1250 (s), 840 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.75 (s, 2 H), 2.7–2.2 (m, 2 H), 1.55 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 206.9, 176.1, 102.2, 87.0, 71.8, 35.3, 29.0, 28.4, −0.4; MS, *m/e* 210 (M$^+$), 195 (M$^+$ − CH$_3$), 111 (Me$_3$SiC≡C=CH$_2{}^+$), 99 (M$^+$ − Me$_3$SiC≡C=CH$_2$), 73 (Me$_3$Si$^+$). Anal. Calcd for C$_{11}$H$_{18}$O$_2$Si: C, 62.81; H, 8.62. Found: C, 62.78; H, 8.50.

4-Hydroxy-5-(trimethylsilyl)-4-phenyl-5,6-heptadienoic Acid Lactone (9). Methyl 3-benzoylpropionate (1.92 g, 10 mmol) obtained from Alfa was used and the reaction was carried out as described for **8** except that the crude α-allenic alcohol in 20 mL of anhydrous ether was treated with 5 drops of BF$_3$·OEt$_2$. Distillation furnished 2.15 g (79% yield) of **9** as a colorless liquid: bp 101 °C (5 × 10^{-3} torr); IR (neat) 1935 (m, C≡C=C), 1780 (s, C=O), 1250 (m), 835 (s), 755 (m), 695 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.45 (s, 5 H), 4.8 (s, 2 H), 3.1–2.1 (m, 4 H), −0.05 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 207.9, 175.9, 143.6, 128.1, 127.3, 124.3, 100.9, 89.4, 72.2, 36.7, 29.1, −0.7; MS, *m/e* 161 (M$^+$ − Me$_3$SiC≡C=CH$_2$), 73 (Me$_3$Si$^+$).

Methyl 3-[2-hydroxy-2-[1-(trimethylsilyl)-1,2-propadienyl]cyclohexyl]propionate (11) was prepared from **10**[8] (1.84 g, 10 mmol) as described for **7**. Distillation afforded 2.43 g (82% yield) of **11** as a white solid: bp 92 °C (2 × 10^{-2} torr); mp 51–52 °C; IR (KBr) 3570 (m, OH), 1930 (s, C≡C=C), 1735 (s, C=O), 1245 (s), 835 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.45 (s, 2 H), 3.65 (s, 3 H), 2.5–2.1 (br, 3 H), 2.1–1.2 (br, 11 H), 0.15 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 206.5, 174.4, 105.6, 76.4, 71.5, 51.5, 44.2, 41.0, 32.3, 26.9, 25.9, 25.7, 21.8, 0.5; MS, *m/e* 296 (M$^+$), 279 (M$^+$ − OH), 185 (M$^+$ − Me$_3$SiC≡C=CH$_2$), 153, 125, 73 (Me$_3$Si$^+$). Anal. Calcd for C$_{16}$H$_{28}$O$_3$Si: C, 64.82; H, 9.52. Found: C, 64.59, H, 9.71.

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Preparation and Single-Crystal X-ray Characterization of 4-Selenanone

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The concept of isosteric exchange has long been used by medicinal chemists as a tool for modifying the activity of biologically important molecules.[1] One very important

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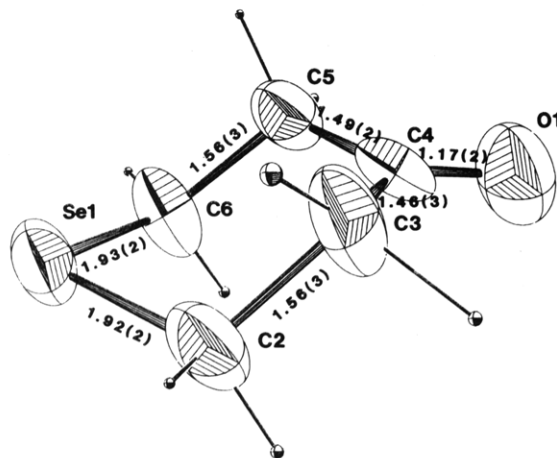
Figure 1. Projection view of 4-selenanone (**4**). The bond distances may be compared to those in **3**:[7a] C(2)–C(3), 1.527 (3) Å; C–S, 1.804 (3) Å.

isosteric pair is that of sulfur and selenium. A wide variety of sulfur-containing compounds have been synthesized in which the sulfur atom has been replaced by a selenium atom.[1]

Tetrahydro-4*H*-thiapyran-4-one (**3**) is a key intermediate
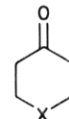
1. X = NCH$_3$
2. X = $^+$N(CH$_3$)$_2$, I$^-$
3. X = S
4. X = Se

in the synthetic scheme of a great many cyclic systems which contain sulfur. An extensive survey of the literature revealed that the *selenium* analogue **4** was heretofore unknown.[2] We now report the first synthesis of 4-selenanone (**4**) which has been accomplished via a reaction sequence that bears a remote similarity to that for **3**.[3] Ketone **4** fills a gap in the family of 1-heterocyclohexanones involving O, S, and now Se.[2d]

The synthetic scheme involved treatment of *N*-methylpiperidone (**1**) with methyl iodide to generate the corresponding oxopiperidinium iodide **2**. A mixture of powdered elemental selenium and NaBH$_4$ was used to generate NaHSe[4] and the resulting mixture was treated with **2**. This type of displacement of a secondary amine has some precedent in the formation of the sulfur analogue **3** as cited previously.[3] Although the yield is modest (56–63%), the reaction is easy to perform.

For comparison purposes, the $\lambda_{C=O}$ for sulfide **3** was 1710 cm^{-1} (KBr). Interestingly, the ^{13}C chemical shifts for C(2,6), C(3,5), and C(4) in **1**[2d] (DCCl$_3$) were 55.3, 41.0, and 207.1 ppm, in **2**[2d] (Me$_2$SO-d_6) were 60.6, 35.0, and 201.7 ppm, in **3**[2d] (DCCl$_3$) were 30.3, 44.0, and 208.0 ppm, and

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(3) (a) Johnson, P. Y.; Berchtold, G. A. *J. Org. Chem.* **1970**, *35*, 584–592. (b) Garst, M. E.; McBride, B. J.; Johnson, A. T. *J. Org. Chem.* **1983**, *48*, 8–16. *CAUTION* should be exercised in the handling of all selenium reagents in the described experiments since it is necessary to presume such materials could be toxic. Ketone **4** does sublime and therefore exposure of this compound to the atmosphere should be avoided.

(4) Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197–199.

Table I. Bond Angles and Dihedral Angles for Ketones 3[7a] and 4

angle	X = S (3), deg	X = Se (4), deg
C(2)–X–C(6)	97.0 (19)	95.0 (9)
X–C(2)–C(3)	113.2 (4)	112.2 (11)
C(5)–C(6)–X		111.1 (13)
C(2)–C(3)–C(4)	112.5 (10)	115.8 (18)
C(4)–C(5)–C(6)		115.5 (14)
C(3)–C(4)–C(5)	118.9 (11)	118.2 (16)
C(3)–C(4)–O		120.1 (16)
C(5)–C(4)–O		121.6 (16)
X–C(6)–C(5)–C(4)	57.1 (16)	58.6 (18)
X–C(2)–C(3)–C(4)		−57.0 (20)
C(6)–C(5)–C(4)–C(3)	50.0 (15)	−54.4 (23)
C(5)–C(4)–C(3)–C(2)		53.1 (22)
C(2)–X–C(6)–C(5)	58.0 (29)	−54.2 (12)
C(6)–X–C(2)–C(3)		53.5 (18)

in cyclohexanone (DCCl₃) were 27.1 (CH₂CH₂C=O), 41.9 (CH₂C=O), and 211.3 (C=O).[5] Thus sulfur appears to be much more electronegative than selenium as suggested by a markedly enhanced downfield shift for C(2,6) in **3** compared to that in **4**. The ⁷⁷Se shift for **4** is 176.6 ppm with PhSe–SePh being used as the external reference.[6] Unfortunately, the literature is void of any ⁷⁷Se data on any related systems for which a comparison might be made in terms of structural characteristics.

As indicated by a single-crystal X-ray diffraction analysis (Figure 1), the six-membered selenanone ring assumes a chair conformation as is has been frequently observed for six-membered rings including most cyclohexanones and thianone **3**.[7] Comparison of the dihedral angles for **4** (Table I) with the angle of 56° known for cyclohexane revealed some puckering of the heterocyclic ring. Comparison with the dihedral angles (Table I) found for the sulfur analogue **3** (from an electron diffraction study of a gaseous sample)[7a] indicated that puckering in the selenium system was achieved by a slightly greater bending of the C–Se–C end of the ring and a slight flattening of the carbonyl end. Interestingly, the C–Se bond lengths [1.92 (2) Å] shown in Figure 1 did not differ significantly from values found in simple dialkyl selenides such as dimethyl selenide [1.943 (1) Å (microwave)].[8] A striking similarity also exists between the C–Se–C in **4** [95.0 (9)°] and that in dimethyl selenide [96.2 (1), microwave].[8] Work is continuing in this area of heterocyclic chemistry.

Experimental Section

All NMR spectra were recorded on a Varian XL-300 spectrometer operating at 299.99 MHz for ¹H and at 75 MHz for ¹³C. The solvents are specified for each compounds. Infrared spectra were recorded on a Perkin-Elmer 681 spectrometer as KBr disks. Elemental analyses were performed by Galbraith Laboratories in Knoxville, TN. All melting points were taken on a Thomas-Hoover apparatus and are uncorrected. 1-Methyl-4-piperidone (Aldrich) was distilled (49–51 °C (0.5 mmHz) prior to use. ⁷⁷Se was recorded at 57.22 MHz on the XL-300 unit.

1,1-Dimethyl-4-oxopiperidinium Iodide (2). A solution of *N*-methyl-4-piperidone (15.0 g, 0.133 mol) in 300 mL of anhydrous ether was placed in a flask equipped with a magnetic stirrer and the usual accessories. Iodomethane (20.0 g, 0.141 mol) was added

in one portion and the resulting solution was stirred for 2 h and then was heated at reflux for another 20 h. A white solid formed during this period and this was filtered and dried under vacuum to give 31.0 g (91.4%) of **2** as a white powder: mp 186–188 °C dec; ¹³C NMR (Me₂SO-d₆) 35.2 [N(CH₃)₂], 51.1 [C(3,5)], 60.1 [C(2,6)], 201.3 [C(4)] ppm. This material was used without further purification. The reported melting point of **2**[9] is 186–188 °C dec.

4-Selenanone (4). *CAUTION. The following procedure should be performed in an efficient fume hood. All effluent gases should be exited from the top of the condenser through a trapping system composed of a blank trap followed by two traps (250 mL) filled to one-half capacity with a solution of potassium hydroxide (saturated) in 95% ethyl alcohol. The traps employed were gas washing bottles equipped with fritted discs (Fischer Scientific Company). When the traps were used as described, no odor was detected from the effluent.*

Powdered elemental selenium (4.35 g, 55.1 mol, Aldrich, 100 mesh, 99.95% purity (*CAUTION. Selenium powder can be absorbed through the lungs and is toxic)*) and NaBH₄ (4.0 g, 106 mmol) were placed in a system equipped with a magnetic stirrer and the usual accessories including an inlet for N₂ the condenser connected to the traps cited above. Absolute alcohol (500 mL) was added and the resulting mixture was stirred at room temperature for 30 min followed by a period of heating at reflux (2 h). A colorless suspension was formed and to this suspension was added solid **2** (12.75 g, 50.0 mmol) in 2–3-g portions over a period of 20 min. A yellow color was developed immediately and this suspension was heated at reflux for an additional 5 h. A dark purple solution was formed which was cooled to room temperature. The volume of the solution was reduced by 80% and the residue was diluted with water. The solution was extracted with ether (5 × 40 mL) and the combined extracts were washed with NaCl (saturated 2 × 30 mL) and dried (K₂CO₃) overnight. Evaporation of the ether produced a dark oil which solidified upon standing. Sublimation of the solid (50 °C (0.1 mmHg) gave 4-selenanone (**4**) in a yield of 4.6–5.1 g (56–63%). The white, crystalline solid had mp 55.0–55.5 °C: IR (KBr) cm⁻¹ 1700 (C=O); ¹H (DCCl₃) δ 2.82 [t, 4 H, H(3,5), *J* = 6.1 Hz], 3.00 [t, 4 H, H(2,6), *J* = 6.1 Hz]; ¹³C (DCCl₃) 19.3 [C(2,6)], 43.7 [C(3,5)], 209.3 [C(4)] ppm; ⁷⁷Se (DCCl₃) 176.6 ppm. Anal. Calcd for C₅H₈OSe: C, 36.81; H, 4.94; Se, 48.44. Found: C, 36.79; H, 4.87; Se, 48.33.

Crystal Data. The structure was solved and refined by using 812 observed reflections on a Syntex P3 automated diffractometer to an *R* value of 0.081. Crystal data for C₅H₈OSe (**4**) are M_r, 163.1, monoclinic, space group $P2_1/n$, *a* = 6.949 (4) Å, *b* = 5.620 (3) Å, *c* = 16.926 (12) Å, α = 90.0°, β = 112.03 (5)°, γ = 90.0°, and *V* = 612.8 (6) Å³, d_{calcd} = 1.767 g cm⁻¹, *Z* = 4, MoKα radiation. Further details of data collection, reduction, and refinement are given in Supplementary Table I.

Supplementary Material Available: Tables of atomic positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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