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Synthesis of 3-Acyl-1-alkyl-2-alkylseleno-1-cyclobutene Using Alkyneselenolate

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Abstract: The reaction of lithium alkyneselenolate with α,β-unsaturated ketone and then alkyl or acyl halide afforded 3-acyl-1-alkyl-2-alkylseleno-1-cyclobutene. The structure of the cyclobutene was elucidated by IR, MS, ^{1}H, ^{13}C, and ^{77}Se NMR, COSY, HMQC, and HMBC data and X-ray analysis.

Alkyneselenolate **1** is an interesting molecule and forms a canonical resonance structure. It has two active sites in the molecule and is important as a precursor of selenoketene. By the control of reaction conditions the

1

ethynylselenolate reacts at different sites and affords different products. The reaction of **1** with alkyl halide (R_1X) readily gave alkyl ethynyl selenide by reacting at the Se atom site.[1] In contrast, the reaction with R_3SiX occurs at the C2 carbon site.[2] The reaction with amine or alcohol led to selenoamide [3] or selenoester,[4] respectively, by reacting at the C1 carbon site. The reaction of **1** with diene[5] occurs at both C1 carbon and Se atom sites to give [2 + 2] cyclic products the same as in the formation reaction of selenoketene dimmer.[6] Compound **1** underwent 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate to give selenophene by reacting at both C2 carbon and Se atom sites.[7] During an investigation of the reactivities of the selenoketene **1**, we also found the reaction of alkyneselenolate with diphenylketene or alkylidene via [2 + 2] cycloaddition occurred at both the C1 and C2 carbon sites of **1**.[8] These reports prompted us to investigate reactivity of alkyneselenolate in detail. Herein, we report the one-pot reaction of the alkyneselenolate **1** with α,β-unsaturated ketone **2** followed by alkyl halide or acyl halide **3**.

SCHEME 1

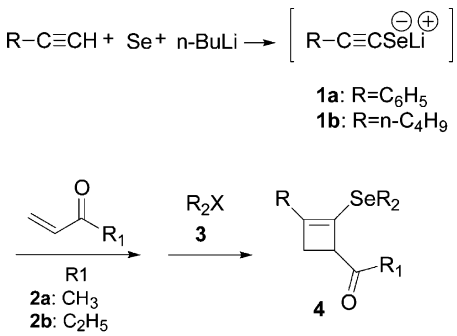

TABLE 1. Synthesis of 3-Acyl-1-alkyl-2-alkylseleno-1-cyclobutenes 4

entry	substrates			yield of **4**[a] (%)
1	**1a**[b]	**2a**[d]	CH_3COCl (**3a**)	84 (**4a**)
2	**1a**[b]	**2a**[d]	4-$CH_3C_6H_4COCl$ (**3b**)	64 (**4b**)
3	**1a**[b]	**2a**[d]	$PhCH_2Br$ (**3c**)	83 (**4c**)
4	**1a**[b]	**2a**[d]	CH_3I (**3d**)	74 (**4d**)
5	**1a**[b]	**2a**[d]	CH_3CH_2I (**3e**)	81 (**4e**)
6	**1a**[b]	**2a**[d]	$CH_3(CH_2)_2I$ (**3f**)	71 (**4f**)
7	**1a**[b]	**2a**[d]	$CH_3(CH_2)_3I$ (**3g**)	78 (**4g**)
8	**1a**[b]	**2a**[d]	$(CH_3)_2CHI$ (**3h**)	40 (**4h**)
9	**1b**[c]	**2a**[e]	**3d**	58 (**4i**)
10	**1a**[b]	**2b**[e]	**3b**	54 (**4j**)
11	**1a**[b]	**2b**[e]	**3c**	46 (**4k**)
12	**1a**[b]	**2b**[e]	**3h**	63 (**4l**)

[a] Isolated yield. [b] $C_6H_5C{\equiv}CSeLi$. [c] n-$C_4H_9C{\equiv}CSeLi$. [d] Methyl vinyl ketone. [e] Ethyl vinyl ketone.

The reaction of lithium alkyneselenolate **1** with α,β-unsaturated ketone **2** followed by alkyl halide **3** was first carried out. Reaction of alkyneselenolate **1** with alkyl halide **3** readily gives an alkyl ethynyl selenide. To avoid the formation of the selenide, various reaction conditions were examined. Under optimal conditions, **2a** (2 equiv) was added to a THF solution of **1**, the mixture was stirred at −25 °C for 30 min, and **3** was then added to afford 3-acyl-1-alkyl-2-alkylseleno-1-cyclobutene **4** (Scheme 1). The reactions were conducted with various substrates. The results are shown in Table 1.

The structure of **4a** was elucidated by studies of IR, MS, ^{1}H, ^{13}C, and ^{77}SeNMR, COSY, HMQC, and HMBC data and X-ray analysis[9] (Figure 1). The structures of

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(1) (a) Koketsu, M.; Kanoh, M.; Itoh, E.; Ishihara, H. *J. Org. Chem.* **2001**, *66*, 4099. (b) Koketsu, M.; Yang, H. O.; Kim, Y. M.; Ichihashi, M.; Ishihara, H. *Org. Lett.* **2001**, *3*, 1705.
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(9) **Crystal structure data for 4a, $C_{14}H_{14}O_2Se$, and 5a, $C_{16}H_{16}O_2Se$.** Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC No. 236473 for **4a** and CCDC No. 236474 for **5a**. Copies of this information can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44 1233 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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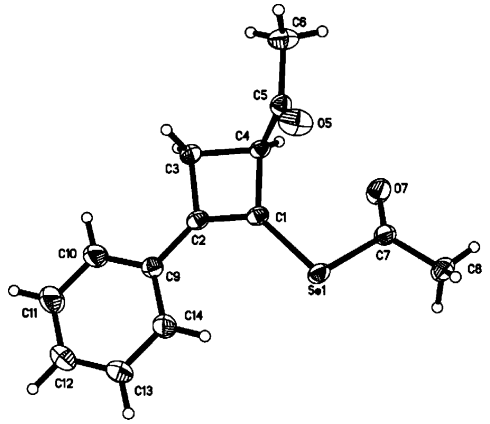
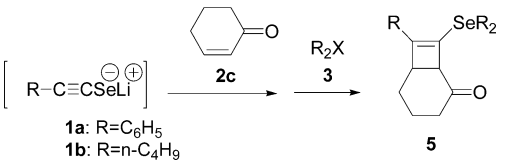


FIGURE 1. X-ray crystal structure of **4a** (ORTEP drawing).

SCHEME 2



products **4b**−**4l** were determined by comparing the spectral data with those of **4a**. In the present reaction, 3-acyl-1-alkyl-2-alkylseleno-1-cyclobutene **4** was obtained as the only product, and neither 3-acyl-2-alkyl-1-alkylseleno-1-cyclobutene nor selenophene was observed. The reaction of **1** with cyclohexenone **2c** also gave a similar product, 8-alkylseleno-7-alkylbicyclo[4.2.0]oct-7-en-2-one **5** (Scheme 2) (Table 2).[9]

The stable product **4** was obtained only when **6** was trapped with alkyl or acyl halide **3**. From these results, formation reaction of **4** could be explained by the addition of the nucleophilic site on ethynylselenolate **1**″ to the most electron-deficient site of α,β-unsaturated ketone **2** (Scheme 3). In the case of the present reaction, the electron pair in the resonance structure **1**″ attacks the β carbon of ketone **2** in a [2 + 2] cycloaddition giving **6** that is quenched with alkyl or acyl halide **3** to afford a single product, 3-acyl-1-alkyl-2-alkylseleno-1-cyclobutene **4**. Reich et al. have reported the regioselectivity of the reaction of allenyllithium and the nature of interaction between the lithium and the carbanionic fragment.[10] According to their results, we speculate that the ethynylselenolate **1** exists as a resonance hybrid between several extreme forms including **1**′, **A**, **B** and **1**″. In the case of the reactions with alkylidenamine, ketene[7] and methyl vinyl ketone **2a**, used in the present reaction, it is believed that delocalized π−electrons of a structure **A** contribute to the attack at the electron-deficient β carbon of ketone **2.** This reaction occurs at the C2 carbon site of **1** and cyclobutene **4** is obtained as the final product.

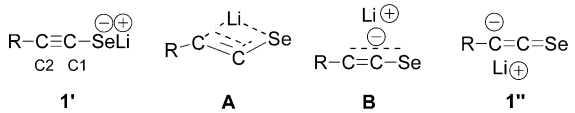


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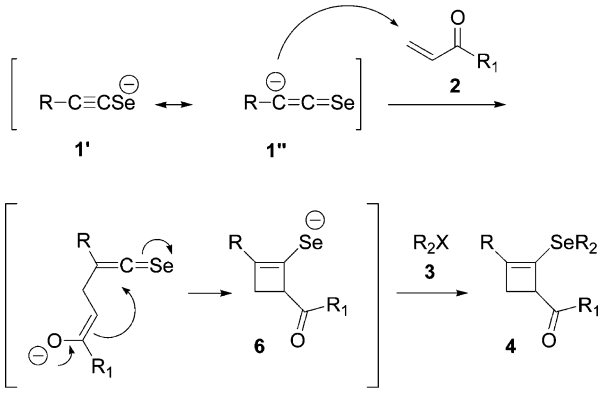
TABLE 2. Synthesis of 8-Alkylseleno-7-alkylbicyclo[4.2.0]oct-7-en-2-ones 5

entry	alkyl or acyl halide (R_2X) **3**		*T* (°C)	time (h)	yield of **5**[a] (%)
1[b]	CH_3COCl	**3a**	−25	1	70 (**5a**)
2[b]	4-$CH_3C_6H_4COCl$	**3b**	−78	2	54 (**5b**)
3[b]	$PhCH_2Br$	**3c**	−25	3	60 (**5c**)
4[b]	CH_3I	**3d**	−25	1	70 (**5d**)
5[b]	CH_3CH_2I	**3e**	−25	1	49 (**5e**)
6[b]	$CH_3(CH_2)_2I$	**3f**	−25	1	43 (**5f**)
7[b]	$CH_3(CH_2)_3I$	**3g**	−25	1	78 (**5g**)
8[c]	CH_3I	**3d**	−40	3	54 (**5h**)

[a] Isolated yield. [b] Phenylacetylene (**1a**) was used. [c] 1-Hexyne (**1b**) was used.

SCHEME 3



The 2-alkylseleno-1-cyclobutene **4** was obtained by the reaction of lithium alkyneselenolate **1** with α,β-unsaturated ketone **2** then alkyl halide **3**. Alkylselenocyclobutene and alkylthiocyclobutene were important molecules as a precursor for the preparation of cyclobutenone.[11] This paper provides not only characterization of 2-alkylseleno-1-cyclobutene **4** but also the preparation method of **4**.

Experimental Section

General Methods. Tetrahydrofuran was distilled from sodium−benzophenone immediately prior to use. The ^{77}Se chemical shifts were expressed in ppm deshielded with respect to neat Me_2Se in $CDCl_3$.

3-Acetyl-2-acetylseleno-1-phenyl-1-cyclobutene 4a. To a THF solution (15 mL) of phenylacetylene (1 mmol) was added *n*-BuLi (1.2 mmol) at 0 °C, and the mixture was stirred for 15 min. Then elemental selenium powder (1 mmol) was added to the mixture. The reaction mixture was warmed to room temperature and stirred for 1 h under argon atmosphere. The obtained lithium alkyneselenoate **1**, formed in situ, was then ready for further reaction. Methyl vinyl ketone **2a** (0.16 mL, 2.0 mmol) was added to the THF solution (15 mL) of **1**. The reaction mixture was stirred at −25 °C for 30 min. Acetyl chloride **3a** (0.07 mL, 1.0 mmol) was added to the reaction mixture. The reaction mixture was stirred at −78 °C for 3 h. The mixture was extracted with diethyl ether and washed with water. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with with diethyl ether/*n*-hexane (1:2) to give **4a** 0.224 g (yield 84%) as white crystals: mp 46.0−47.0 °C; IR (KBr) 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.45 (s, 3H), 3.04 (dd,

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J = 1.8, 12.4 Hz, 1H), 3.24 (dd, J = 5.0, 12.4 Hz, 1H), 4.21 (dd, J = 1.8, 5.0 Hz, 1H), 7.24−7.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 33.4, 34.8, 53.5, 120.6, 126.2, 126.5, 128.5, 133.3, 150.8, 195.3, 207.5; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 587.7; MS (CI) m/z 295 (M^+ + 1), 252 (M^+ − $COCH_3$). Anal. Calcd for $C_{14}H_{14}O_2Se$: C, 57.35; H, 4.81. Found: C, 57.12; H, 4.72.

3-Acetyl-1-phenyl-2-(*p*-toluoylseleno)-1-cyclobutene 4b: yellow solid; mp 72.8−74.0 °C; IR (KBr) 1693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.43 (s, 3H), 3.10 (dd, J = 1.8, 12.4 Hz, 1H), 3.26 (dd, J = 5.1, 12.4 Hz, 1H), 4.34 (dd, J = 1.8, 5.1 Hz, 1H), 7.24−7.78 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 28.9, 34.5, 54.8, 121.6, 127.3, 128.7, 129.5, 129.8, 130.8, 134.5, 136.8, 146.4, 152.7, 192.5, 208.5; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 552.2; MS (EI) m/z 370 (M^+), 251 (M^+ − $COPhCH_3$). Anal. Calcd for $C_{20}H_{18}O_2Se$: C, 65.04; H, 4.81. Found: C, 65.24; H, 4.88.

3-Acetyl-2-benzylseleno-1-phenyl-1-cyclobutene 4c: yellow liquid; IR (neat) 1704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 2.92 (dd, J = 2.0, 12.6 Hz, 1H), 3.08 (dd, J = 5.0, 12.6 Hz, 1H), 3.71 (dd, J = 2.0, 4.8 Hz, 1H), 4.04 (s, 2H), 7.16−7.49 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 29.4, 32.0, 54.4, 124.6, 125.8, 127.2, 128.5, 128.7, 129.0, 133.9, 138.2, 147.7, 208.8; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 319.7; MS (CI) m/z 343 (M^+ + 1), 252 (M^+ − CH_2Ph). Anal. Calcd for $C_{19}H_{18}OSe$: C, 66.86; H, 5.32. Found: C, 66.91; H, 5.33.

3-Acetyl-2-methylseleno-1-phenyl-1-cyclobutene 4d: yellow liquid; IR (neat) 1698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 2.20 (s, 3H), 3.10 (dd, J = 1.8, 12.4 Hz, 1H), 3.10 (dd, J = 5.2, 12.4 Hz, 1H), 3.82 (dd, J = 1.8, 5.2 Hz, 1H), 7.24−7.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.84, 25.6, 31.5, 53.7, 125.4, 127.8, 128.5, 134.1, 145.2, 209.0; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 177.6; MS (CI) m/z 267 (M^+ +1), 251 (M^+ − CH_3), 223 (M^+ − $COCH_3$). Anal. Calcd for $C_{19}H_{18}OSe$: C, 58.87; H, 5.32. Found: C, 58.74; H, 5.41.

3-Acetyl-2-ethylseleno-1-phenyl-1-cyclobutene 4e: yellow liquid; IR (neat) 1699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (t, J = 7.0 Hz, 3H), 2.23 (s, 3H), 2.67−2.93 (m, 3H), 3.14 (dd, J = 4.8, 12.6 Hz, 1H), 3.81 (dd, J = 1.6, 4.8 Hz, 1H), 7.23−7.49 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.4, 19.3, 25.7, 31.7, 54.1, 125.1, 125.6, 128.0, 128.5, 134.1, 146.6, 209.3; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 285.3; MS (EI) m/z 280 (M^+), 251 (M^+ − C_2H_5), 237 (M^+ − $COCH_3$). Anal. Calcd for $C_{14}H_{16}OSe$: C, 60.22; H, 5.78. Found: C, 60.21; H, 5.63.

3-Acetyl-1-phenyl-2-propylseleno-1-cyclobutene 4f: yellow liquid; IR (neat) 1702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.3 Hz, 3H), 1.71 (sixtet, J = 7.3 Hz, 2H), 2.21 (s, 3H), 2.63−2.91 (m, 3H), 3.07 (dd, J = 4.9, 12.5 Hz, 1H), 3.79 (dd, J = 1.8, 4.9 Hz, 1H), 7.22−7.49 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 24.3, 25.7, 27.7, 31.6, 54.1, 125.3, 125.6, 128.0, 128.5, 134.1, 146.3, 209.2; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 251.9; MS (EI) m/z 294 (M^+), 251 (M^+ − C_3H_7). Anal. Calcd for $C_{15}H_{18}$-OSe: C, 61.43; H, 6.19. Found: C, 61.44; H, 6.21.

3-Acetyl-2-butylseleno-1-phenyl-1-cyclobutene 4g: yellow liquid; IR (neat) 1702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3H), 1.41 (sixtet, J = 7.3 Hz, 2H), 1.68 (quintet, J = 7.4 Hz, 2H), 2.22 (s, 3H), 2.66−2.91 (m, 3H), 3.11 (dd, J = 4.9, 12.5 Hz, 1H), 3.80 (dd, J = 1.6, 4.9 Hz, 1H), 7.22−7.49 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 22.8, 25.3, 25.7, 31.6, 33.0, 54.1, 125.4, 125.6, 127.9, 128.5, 134.1, 146.2, 209.2; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 255.4; MS (EI) m/z 308 (M^+), 251 (M^+ − Bu). Anal. Calcd for $C_{16}H_{20}OSe$: C, 62.54; H, 6.56. Found: C, 62.32; H, 6.47.

3-Acetyl-2-isopropylseleno-1-phenyl-1-cyclobutene 4h: yellow liquid; IR (neat) 1700 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, J = 6.8 Hz, 3H), 1.51 (d, J = 6.8 Hz, 3H), 2.24 (s, 3H), 2.96 (dd, J = 2.0, 12.7 Hz, 1H), 3.15 (dd, J = 4.9, 12.7 Hz, 1H), 3.46 (seventet, J = 6.8 Hz, 1H), 3.84 (dd, J = 2.0, 4.9 Hz, 1H), 7.25−7.56 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.1, 26.0, 26.2, 31.9, 33.0, 54.7, 125.1, 125.8, 128.2, 128.4, 134.1, 148.3, 209.2; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 368.4; MS (EI) m/z 294 (M^+), 251 (M^+ − $CH(CH_3)_2$). Anal. Calcd for $C_{15}H_{18}OSe$: C, 61.43; H, 6.19. Found: C, 61.58; H, 6.17.

3-Acetyl-1-butyl-2-methylseleno-1-cyclobutene 4i: yellow oil; IR (neat) 1700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3H), 1.31 (m, 2H), 1.41 (m, 2H), 2.03 (s, 3H), 2.10−2.14 (m, 5H), 2.54 (dd, J = 1.2, 11.5 Hz, 1H), 2.68 (dd, J = 4.9 Hz, 1H), 3.6 (m, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 5.03, 13.9, 22.6, 26.3, 28.9, 29.5, 33.5, 54.4, 123.8, 154.6, 209.4; ^{77}Se NMR (95.4 MHz, $CDCl_3$) δ 120.8; MS (CI) m/z 246 (M^+ + 1); HRMS m/z = 246.0522 calcd for $C_{11}H_{18}OSe$, found 246.0516.

1-Phenyl-3-propionyl-2-(*p*-toluoylseleno)-1-cyclobutene 4j: yellow liquid; IR (neat) 1706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (t, J = 8.3 Hz, 3H), 2.40 (m, 4H), 2.60 (m, 2H), 3.01 (dd, J = 1.8, 12.4 Hz, 1H), 3.12 (dd, J = 5.1, 12.4 Hz, 1H), 4.38 (m, 1H), 7.25−8.01 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.6, 21.7, 33.4, 33.9, 52.8, 120.3, 126.1−130.2, 133.4, 135.8, 144.5, 145.2, 191.5, 210.0; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 552.0; MS (CI) m/z 384 (M^+ + 1). Anal. Calcd for $C_{21}H_{20}O_2Se$: C, 65.80; H, 5.26. Found: C, 65.68; H, 5.31.

2-Benzylseleno-1-phenyl-3-propionyl-1-cyclobutene 4k: yellow liquid; IR (neat) 1703 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J = 7.3 Hz, 3H), 2.52 (m, 2H), 2.91 (dd, J = 1.8, 12.5 Hz, 1H), 3.04 (dd, J = 4.8, 12.5 Hz, 1H), 3.84 (dd, J = 1.8, 4.8 Hz, 1H), 4.02 (s, 2H), 7.25−7.76 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.6, 29.5, 32.1, 32.4, 53.6, 124.4, 125.7, 127.0, 128.0, 128.5, 133.8, 135.8, 136.4, 138.1, 147.8, 210.8; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 316.4; MS (CI) m/z 356 (M^+ + 1). Anal. Calcd for $C_{20}H_{20}OSe$: C, 67.60; H, 5.67. Found: C, 67.43; H, 5.61.

2-Isopropylseleno-1-phenyl-3-propionyl-1-cyclobutene 4l: yellow liquid; IR (neat) 1701 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, J = 6.3 Hz, 3H), 1.46 (m, 6H), 2.61 (m, 2H), 2.98 (m, 1H), 3.10 (m, 1H), 3.43 (m, 1H), 3.85 (dd, J = 1.8, 5.0 Hz, 1H), 7.25−7.55 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.6, 24.2, 26.1, 32.0, 32.2, 33.2, 54.0, 124.9, 125.8, 128.1, 128.3, 143.6, 212.3; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 368.4; MS (CI) m/z 308 (M^+ + 1). Anal. Calcd for $C_{16}H_{20}OSe$: C, 62.54; H, 6.56. Found: C, 62.81; H, 6.44.

8-Acetylseleno-7-phenylbicyclo[4.2.0]oct-7-en-2-one 5a: yellow solid; mp 97.2−97.5 °C; IR (KBr) 1693, 1720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65−1.83 (m, 2H), 1.97−2.03 (m, 1H), 2.12−2.24 (m, 2H), 2.43 (s, 3H), 2.62−2.69 (m, 1H), 3.66 (d, J = 4.0 Hz, 1H), 3.93 (m, 1H), 7.30−7.58 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 24.7, 34.4, 40.3, 42.5, 55.2, 118.1, 126.3, 128.3, 128.9, 131.9, 157.1, 194.6, 208.8; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 578.2; MS (CI) m/z 321 (M^+ +1). Anal. Calcd for $C_{16}H_{16}O_2Se$: C, 60.19; H, 5.05. Found: C, 60.33; H, 5.12.

7-Phenyl-8-(*p*-toluoylseleno)bicyclo[4.2.0]oct-7-en-2-one 5b: yellow solid; mp 95.0−95.5 °C; IR (KBr) 1689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66−1.87 (m, 2H), 2.10−2.03 (m, 3H), 2.44 (s, 3H), 2.74 (d, J = 16.8 Hz, 1H), 3.76 (d, J = 4.0 Hz, 1H), 4.00 (brs, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.28−7.39 (m, 3H), 7.58 (d, J = 7.9 Hz, 2H), 7.76 (d, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 21.6, 24.9, 40.5, 42.8, 55.7, 118.0, 126.5, 126.8, 128.0, 128.4, 129.0, 129.4, 132.2, 145.0, 158.5, 191.2, 209.2; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 543.6; MS (CI) m/z 397 (M^+ +1), 279. Anal. Calcd for $C_{22}H_{20}O_2Se$: C, 66.84; H, 5.10. Found: C, 66.98; H, 5.24.

8-Benzylseleno-7-phenylbicyclo[4.2.0]oct-7-en-2-one 5c: yellow solid; mp 86.5−86.8 °C; IR (KBr) 1690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66−1.87 (m, 3H), 2.13−2.23 (m, 2H), 2.53 (dd, J = 4.0, 18.7 Hz, 1H), 3.71 (d, J = 4.4 Hz, 1H), 3.78 (d, J = 4.4 Hz, 1H), 4.27 (s, 2H), 7.18−7.44 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 24.9, 29.1, 40.3, 41.5, 55.1, 123.7, 126.1, 126.9, 127.8, 128.4, 128.5, 129.0, 133.0, 138.2, 148.9, 210.7; ^{77}-Se NMR (76.2 MHz, $CDCl_3$) δ 312.3; MS (CI) m/z 369 (M^+ + 1), 279. Anal. Calcd for $C_{21}H_{20}OSe$: C, 68.66; H, 5.49. Found: C, 68.53; H, 5.53.

8-Methylseleno-7-phenylbicyclo[4.2.0]oct-7-en-2-one 5d: yellow solid; mp 81.0−81.5 °C; IR (KBr) 1692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61−1.73 (m, 2H), 1.76−1.89 (m, 1H), 2.13−2.28 (m, 2H), 2.30 (s, 3H), 2.61 (dd, J = 4.0, 10.1 Hz, 1H), 3.69 (d, J = 4.0 Hz, 1H), 3.75 (d, J = 4.0 Hz, 1H), 7.25−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.1, 17.5, 24.7, 39.9, 41.1, 54.4, 123.7, 125.6, 127.5, 128.4, 133.0, 147.8, 210.6; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 169.6; MS (CI) m/z 293 (M^+ + 1), 279. Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 61.63; H, 5.42.

8-Ethylseleno-7-phenylbicyclo[4.2.0]oct-7-en-2-one 5e: yellow solid; mp 82.5−84.1 °C; IR (KBr) 1693 cm^{-1}; ^{1}H NMR (400

MHz, $CDCl_3$) δ 1.42 (t, $J = 7.3$ Hz, 3H), 1.63−1.77 (m, 2H), 1.78−1.92 (m, 1H), 2.13−2.28 (m, 2H), 2.60 (dd, $J = 4.4$, 21.1 Hz, 1H), 2.84−2.93 (m, 1H), 3.01−3.14 (m, 1H), 3.68 (d, $J = 4.0$ Hz, 1H), 3.80 (d, $J = 4.0$ Hz, 1H), 7.25−7.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 17.6, 19.2, 24.8, 40.0, 41.4, 54.9, 123.5, 125.9, 127.7, 128.4, 133.1, 148.8, 210.7; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 279.9; MS (CI) *m/z* 307 (M^+ 1), 279. Anal. Calcd for $C_{16}H_{18}OSe$: C, 62.95; H, 5.94. Found: C, 62.07; H, 5.67.

7-Phenyl-8-propylselenobicyclo[4.2.0]oct-7-en-2-one 5f: yellow solid; mp 85.0−85.5 °C; IR (KBr) 1692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, $J = 7.3$ Hz, 3H), 1.63−1.78 (m, 4H), 1.78−1.92 (m, 1H), 2.15−2.27 (m, 2H), 2.60 (dd, $J = 4.4$, 10.1 Hz, 1H), 2.82−2.88 (m, 1H), 3.05−3.12 (m, 1H), 3.67 (d, $J = 4.4$ Hz, 1H), 3.78 (d, $J = 4.4$ Hz, 1H), 7.25−7.45 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 17.6, 24.3, 24.8, 27.6, 39.9, 41.4, 55.0, 123.7, 125.8, 127.6, 128.4, 133.2, 148.6, 210.8; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 247.0; MS (CI) *m/z* 321 ($M^+ + 1$), 279. Anal. Calcd for $C_{17}H_{20}OSe$: C, 63.95; H, 6.31. Found: C, 63.78; H, 6.22.

8-Butylseleno-7-phenylbicyclo[4.2.0]oct-7-en-2-one 5g: yellow solid; mp 85.0−85.5 °C; IR (KBr) 1691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, $J = 7.3$ Hz, 3H), 1.38−1.44 (sextet, $J = 7.3$ Hz, 2H), 1.63−1.75 (m, 4H), 1.81−1.88 (m, 1H), 2.17−2.27 (m, 2H), 2.61 (dd, $J = 5.4$, 9.0 Hz, 1H), 2.85−2.92 (m, 1H), 3.06−3.13 (m, 1H), 3.67 (d, $J = 4.4$ Hz, 1H), 3.79 (d, $J = 4.4$ Hz, 1H), 7.26−7.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 17.6, 22.7, 24.8, 25.3, 33.0, 40.0, 41.4, 55.0, 123.8, 125.9, 127.7, 128.5, 133.2, 148.6, 210.9; ^{77}Se NMR (76.2 MHz, $CDCl_3$) δ 249.8; MS (CI) *m/z* 335 ($M^+ + 1$), 279. Anal. Calcd for $C_{18}H_{22}OSe$: C, 64.86; H, 6.65. Found: C, 64.92; H, 6.48.

7-Butyl-8-methylselenobicyclo[4.2.0]oct-7-en-2-one 5h: yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, $J = 7.4$ Hz, 3H), 1.31 (m, 2H), 1.43 (m, 2H), 1.58 (m, 1H), 1.70 (m, 1H), 1.80 (m, 1H), 1.90 (m, 1H), 1.99 (m, 1H), 2.08−2.16 (m, 5H), 2.53 (dd, $J = 1.2$ Hz, 5.1 Hz, 1H), 3.27 (m, 1H), 3.44 (m, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 4.87, 13.9, 17.9, 22.9, 24.7, 28.2, 28.8, 40.0, 42.6, 55.0, 122.0, 155.8, 211.3; ^{77}Se NMR(95.4 MHz, $CDCl_3$) δ 155.8; MS (CI) *m/z* 273 ($M^+ + 1$); HRMS *m/z* 272.0679, calcd for $C_{13}H_{20}OSe$, found 272.0695.

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Supporting Information Available: Complete tables of crystallographic data, structure-refinement parameters, final atomic coordinates and equivalent isotropic thermal parameters, bond distances, bond angles, torsion angles, and ORTEP figures of **4a** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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