$ across a selenophene carbon–carbon double bond to Se exo to the selenophene ring was less than the observed line width (<2 Hz), a recent report[10] by Johannsen and Eggert showed a pronounced stereochemical dependence of $^3J_{\mathrm{SeSe}}$ across the carbon–carbon double bond in *cis*- and *trans*-1,2-(methylseleno)-1-phenylethylene ($^3J_{\mathrm{SeSe}}$(cis) = 12.0 Hz, $^3J_{\mathrm{SeSe}}$(trans) = 96.5 Hz) with similar values found for $^3J_{\mathrm{SeSe}}$ in various substituted tetraselenofulvalenes. In view of the recent interest in organoselenium chemistry[11,12] and selenium biochemistry[11-13] and the ongoing development in

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our[14,15] and other[16] laboratories of ^{77}Se NMR spectroscopy for the study of biologically important selenium-containing compounds, a detailed investigation of the effect on the ^{77}Se NMR parameters caused by subtle, systematic changes in the organic moieties of two separate series of unsymmetrical compounds, alkyl methyl and alkyl phenyl diselenides, was conducted and the results are reported herein.

Experimental Section

General Data. All syntheses were performed under an atmosphere of dry nitrogen using standard Schlenk or high-vacuum line techniques.[17] Selenium metal was used in its gray, powdered, elemental form. Tetrahydrofuran (THF) and hexane were dried by distillation from sodium benzophenone ketyl[18] immediately prior to use. *tert*-Butyl alcohol was dried by distillation from CaH$_2$ and stored over 4-Å molecular sieves. All alkyl halides were obtained commercially, except *tert*-butyl chloride, which was prepared by addition of concentrated hydrochloric acid to *tert*-butyl alcohol,[19] dried over CaCl$_2$, and distilled (bp 50–50.5 °C). *tert*-Butyl iodide was redistilled immediately prior to use while all other alkyl halides were used as received. Ammonia was dried by distilling from Na metal immediately prior to use. Sample purity was checked by mass and ^{1}H NMR spectroscopy.

Proton NMR spectra were obtained on a Varian EM-390 spectrometer or on an IBM NR 80B spectrometer. Carbon-13 NMR spectra were obtained on an IBM NR 80B spectrometer (20.13 MHz) operating in the Fourier transform mode and employing continuous broad-band noise-modulated ^{1}H decoupling. Selenium-77 NMR spectra were obtained either on a highly modified[15] Varian Associates XL-100-15 spectrometer (18.9 MHz) or on an IBM NR 80B spectrometer (15.27 MHz) operating in the Fourier transform mode. Broad-band noise-modulated ^{1}H decoupling was utilized when appropriate. Temperature control for ^{77}Se NMR spectra was accomplished by using standard VT units and an appropriate cold bath. The temperature was measured with a copper–constantan thermocouple immersed in a 10- or 12-mm NMR tube filled with ethylene glycol and is estimated as being accurate to ±0.5 °C.

Proton and ^{13}C spectra were run as dilute (ca. 5–15%) CDCl$_3$ solutions in 5-mm sample tubes. All ^{77}Se spectra were run as ca. 50–70% solutions by volume in CDCl$_3$ in 10- or 12-mm NMR tubes unless otherwise stated. All samples were freeze–pump–thaw degassed and sealed under dynamic vacuum. The ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) with respect to (CH$_4$)$_4$Si at 0.0 ppm. The ^{1}H chemical shifts were measured from the ^{1}H resonance of the residual CHCl$_3$ solvent impurity (δ 7.24), and the ^{13}C chemical shifts were measured from the central CDCl$_3$ solvent triplet resonance (δ 76.9). The ^{77}Se chemical shifts were externally referenced to dimethyl selenide (60% in CDCl$_3$ at 25 °C, δ 0.0)[20] by the sample tube replacement technique.[21] A positive chemical shift denotes a resonance to lower shielding (higher frequency).

For selected compounds ^{77}Se INEPT[22] and ^{77}Se refocused INEPT[22b,23] NMR spectra were obtained, as were ^{77}Se INADEQUATE[24] or ^{77}Se INADEQUATE ENHANCED-WITH-INEPT[25] NMR spectra. Chemical exchange was also probed by using ^{77}Se NMR spectroscopy via a combined[26a] DANTE selectively excited[26b] spin saturation transfer[27] pulse sequence in a difference spectra mode (vide infra).

Mass spectra were obtained as neat liquids on an Hitachi Perkin-Elmer RMU-6 mass spectrometer or GC/MS was performed as dilute diethyl ether solutions on a Finnigan 4021 GC/mass spectrometer utilizing electron-impact ionization with an ionization voltage of 70 eV. The gas chromatography utilized a 25 M, 0.2-mm i.d. fused silica capillary column coated with cross-linked SE-54 polymer having a film thickness of 0.25 μm and an inlet helium carrier gas pressure of 10 psi. The temperature program consisted of an injection temperature of 150 °C followed by a column temperature of 50 °C for 1 min and then ramped at 15 °C/min. GC/MS analyses and mass spectral computer simulations of the theoretical ion pattern due to the natural isotope abundance for two Se atoms were performed by Mike Walla of this department.

Selenium Compounds. All selenols[28,29] and symmetrical diselenides[29b,c,30,31] used as starting materials in the preparation of the unsymmetrical diselenides were prepared by known methods (except di-*tert*-butyl diselenide, vide infra) or obtained commercially (dimethyl diselenide, Strem Chemicals, Inc.). Diphenyl diselenide was a gift from Dr. N. P. Luthra of this department.

Di-*tert*-butyl Diselenide. Attempts to prepare di-*tert*-butyl diselenide directly from *tert*-butyl halide (X = Cl, Br, I) and Li$_2$Se$_2$[31b] met with limited success. Reaction of *tert*-butyl chloride with Li$_2$Se$_2$ gave little to no di-*tert*-butyl diselenide, whereas the reaction of either *tert*-butyl bromide or *tert*-butyl iodide with Li$_2$Se$_2$ required high temperatures (ca. 80 °C) and long reaction times (ca. 3 days) providing only moderate yields (<30%) of di-*tert*-butyl diselenide contaminated with impurities that proved extremely difficult to remove. Preparative scale elution chromatography (silica gel or alumina) tended to decompose the diselenide to the selenide. A limited quantity of pure sample *could*, however, be obtained by oxidizing[32] carefully purified 2-methyl-2-propaneselenol with alkaline hydrogen peroxide to the diselenide. However, 2-methyl-2-propaneselenol proved to be practically inseparable from the organic solvents used in its preparation (e.g., pentane, diethyl ether, or THF), requiring repeated high vacuum trap-to-trap fractionations and use of a modified low-temperature fractionation column[33] resulting in only very small, isolated quantities of pure 2-methyl-2-propaneselenol.

Initial attempts to prepare di-*tert*-butyl diselenide from *tert*-butyllithium and elemental selenium in dry THF were fraught with difficulties. Small yields of di-*tert*-butyl diselenide were obtained contaminated with di-*tert*-butyl selenide and a compound that has only been partially characterized (by GC/mass spectrometry) as being a diselenide containing a neohexyl group and possibly a separate *tert*-butyl group. The largest molecular ion at *m/e* 302 is the correct molecular ion for the unsymmetrical *tert*-butyl neohexyl diselenide. Subsequent to our work and using similar experimental conditions with tellurium metal, Jones and Sharma[34] reported that *tert*-butyllithium seems to react at room temperature initially with THF to form neohexyllithium that then reacts with the tellurium metal to form dineohexyl ditelluride.

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Table I. Selenium-77 NMR Parameters Determined for Unsymmetrical Alkyl Methyl and Alkyl Phenyl Diselenides, $R_aSe_aSe_bR_b$

	diselenide						
no.	R_a	R_b	$\delta(Se_a)$[a]	$\delta(Se_b)$[a]	$^1J_{SeSe}$[b]	prep[c]	remarks
1	n-C_4H_9	CH_3	361.7	217.9	36.3 ± 0.6	3	*d*
2	n-C_5H_{11}	CH_3	366.8	221.4	*e*	3	*f*
3	n-$C_{10}H_{21}$	CH_3	366.4	221.3	35.9 ± 0.25	3	*f*
4	n-$C_{16}H_{33}$	CH_3	367.2	221.8	35.4 ± 0.25	3	*f*
5	C_2H_5	CH_3	398.8	207.6	33.2 ± 0.2	4	*d*
6	i-C_3H_7	CH_3	492.5	177.9	16.3 ± 0.2	3	*d*
7	t-C_4H_9	CH_3	584.0	179.1	ca. 2.7[g]	3, 5	*d*
8	C_6H_5	n-C_4H_9	392.7	372.5	10.0 ± 0.1	2	*d*
9	C_6H_5	n-C_5H_{11}	389.1	370.7	*e*	2	*f*
10	C_6H_5	n-$C_{10}H_{21}$	392.6	372.7	8.4 ± 0.2	2	*d*
11	C_6H_5	n-$C_{16}H_{33}$	396.1	375.6	*e*	2	*f*
12	C_6H_5	CH_3	446.8	294.5	21.5 ± 0.25	1	*f*
13	C_6H_5	CH_2CH_3	382.5	406.4	7.0 ± 0.2	1	*d*
14	C_6H_5	i-C_3H_7	357.4[h]	488.0[h]	13.0 ± 0.15[h]	2	*d*
15	C_6H_5	t-C_4H_9	355.6	567.5	34.9 ± 0.1	5	*d*

[a] In ppm, deshielded with respect to 60% dimethyl selenide in $CDCl_3$ (v/v) at 25 °C. All samples were run as mixtures containing the unsymmetrical diselenide and both of the corresponding symmetrical diselenides, ca 50–70% total diselenides in $CDCl_3$ (v/v) at 25 °C. [b] In Hz, the value reported is the average of the coupling measured for both unsymmetrical resonances. [c] This number corresponds to the number of the equation in the text that describes the particular method used to prepare the unsymmetrical diselenide. [d] Measured at 15.27 MHz. [e] Not obtained. [f] Measured at 18.90 MHz. [g] The high-field satellite peak could only be resolved as a shoulder on the main resonance. [h] Measurements performed on sample *after* aqueous workup (see text).

With use of experimental conditions similar to Engman and Cava[35] for preparing di-*tert*-butyl ditelluride from *tert*-butyllithium and tellurium metal in dry THF, modest yields (15–23%) of pure di-*tert*-butyl diselenide could be prepared by the following procedure: under a purge of dry nitrogen, elemental selenium (17.41 g, 220.5 mmol) was added to 100 mL of dry THF. After the solution was cooled to 0 °C with stirring, 116.1 mL of *tert*-butyllithium (1.9 M in pentane, 220.5 mmol) was slowly syringed into the solution that was then allowed to warm and stir for 1 h at room temperature. The solution was again cooled to 0 °C, and 27.7 mL of 8.8 N NaOH precooled to 0 °C was added followed by 65 mL of precooled 1.7 M aqueous hydrogen peroxide. The mixture was warmed to room temperature and 50 mL of H_2O added. The organic layer was separated, washed (four times, 50 mL of H_2O), dried ($MgSO_4$), and filtered (glass wool plug and Celite), and the solvents were removed under vacuum. Careful distillation on a small (30 plate) Teflon spinning band distillation column (B/R Instrument Corp.) resulted in two fractions. Di-*tert*-butyl selenide:[36] a colorless, slightly ethereal-smelling liquid; bp 30–34 °C (1.9-2.1 torr); 6.45 g (15% based on Se); ^1H NMR (15% in $CDCl_3$) δ 1.48 (s); ^{13}C NMR (15% in $CDCl_3$) δ 33.8 (CH_3, $^1J_{CH} = 126.36 \pm 0.13$ Hz, $^3J_{CH} = 4.73 \pm 0.13$ Hz), 42.1 (quaternary, $^3J_{CH} = 4.36 \pm 0.12$ Hz); ^{77}Se NMR (71% in $CDCl_3$, 25 °C) δ 613.8 ($^3J_{^{77}Se^1H} = 9.87 \pm 0.03$ Hz). Di-*tert*-butyl diselenide:[36] a bright, clear yellow liquid; bp 53–56 °C (0.15 torr) [lit.[37] 63–67 °C (3–4 torr)]; 6.77 g (22.6% based on Se).

Unsymmetrical Diselenides. The five general methods used for the preparation of unsymmetrical diselenides as outlined in eq 1–5 are described in detail below for a representative preparation by each method. The particular method used for each of the compounds reported in this work is noted in Table I.

Method 1. Preparation of methyl phenyl diselenide:[6] benzeneselenol (1.10 g, 7.00 mmol) and dimethyl diselenide (1.11 g, 5.90 mmol) under an atmosphere of dry nitrogen were placed in a small glass reaction vessel sealed to a Teflon and glass vacuumn valve (J. Young L.T.D.) having an o-ring/Teflon joint (Fischer and Porter Co.).[38] The vessel was then attached to a vacuum line and degassed by several freeze–pump–thaw cycles. Over the course of several days the vessel was periodically cooled to −78 °C (dry ice/isopropyl alcohol bath) and the volatile methaneselenol (identified by mass spectrometry) was pulled onto the vacuum line under a dynamic vacuum and trapped at −196 °C (liquid-nitrogen bath).

Method 2. Preparation of phenyl isopropyl diselenide: phenyl selenenyl chloride[39] was formed in situ by bubbling chlorine gas into a magnetically stirred solution of diphenyl diselenide (1.24 g, 4.00 mmol) in ca. 60 mL of dry pentane (or $CHCl_3$) under an atmosphere of dry nitrogen until a white precipitate of $C_6H_5SeCl_3$ just formed. At this point diphenyl diselenide, a small portion of which had previously been held back for this purpose, was added portionwise until the white precipitate just disappeared. The repeated formation of precipitate and addition of diphenyl diselenide were continued until a clear, dark red solution of C_6H_5SeCl resulted, having consumed exactly 4.00 mmol of diphenyl diselenide. The reaction vessel was cooled to −78 °C and partially evacuated, and 2-propaneselenol (1.07 g, 8.70 mmol) was condensed into it from a Schlenk tube via a U-tube. The vessel was placed under a slight nitrogen overpressure, and the solution was allowed to warm to room temperature and allowed to stir for ca. 18 h. The initial deep, dark red of the solution changed to a pale yellow. Removal of the solvent on a rotary evaporator resulted in an orange oil that was transferred to an NMR tube, dissolved in $CDCl_3$, degassed, and sealed under dynamic vacuum.

Method 3. Preparation of *tert*-butyl methyl diselenide: dimethyl diselenide (0.49 g, 2.61 mmol) and 2-methyl-2-propaneselenol (0.36 g, 2.63 mmol) were placed into a small reaction vessel. The vessel was attached to a vacuum line, degassed, and allowed to warm to room temperature. Periodically the reaction vessel was cooled to ca. −40 °C, and the methaneselenol byproduct was removed to the vacuum line.

Method 4. Preparation of ethyl methyl diselenide: methyllithium (32 mL of 1.9 M solution in diethyl ether, 60.80 mmol) was placed into a three-neck 250-mL round-bottom flask under a dry nitrogen atmosphere. The diethyl ether was removed under vacuum and replaced with THF. Se metal (9.5 g, 120.31 mmol) was added portionwise at 0 °C with magnetic stirring. The solution turned very dark red characteristic of Se_2^{2-}. Ethyl iodide (5.0 mL, 60.91 mmol) was added dropwise at 0 °C. The solution was allowed to warm to room temperature and to stir overnight. The solvent was removed at reduced pressure, yielding an orange oil that turned red upon standing, presumably due to deposition of red, elemental Se. The red oil was distilled (ca. 20 torr) yielding fraction I (boiling range 60–75 °C) and fraction II (bp 79–80 °C). Fraction I was identified spectroscopically (^1H, ^{77}Se, and ^{13}C NMR and mass spectroscopy) to be a mixture of diethyl diselenide, dimethyl diselenide, and ethyl methyl diselenide. Fraction II was

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(38) Note: the total avoidance of the use of any stopcock grease whatsoever in preparing, transferring, or handling volatile liquid organoselenium compounds makes for a much more pleasant atmosphere in the laboratory.

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similarly identified to be mostly diethyl diselenide. Redistilling fraction I did not change its ^{1}H NMR or mass spectral data.

Method 5. Preparation of *tert*-butyl phenyl diselenide: sodium 2-methyl-2-propaneselenolate was formed in situ by adding Na metal (0.28 g, 12 mmol) to di-*tert*-butyl diselenide (1.63 g, 6 mmol) in liquid ammonia at −78 °C with stirring under dry nitrogen. The ammonia was allowed to evaporate, ca. 30 mL dry hexane was added, and the mixture was cooled to −78 °C. Benzeneselenenyl chloride (1.87 g, 6 mmol), prepared as in method 2 above, dissolved in ca. 70 mL of dry hexane, was slowly added from a dropping funnel. The solution was stirred for 20 min and then allowed to warm to room temperature. Water (ca. 30 mL) was added, and the organic layer was collected, washed (three times with 30 mL of H_2O), dried ($MgSO_4$), and filtered (glass wool plug and Celite), and solvent was removed on a rotary evaporator.

Results and Discussion

The unsymmetrical diorganyl diselenides investigated in this study were prepared by the five different methods outlined in eq 1–5 and described in detail in the Experimental Section.

$$C_6H_5SeH + R_2Se_2 \rightarrow C_6H_5SeSeR + RSeH \quad (1)$$

$$C_6H_5SeCl + RSeH \rightarrow C_6H_5SeSeR + HCl \quad (2)$$

$$(CH_3)_2Se_2 + RSeH \rightarrow CH_3SeSeR + CH_3SeH \quad (3)$$

$$RSe_2Li + R'I \rightarrow RSeSeR' + LiI \quad (4)$$

$$RSeX + R'SeNa \rightarrow RSeSeR' + NaX \quad (5)$$

$$X = Cl, Br$$

Equation 1 is essentially the procedure originally used by McFarlane[6] to prepare methyl phenyl diselenide while the remaining four methods are new and reported here for the first time. All of the methods have as a common theme the formation of a sacrificial coproduct that either is more volatile than the starting materials and the desired unsymmetrical diselenide product and easily removed on a high vacuum system (e.g., methane- or ethaneselenol, HCl) or is an alkali halide insoluble in the reaction mixture and consequently washed away in the aqueous workup.

As noted by McFarlane,[6] unsymmetrical diselenides are easily formed but are thermally labile. Attempts to purify the unsymmetrical diselenides by distillation results in disproportionation of the unsymmetrical diselenide and isolation of only the corresponding symmetrical diselenides. However, in the case of ethyl methyl diselenide, reduced pressure distillation (ca. 20 torr) produces a separate fraction containing a mixture of dimethyl diselenide, diethyl diselenide, and ethyl methyl diselenide whose spectroscopic properties (^{1}H NMR and mass spectroscopy) do not change on redistillation. Distillation of ethyl phenyl diselenide (high vacuum) and methyl phenyl diselenide (ca. 20 torr) results in disproportionation to the symmetrical diselenides. Except for the single case of phenyl isopropyl diselenide (vide infra), the ^{13}C and ^{77}Se NMR spectra indicate that the unsymmetrical compounds are stable in solution on the "NMR time scale". As these compounds were too thermally labile to distill and the symmetrical diselenides are known to be unstable to liquid chromatography on silica gel or alumina, it was of interest to determine if the mixture containing the more stable ethyl methyl diselenide could be resolved by gas chromatography. The results are shown in Figure 1 for the GC/mass spectra of a dilute diethyl ether sample of the redistilled ethyl methyl diselenide mixture. The order of elution and the "retention" time for GC peaks 1, 2, and 3 (Figure 1a) are qualitatively similar to the results reported by Evans and Johnson[40] for dimethyl and diethyl diselenide in their gas chromatography study of the separation of alkylselenium compounds. The mass spectra for GC peaks 1, 2, and 3 (Figure 1b–d) identify the peaks as dimethyl, ethyl methyl, and diethyl diselenide, respectively. The three clusters of ion patterns found at highest m/e in each mass spectrum reproduce fairly well the expected relative internal intensities for fragments containing two selenium atoms at natural abundance and correspond to $[RSe_2R]^+$, $[RSe_2H]^+$, and $[HSe_2H]^+$ when the organic group lost is C_2H_4 and correspond to $[RSe_2R]^+$, $[RSe_2]^+$, and $[Se_2]^+$ when the organic group lost is CH_3. The difference presumably is due to the reluctance of the methyl group to undergo an intramolecular 1,2-hydrogen shift as has been observed for alkyl methyl disulfides.[41] This is also consistent with the fragmentation reported for di-*n*-butyl diselenide.[42]

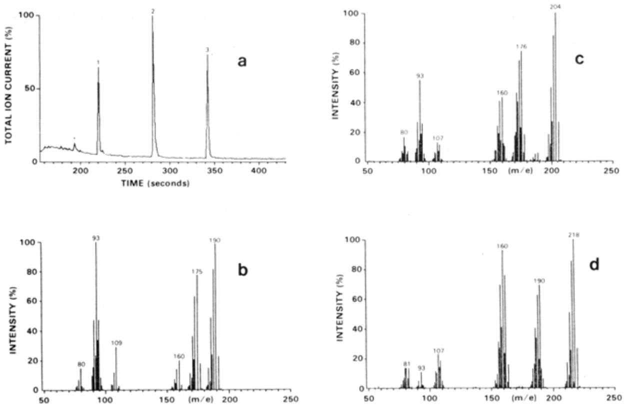

Figure 1. Separation by GC/MS of the diselenides present in the low boiling fraction of the distillation of ethyl methyl diselenide. (a) Chromatograph of the total mass spectral ion current vs. elution time of the components in the mixture: (*) known solvent decomposition product, (1) dimethyl diselenide, (2) ethyl methyl diselenide, (3) diethyl diselenide. (b) Mass spectrum of peak 1. (c) Mass spectrum of peak 2. (d) Mass spectrum of peak 3 (70 eV).

The only unsymmetrical diselenide to display evidence of exchange in an NMR spectrum was a sample of phenyl isopropyl diselenide prepared by the method of eq 2 in which the reaction mixture was *not* extracted into an organic solvent during an aqueous workup upon completion of the preparation. Instead, the reaction mixture had been filtered through a fine sintered glass frit, the solvent removed on a rotary evaporator, and a sealed NMR sample prepared directly from the resulting mixture. The room-temperature ^{13}C NMR spectrum exhibited a broad coalescence of the two isopropyl C_α signals due to the symmetrical and unsymmetrical diselenides and a single, sharp, "collapsed" signal due to the two isopropyl C_β resonances. The exchange could be slowed sufficiently to observe sharp, distinct signals for all ^{13}C resonances of diisopropyl diselenide, phenyl isopropyl diselenide, and diphenyl diselenide by cooling the sample to ca. −10 °C. The demonstrated exchange[43] in the ^{13}C NMR spectra did not seem to indicate whether a Se–C bond or the Se–Se bond was being broken and reformed. Variable-temperature ^{77}Se NMR spectroscopy, in principle, could probe this question directly. However, due to the extremely large chemical shift differences between the exchanging resonances (>1200 Hz), the change in rate due to varying the temperature between −60 and +60 °C was too small to produce an

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(40) Evans, C. E.; Johnson, C. M. *J. Chromatogr.* **1966**, *21*, 202.

(41) Gupta, D.; Knight, A. R.; Smith, P. J. *Can. J. Chem.* **1981**, *59*, 543 and references cited therein.

(42) Agenäs, L.-B. *Ark. Kemi* **1969**, *30*, 497.

(43) Anderson, J. A.; Odom, J. D.; Zozulin, A. J., manuscript in preparation.

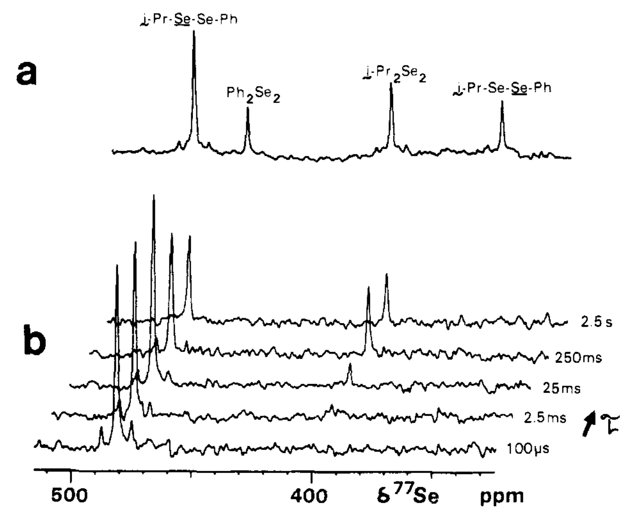

Figure 2. ^{77}Se NMR study of the chemical exchange in phenyl isopropyl diselenide by selective magnetization transfer. (a) Full proton-decoupled ^{77}Se spectrum of the phenyl isopropyl diselenide sample displaying all four resonances of the two symmetrical diselenides and the unsymmetrical diselenide. (b) Proton-decoupled ^{77}Se magnetization transfer difference spectra, using a 180° DANTE selective pulse sequence of 37 pulses of flip angle $\pi/37$ rad, lasting 7.4 ms. The time axis is the delay τ after selective inversion of the low-field (isopropyl) selenium-77 resonance of the unsymmetrical phenyl isopropyl diselenide, showing transfer of negative Z magnetization to the high-field (phenyl) selenium-77 resonance of the unsymmetrical diselenide.

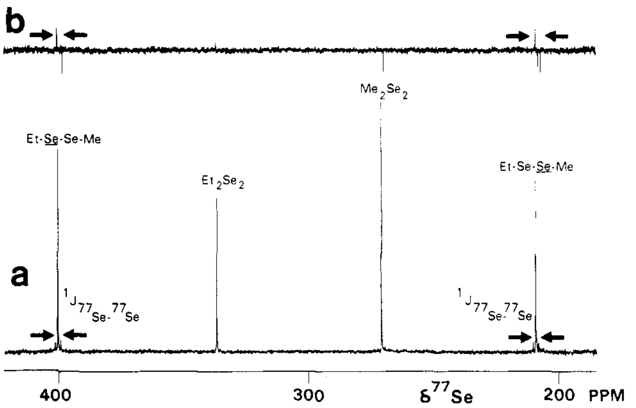

Figure 3. Proton-decoupled ^{77}Se NMR spectra of the ethyl methyl diselenide mixture. (a) Normal ^{77}Se Fourier transform spectrum displaying two singlets for the two symmetrical diselenides plus two singlets for the two unsymmetrical diselenide resonances flanked by low-intensity doublets arising from homonuclear spin–spin coupling in the unsymmetrical diselenide bond when both selenium nuclei are ^{77}Se. (b) ^{77}Se INADEQUATE (enhanced with INEPT) spectrum of ethyl methyl diselenide showing that the satellites in (a) are due solely to homonuclear ^{77}Se–^{77}Se coupling. The double quantum transitions due to two adjacent, chemically shift nonequivalent ^{77}Se nuclei are selectively enhanced as +1:–1 doublets while all other transitions are suppressed. The INEPT delays were τ_1 = 20.83 ms ($^2J_{SeH} \simeq$ 12 Hz) and $2\tau_2$ = 27.78 ms (optimal for refocusing the methylene proton coupling, $^2J_{SeH} \simeq$ 9 Hz). The INADEQUATE delay $\tau_4 = (2n + 1)/4J_{SeSe}$ was 37.88 ms (optimal double quantum conversion for $^1J_{SeSe} \simeq$ 33 Hz and n = 2). The abbreviated pulse sequence of ref 25 was used employing a "64-step phase sequence".

easily interpretable perturbation in the ^{77}Se resonances. In order to solve this problem, a ^{77}Se DANTE selective magnetization transfer experiment[44] was performed and recorded in the difference mode so that only the perturbed resonances contributed to the observed spectrum. The unperturbed room-temperature FT ^{77}Se spectrum is shown in Figure 2a for comparison and displays all four ^{77}Se resonances attributable to diphenyl, phenyl isopropyl, and diisopropyl diselenide. The magnetization transfer was initiated by selectively inverting the isopropyl ^{77}Se resonance in phenyl isopropyl diselenide, and then the amount of magnetization transferred was monitored as a function of the delay time τ. At small values of τ (Figure 2b) no magnetization transfer has occurred, but as τ is increased, magnetization is transferred from the selectively excited isopropyl ^{77}Se resonance of phenyl isopropyl diselenide to the ^{77}Se resonance in diisopropyl diselenide with no transfer of magnetization to either of the phenyl ^{77}Se resonances occurring. This result suggests that Se–Se bonds are being broken and remade during the exchange as any plausible mechanism involving scission of the Se–C bonds would allow scrambling of the Se atoms in the unsymmetrical diselenide and hence should transfer magnetization to all four of the ^{77}Se resonances. If the sealed NMR sample of phenyl isopropyl diselenide is now opened and subjected to an aqueous workup, dried, and filtered and solvent removed on a rotary evaporator, the chemical exchange is destroyed as evidenced by all of the ^{13}C resonances of the symmetrical and unsymmetrical diselenides being sharp and distinct at room temperature.[43]

The ^{77}Se chemical shift and ^{77}Se–^{77}Se scalar coupling constant ($^1J_{SeSe}$) data for the 15 unsymmetrical diselenides studied in this investigation are presented in Table I. A representative Fourier transform ^{77}Se NMR spectrum of a mixture of an unsymmetrical dialkyl diselenide, ethyl methyl diselenide, and the corresponding symmetrical diselenides is shown in Figure 3 and compared with a ^{77}Se INADEQUATE (enhanced with INEPT) spectrum of the same compound. The INADEQUATE pulse sequence has selectively suppressed the single quantum transitions due to a ^{77}Se resonance arising from Se–Se bonds containing only one ^{77}Se isotope while enhancing the +1:–1 doublets with separation of $^1J_{SeSe}$ for the double quantum transitions due to those ^{77}Se resonances that are directly bonded to a second, chemically nonequivalent ^{77}Se isotope. The data for the two series of compounds, alkyl methyl diselenides and alkyl phenyl diselenides, follow parallel trends. For example, repeated methyl substitution at an α-carbon consistently has a deshielding effect on the near selenium resonance (e.g., +111.9 ppm for conversion of dimethyl diselenide into ethyl methyl diselenide) while having a shielding effect on the remote selenium resonance (e.g., –64.3 ppm in going from dimethyl diselenide to ethyl methyl diselenide). The deshielding effect on the near selenium, however, is consistently ca. 13% less (16.5 ppm) in the alkyl phenyl series than in the dialkyl series of diselenides. An apparent anomaly is that the third α-methyl substitution has only a slight effect on the remote selenium. The effect on the ^{77}Se chemical shift of varying the alkyl chain length past four carbons is small in both series of compounds.

The effect of sequential α-methyl substitution is clearly illustrated in Figure 4 where the ^{77}Se chemical shifts in the unsymmetrical diselenides have been plotted against the number of protons on the two α-carbons. The two series of compounds create two essentially parallel sets of curves. The selenium resonance adjacent to the point of α-methyl substitution undergoes a smooth monotonic deshielding while the remote selenium resonance displays a dramatic nonlinear shielding effect. The regularity of the change in shielding of the selenium resonance adjacent to the point of α-methyl substitution suggests that multiple C_α methyl substitution is an additive effect as has been found for the

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[44] The only other reported examples of magnetization transfer applied to "heavy" nuclei are ^{113}Cd (see: Ellis, P. D.; Yang, P. P.; Palmer, A. R. *J. Magn. Reson.* **1983**, *52*, 254) and ^{119}Sn (see: Knight, C. T. G.; Merbach, A. E. *J. Am. Chem. Soc.* **1984**, *106*, 804).

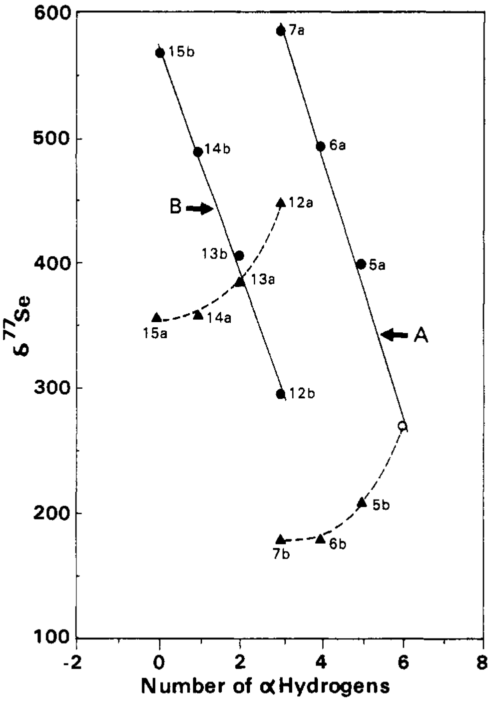

Figure 4. Correlation of ^{77}Se chemical shifts with the number of hydrogens on the α-carbons of the two substituents (methyl, ethyl, isopropyl, *tert*-butyl, and phenyl) in the two series of compounds, alkyl methyl diselenides (curves A) and alkyl phenyl diselenides (curves B): ●, ^{77}Se resonance adjacent to point of α-methyl substitution; ▲, ^{77}Se resonance remote to point of substitution; ○, dimethyl diselenide.

^{13}C chemical shifts[45] of linear and branched alkanes and recently for the ^{125}Te resonances in unsymmetrical diorganyl ditellurides[46] and tellurides[47] and for the ^{77}Se resonance in unsymmetrical diorganyl selenides.[47] A second and better correlation is shown in Figure 5 where the ^{77}Se chemical shift data for the unsymmetrical diselenides in Table I and the corresponding symmetrical diselenides are plotted against the number of hydrogens on the carbon α to the selenium atom minus the sum of all hydrogens on carbons in a position that is β to the selenium. This same type of linear correlation has also been shown to hold for the group contribution of branched alkyl groups on the ^{31}P chemical shift in substituted triorganylphosphines.[48] The ^{31}P chemical shift study also demonstrated the equivalence of the number of α- minus β-protons to the number of β-minus γ-carbons.

The opposite shielding effects of α-methyl substitution on the near and remote selenium resonances can be rationalized as being similar to that found for ^{13}C substituent effects[45b] in linear and branched alkanes. This is illustrated in Figure 6a for the effects of α-methyl substitution in converting dimethyl diselenide into ethyl methyl diselenide compared with the analogous conversion of *n*-butane into *n*-pentane. The effect of replacement of hydrogen for methyl at the C_α position deshields the near selenium resonance by 129.3 ppm and shields the remote selenium resonance by 61.9 ppm analogous to the β- and γ-effects of ^{13}C NMR spectroscopy; e.g., in *n*-pentane the C-2 resonance is deshielded by 9.5 ppm and the C-3 resonance is shielded by 2.6 ppm by α-methyl substitution (at C-1) of *n*-butane.[45a] The β-effect in ^{13}C NMR spectroscopy is usually observed to be independent of substituent electronegativity but has not otherwise been satisfactorily explained. The γ-gauche effect, however, is usually considered to be steric in nature[49] (Figure 6b) where a methyl or other simple substituent (i.e., SH, NH_2, Br, Cl, etc.) can compress the C–H bond of the γ-carbon due to near

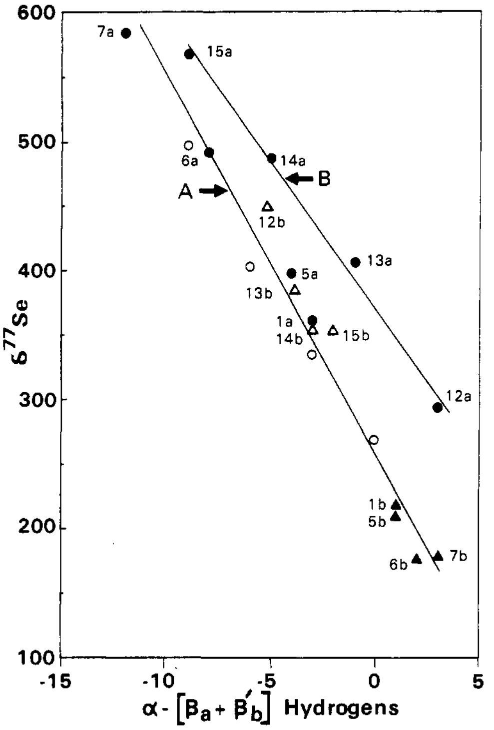

Figure 5. Correlation of ^{77}Se chemical shifts with the hydrogens on an α-carbon minus the sum of all hydrogens on a carbon β (β' = remote substituent) to the Se atom in the two substituents (methyl, ethyl, isopropyl, *tert*-butyl, phenyl) of the two series of unsymmetrical compounds (alkyl methyl and alkyl phenyl diselenides) and the symmetrical dialkyl diselenides. Curve A is the correlation (r^2 = 0.9649) of all ^{77}Se resonances excluding the alkyl ^{77}Se resonance in the alkyl phenyl series, which is plotted separately as curve B (r^2 = 0.9926): ●, ^{77}Se resonance adjacent to point of α-methyl substitution; ▲, methyl ^{77}Se resonance of the alkyl methyl diselenides; △, phenyl ^{77}Se resonance of the alkyl phenyl diselenides; ○, symmetrical dialkyl diselenide.

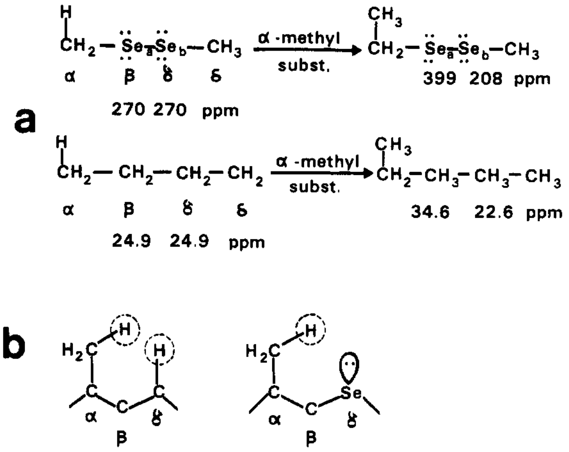

Figure 6. The β- and γ-effects illustrated for ^{13}C and ^{77}Se shielding. (a) The β- and γ-effects of replacing an α-proton with a methyl group in linear alkanes contrasted with the equivalent transformation in alkyl methyl diselenides. (b) Steric requirement for the γ-effect in ^{13}C and ^{77}Se shielding.

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[45] (a) Paul, E. G.; Grant, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 1701. (b) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.

[46] O'Brien, D. H.; Dereu, N.; Grigsby, R. A.; Irgolic, K. J.; Knapp, F. F., Jr. *Organometallics* **1982**, *1*, 513.

[47] O'Brien, D. H.; Dereu, N.; Huang, C.-K.; Irgolic, K. J.; Knapp, F. F., Jr. *Organometallics* **1983**, *2*, 305.

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[49] Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315.

Table II. ^{77}Se Chemical Shift Changes Due to Sequential α-Methyl Substitution in Diorganyl Diselenides, $R_aSe_aSe_bPh$ and $R_aSe_aSe_bMe$

sequence of α-methyl substitutions	alkyl phenyl parameters[a]		alkyl methyl parameters[a]		example R_a conversn
	$\Delta\delta(Se_a)$	$\Delta\delta(Se_b)$	$\Delta\delta(Se_a)$	$\Delta\delta(Se_b)$	
1st[b]	111.9	−64.3	129.3	−61.9	Me to Et
2nd[b]	81.6	−25.1	93.7	−29.7	Et to *i*-Pr
3rd[b]	79.5	−1.8	91.5	1.2	*i*-Pr to *t*-Bu

[a] In ppm. [b] Equivalent to α_1, α_{2-1}, and α_3, respectively, of ref 44.

Table III. α-Methyl ^{77}Se Chemical Shift Substituent Parameters A_l and Branching Correction Terms S_{kl} for Eq 6 in Dialkyl Diselenides, $R_aSe_aSe_bR_b$

substituent parameters		correctn terms			
carbon position l (Se atom k)	A_l,[a] ppm	$k(l)$	S_{kl},[a] ppm	$k(l)$	S_{kl},[a] ppm
β_a	129.3	a(3°)	−34.7	b(3°)	33.1
γ_a	−61.9	a(4°)	−71.6	b(4°)	97.1

[a] For δ_{ref} in eq [6] = 269 ppm for dimethyl diselenide (relative to 60% dimethyl selenide in $CDCl_3$ at 25 °C).

proximity of the substituent's covalent element–hydrogen bonds and/or unshared pairs of electrons. This forces electron density toward the γ-carbon resulting in an increased shielding of the resonance of this carbon. This same type of steric compression could be operative in the increased shielding of a selenium atom γ to a methyl group by forcing the electron density of the unshared pair closer to the selenium nucleus. The chemical shift changes in alkyl methyl and alkyl phenyl diselenides caused by sequential α-methyl substitution are summarized in Table II. The changes at the remote selenium are very similar among the two series of unsymmetrical diselenides; however, as mentioned previously, the changes at the selenium nearest to the point of substitution are consistently smaller in the phenyl series as compared to the methyl series. This anomaly is also evident in Figure 5 where the alkylselenium resonances in the phenyl series are displaced significantly away from the line drawn for the correlation of both of the resonances in the dialkyl series. A tentative explanation for the anomalously lower deshielding effect in the alkyl phenyl series on the near ^{77}Se resonance by α-methyl substitution could be a simple decrease with distance in the long-range deshielding effect arising from ring currents in the π-electron system of the phenyl ring.[50] This could be due to an increasing Se–Se–C_{ipso}(phenyl) bond angle upon sequential α-methyl substitution causing a lesser deshielding effect on the Se resonance remote from the phenyl ring. Perhaps of more interest than the absolute magnitude of the difference in the $\Delta\delta(Se_a)$ parameters for the two series of compounds is the near consistency of this difference (16.5, 12.5, and 12.0 ppm, respectively) as the number of α-methyl substitutions increases from one to three. This decrease in deshielding by the ring current with increasing α-methyl substitution would have to be a consistently larger effect with each new substitution as a constant effect would only cancel and hence not be detected. However, as pointed out recently,[51] a definitive explanation of an effect this small (~15 ppm) compared to the total chemical shift range of ^{77}Se (~3000 ppm) and for these unsymmetrical diselenides (~405 ppm) is probably not possible. Furthermore, the extreme difficulty in isolating pure samples of these thermally labile compounds makes it doubtful whether accurate structural data will ever become available to substantiate this hypothesis.

The concept of the Grant–Paul additivity relationship used in predicting ^{13}C chemical shifts of alkanes[45b] can be extended to the ^{77}Se NMR spectroscopy of diselenides by formulating the following additivity relationship

$$\delta_{Se}(k) = \delta_{ref} + \sum_l A_l n_{kl} + \sum S_{kl} \qquad (6)$$

where $\delta_{Se}(k)$ is the calculated chemical shift of the kth Se atom, δ_{ref} is the chemical shift of the reference compound dimethyl diselenide (269 ppm), A_l is the additive shift parameter for C atom l, n_{kl} is the number of C atoms in position l with respect to Se atom k, and S_{kl} is the correction parameter for branching at C atom l on the chemical shift of Se atom k. The parameters necessary for calculation of ^{77}Se chemical shifts in dialkyl diselenides with α-branching have been determined from the chemical shift data for alkyl methyl diselenides and are listed in Table III. An example calculation for the isopropyl ^{77}Se resonance in isopropyl methyl diselenide is $\delta_{Se}(a) = \delta_{ref} + 2\beta_a + S_{a3°} = 269 + 2(129.3) - 34.7 = 492.9$ ppm, in excellent agreement with the experimental value of 492.5 ppm. This method also accurately predicts the ^{77}Se chemical shifts of the symmetrical diselenides. Both correction terms in ^{77}Se chemical shifts for α-branching listed in Table III are shielding effects as are all of the branching correction terms used in the calculation of ^{13}C chemical shifts of branched alkanes. The ^{13}C correction for isopropyl next to a methylene carbon $S_{2°(3°)}$ is −2.50 ppm while the ^{77}Se term $S_{a3°}$ is −35.6 ppm. This ^{13}C correction factor has the same shielding effect as the ^{13}C γ-effect (−2.50 ppm) while the ^{77}Se correction factor is less shielding than the ^{77}Se γ_b-effect by 27 ppm. It is interesting to note that correction factors for *remote* branching are necessary to calculate ^{77}Se chemical shifts in these diselenides. No such remote branching correction factors are required in calculating ^{13}C chemical shifts. However, separate α- and β-substituent parameters *are* necessary to account for heteroatom location,[52] i.e., whether substitution occurs at the end, or in the middle of, an alkyl chain. Furthermore, ^{13}C chemical shift additivity schemes require many more branching correction factors in order to account for all of the available combinations of the different degrees of branching (1°, 2°, 3°, 4°) possible at two adjacent carbon atoms.

The $^1J_{SeSe}$ data in Table I follow the same type of correlation as the chemical shift data if the relative signs of three of the coupling constants (*tert*-butyl methyl-, phenyl isopropyl, and *tert*-butyl phenyl diselenide) are assumed to be of opposite sign than the remainder of the ^{77}Se–^{77}Se coupling constants. The correlation of the $^1J_{SeSe}$ values with the sum of the *near* [α–β] hydrogens for both selenium atoms, i.e.

$$[\alpha_a(R) + \alpha_a(R')] - [\beta_a(R) + \beta_a(R')]$$

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(52) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1978; p 37.

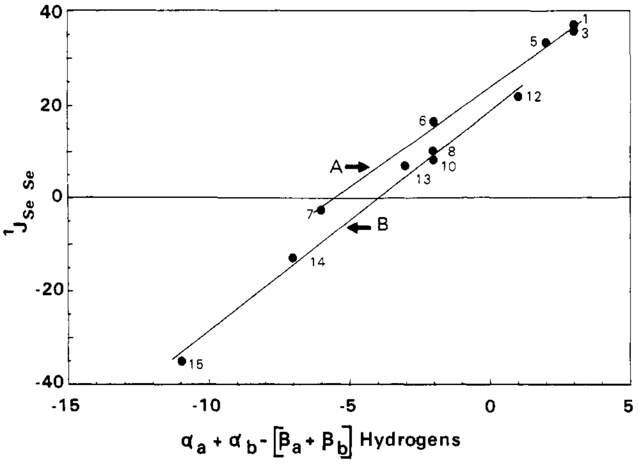

Figure 7. Correlation of one-bond spin–spin coupling constants in unsymmetrical diselenides with the sum of the α- minus β-protons on the two substituents assuming a change in sign of $^1J_{SeSe}$ (see text). Curve A is the alkyl methyl diselenide series (r^2 = 0.9973). Curve B is the alkyl phenyl diselenide series (r^2 = 0.9924).

is shown in Figure 7. Both series of unsymmetrical diselenides appear to fall very near the same line. Inclusion of the *remote* β-hydrogens into the calculated difference of α- and β-hydrogens displaces the alkyl methyl series significantly to the left of the line in Figure 7 while the alkyl phenyl series undergoes a negligible shift, once again showing similar and essentially parallel trends for both series of unsymmetrical diselenides.

In contrast to the large effect that α-methyl substitution has on the ^{77}Se chemical shifts, there initially appears to be a relatively small effect on the ^{77}Se–^{77}Se coupling constants. For example, the selenium resonance nearest to the point of α-methyl substitution is deshielded by 94 ppm in going from $EtSe_2Me$ to *i*-$PrSe_2Me$ while $^1J_{SeSe}$ is decreased by only 16.9 Hz; however, the fractional changes (computed from the total range of chemical shifts (ca. 405 ppm) and coupling constants (71.2 Hz)) are both approximately 23%. At first glance the small coupling constants appear to be contrary to expectation, as indeed McFarlane has already shown fairly convincingly that, even though a diselenide Se–Se bond probably has a relatively high degree of s character, the one-bond ^{77}Se–^{77}Se coupling constant for methyl phenyl diselenide is positive in sign as predicted by Jameson and Gutowsky[53] but is much smaller than expected for such a relatively large, third-row element.[6] In fact, $^1J_{SeSe}$ is very similar in magnitude, though opposite in sign, to $^1J_{^{31}P^{31}P}$ measured in tetraorganyldiphosphine disulfides (−19 Hz for $(CH_3)_2P(S)\cdot P(S)(CH_3)_2$).[54] McFarlane attributed the small magnitude of $^1J_{SeSe}$ in methyl phenyl diselenide to opposite and roughly equal contributions to the Fermi contact term from different excitations.[6] Molecular orbital studies on disulfides,[55] which presumably would hold qualitatively for diselenides, have shown that the energy levels of the two highest occupied molecular orbitals (HOMO), which are the two p_π orbitals of the unshared electron pairs of selenium, change in energy in an opposite and approximately equal sense as the dihedral angle changes from 0° to 180° with a crossover in energy levels occurring at ca. 90°. The lowest unoccupied molecular orbital (LUMO) is a σ^* orbital with an essentially unchanging energy level. This feature of the electronic structure has been used successfully to explain many features of the UV absorption spectra, and a similar conformational dependence was found for the valence electronic energy levels in disulfides in a recent X-ray photoelectron spectroscopy study.[56] As the dihedral angle found for most acyclic diselenides is near 90°, these molecular orbital results lend support to the idea that there could be approximately equal and opposite contributions to the coupling constants with a corresponding conformational dependence. The interplay of cancelling terms in determining the coupling constant is more probably due to one of the noncontact terms having a substantial contribution opposite in sign to the Fermi contact term. This has been shown to have an important effect in recent SCF-INDO-FPT calculations[57] on the magnitude and sign of one-bond ^{31}P–^{31}P spin–spin coupling constants in substituted diphosphines, and also in a similar study on the calculated dihedral angle dependence[58] of ^{31}P–^{31}P coupling constants. Although the extra unshared pair of electrons on each selenium makes comparisons between diselenides and diphosphines somewhat tenuous, it is satisfying to note that the effect of increasing α-methyl substitution in unsymmetrical dialkyldiphosphines is in the same sense (less positive)[54] as in the unsymmetrical diselenides although the absolute sign of the ^{77}Se–^{77}Se coupling constant is opposite that of $^1J_{P-P}$ in compounds containing similar substituents. In any event, the change in sign of the ^{77}Se–^{77}Se coupling constants with multiple α-methyl substitution is only *suggested* by the linear correlation of Figure 7 and needs experimental verification. Likewise the origin of the decrease in magnitude (and possible sign change) of $^1J_{SeSe}$ needs to be probed theoretically.

In summary, it has been shown that the effect of sequential α-methyl substitution on the two ^{77}Se resonances of unsymmetrical alkyl methyl and alkyl phenyl diselenides can be explained as being due to a β- (deshielding) effect on the near ^{77}Se resonance and a γ- (shielding) effect on the remote ^{77}Se resonance qualitatively similar to the named effects in ^{13}C chemical shifts. However, contrary to what is found for ^{13}C chemical shifts, remote branching is seen to effect ^{77}Se chemical shifts (a deshielding effect). The one-bond ^{77}Se–^{77}Se coupling constant is shown to consistently decrease with sequential α-methyl substitution being near zero (±2.7 Hz) for *tert*-butyl methyl diselenide and possibly changing sign between ethyl phenyl diselenide and phenyl isopropyl diselenide. Clearly more work, both theoretical and experimental, is needed in this area.

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Registry No. **1**, 90971-31-6; **2**, 90971-32-7; **3**, 90971-33-8; **4**, 90971-34-9; **5**, 90971-35-0; **6**, 90971-36-1; **7**, 90971-37-2; **8**, 90971-38-3; **9**, 90971-39-4; **10**, 90971-40-7; **11**, 90971-41-8; **12**, 22687-48-5; **13**, 90971-42-9; **14**, 90971-43-0; **15**, 90971-44-1; di-*tert*-butyl diselenide, 34172-61-7; selenium, 7782-49-2; *tert*-butyllithium, 594-19-4; di-*tert*-butyl selenide, 34172-60-6; benzeneselenol, 645-96-5; dimethyl diselenide, 7101-31-7; phenyl selenenyl chloride, 5707-04-0; 2-propaneselenol, 29749-04-0; 2-methyl-2-propaneselenol, 34172-59-3; methyllithium, 917-54-4; ethyl iodide, 75-03-6; sodium 2-methyl-2-propaneselenolate, 37773-07-2.

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