138. On the *Claisen* Rearrangement of Allyl Ethyl Ketene Acetals Generated *in situ via* Benzeneselenenic Acid Elimination

by **Rita Pitteloud** and **Martin Petrzilka**

Département de Chimie Organique, Université de Genève, CH-1211 Genève 4

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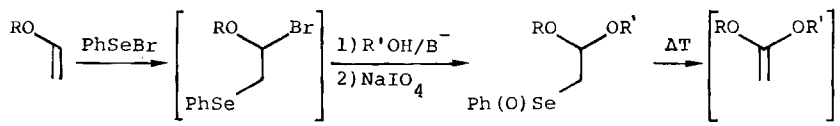
Summary

Mixed acetals 7 of benzeneseleninylacetaldehyde, prepared by a simple 2-step procedure from mono- and bicyclic allylic alcohols **5**, undergo benzeneselenenic acid elimination to transient ketene acetals **8** which afford γ,δ-unsaturated esters **9** *via* the ester *Claisen* rearrangement *(Scheme 2)*. Under the same conditions selenoxide **7h** derived from benzyl alcohol **5h** is converted back to benzyl alcohol with the concomitant formation of ethylphenylselenoacetate **12**.

The remarkable potential of the *Claisen* rearrangement lies in the generation of 2 functional groups of different reactivity in a stereo- and regiospecific manner with the additional possibility of selectively creating a desired configuration about the newly formed C–C single bond [1]. The central problem in devising new variants of this useful synthetic method consists in connecting an allylic alcohol[1]) with a carbonyl enol equivalent in a simple and direct manner. In this context we have recently contributed one solution, which led to the efficient preparation of acyclic γ,δ-unsaturated acids [3] and, when carried out intramolecularly, provided a new method for the construction of macrolides [4]. The introduction of the required ketene acetal part into the putative rearrangement precursors is summarized in *Scheme 1*.

Scheme 1



1 **2** **3** **4**

We now report the application of this new 3-step procedure to a series of mono- and bicyclic allylic alcohols. Consequently we have chosen examples to cover a wide range of carbocyclic ring systems; 1–3 carbon atoms of the allyl alcohol unit are always part of a 5- or 6-membered ring, *i.e.* in all examples 2 of the 5 substituents R^1 to R^5 in **5** *(Scheme 2)* are connected to each other.

[1]) For a recent variation which starts from allylic ethers, see [2].

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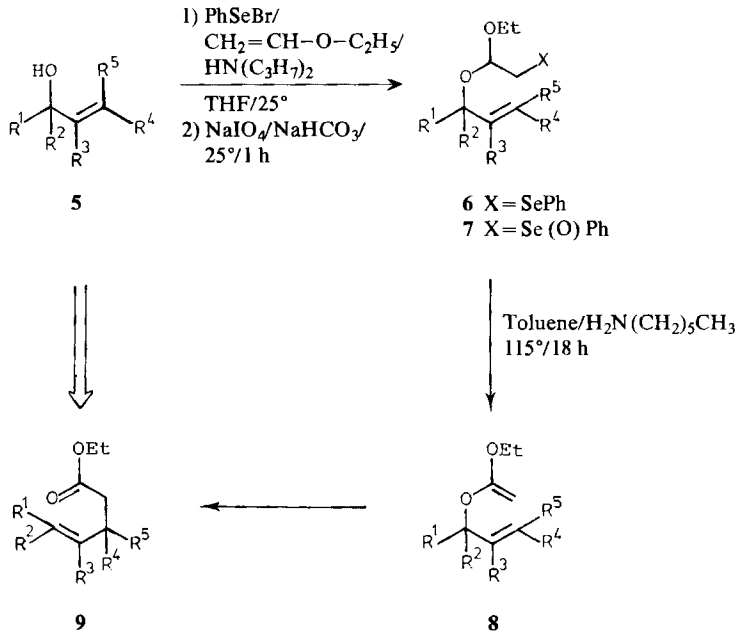
Scheme 2



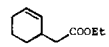
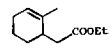
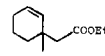
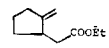
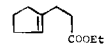
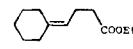
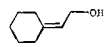
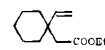
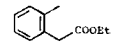
5

6 X = SePh
7 X = Se (O) Ph

9

8

Table 1

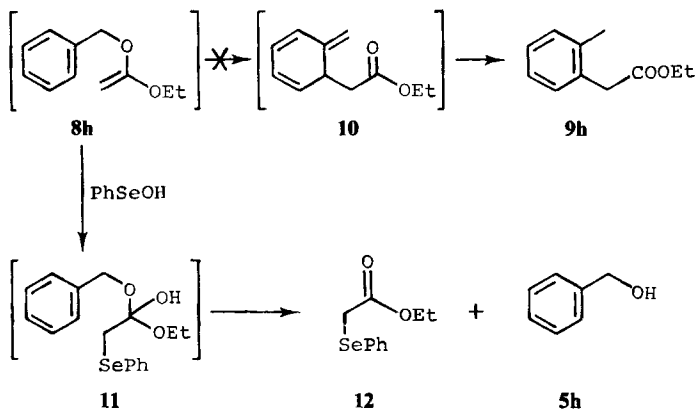
Allylic alcohol		Selenide	Yield[a])	Ethyl ester		Yield[a])[b])
5a		**6a**	91%	**9a**		86%
5b		**6b**	95%	**9b**		78%
5c		**6c**	92%	**9c**		80%
5d		**6d**	98%	**9d**		95%
5e		**6e**	98%	**9e**		97%
5f		**6f**	86%	**9f**		95%
5g		**6g**	90%	**9g**		91%
5h		**6h**	98%	**9h**		0%

[a]) Yields refer to isolated products purified by column chromatography and are not optimized.
[b]) Based on selenides **6**.

Under the conditions described previously [3] (see also experimental part), the allylic alcohols **5a–5g** were cleanly converted to the corresponding γ,δ-unsaturated ethyl esters **9a–9g** in high overall yields *(Table 1)*. The formation of dienic elimination products was not observed[2]). Primary (**5d**, **5g**) secondary (**5a**, **5b**, **5c**, **5e**) and even tertiary (**5f**) allylic alcohols undergo the rearrangement with remarkable ease and the specific substitution pattern of the allylic double bond (*cf.* **5a**, **5b**, **5c**) does not significantly influence the course of the reaction. However, attempted rearrangement of the ketene acetal **8h** derived from benzyl alcohol **5h** deserves special mention. Although the corresponding selenide **6h** and selenoxide **7h** could be prepared in almost quantitative yield, thermolysis of the latter using our standard conditions gave predominantly benzyl alcohol **5h** and ethyl phenylselenoacetate **12** (IR. (CCl_4): 1732 cm^{-1}. – ^{1}H-NMR. ($CDCl_3$): 3.51 (*s*, 2 H). – MS.: 244 and 242 ($C_{10}H_{12}O_2Se^+$)) and none of the desired ethyl *o*-tolylacetate **9h** *(Scheme 3)*[3]).

The formation of **5h** and **12** can be rationalized by the re-addition of benzeneselenenic acid, formed *in situ*, to the enol ether double bond, followed by elimination of benzyl alcohol **5h** from the intermediate **11**[4]). As we have not yet found an effective trapping agent for this very weakly acidic by-product of the selenoxide *syn*-elimination, the reasons for the non-occurrence of the *Claisen* rearrangement of the ketene acetal **8h** (apparently formed *in situ*) are not obvious. Owing to a possibly higher activation energy barrier (formation of a dearomatized intermediate **10**) the rearrangement of **8h** to **9h** might either be no longer favored or may not occur at all at this temperature. Alternatively free-radical processes might be involved as reported previously[3]).

Scheme 3



8h **10** **9h**

11 **12** **5h**

[2]) The ketene acetals **8** of allylic alcohols incorporating all 3 carbon atoms of the allylic unit in the same ring (*e.g.* **5a**, **5b**, **5c**, **5i**, **5k**, **5l**) would be especially prone to this side reaction. For leading references see [1b] [5] [6].

[3]) The difficulties encountered with the [3,3]-sigmatropic rearrangement of benzyl vinyl ether type systems are numerous, see [10] and references cited therein; for 2 notable exceptions see [11] [12].

[4]) For a mechanistically related case see [7]. The addition of benzeneselenenic acid to olefins has been extensively studied by *Sharpless* [8] and *Reich* [9].

Table 2

Allylic alcohol		Selenide	Yield[a])	Ethyl ester		Yield[a])[b])
5i		**6i**	93%	**9i**		92%
5k[c])		**6k**	99%	**9k**		74%[d])
5l[c])		**6l**		**9l**		

[a]) Yields refer to isolated products purified by column chromatography and are not optimized.
[b]) Based on selenides **6**. [c]) **5k/5l** ≅ 10:1. [d]) **9k/9l** ≅ 10:1.

Finally, the continued need for methods for the stereoselective angular functionalization of polycyclic ring systems[5]) led us to examine some suitably constituted bicyclic allylic alcohols (**5i**, **5k/5l** *(Table 2)*).

Under the usual conditions the corresponding γ,δ-unsaturated ethyl esters **9i**[6]) and **9k/9l** [5] were formed in equally high overall yields. Although starting from an epimeric mixture of **5k** and **5l** (β-OH/α-OH ≅ 10:1) the stereospecific course of the rearrangement for the single isomers is strongly indicated by GC. analysis of the resulting mixture of esters **9k** and **9l**, which showed the same relative amounts of epimers.

The present communication further demonstrates the synthetic value of this new version of the ester *Claisen* rearrangement. With regard to other existing procedures effecting the same type of transformation (*cf.* [1]) its noteworthy features are: 1) none of the reaction partners has to be used in large excess; moreover, the only expensive reagent, benzeneselenenyl bromide,[7]) may be recycled; 2) the reaction conditions (weakly basic throughout the whole sequence) are compatible with a wide array of functional groups; 3) during the course of a more complex synthesis, an allylic alcohol moiety may be protected as a stable, masked ketene acetal prior to rearrangement at a later stage; 4) in general overall yields are high and often superior to those obtained using other variations; 5) the procedure may be applied intramolecularly and thus offers a new method for the construction of macrolides (see [4]); 6) the whole reaction sequence may be carried out conveniently without purification of the intermediates **7** and **8**.

We thank Dr. *R.L. Snowden, Firmenich SA*, for helpful comments and suggestions on the manuscript and Mr. *J.-P. Saulnier* and Mrs. *F. Klöti* for careful ^{1}H-NMR. and mass spectra measurements.

5) For the use of the *Claisen* rearrangement in this connection see [5] [6] [13].
6) The corresponding aldehyde has been prepared previously in 30% overall yield *via* the *Claisen* rearrangement of vinylated **5i** [6].
7) Our preferred mode of preparation and purification of this reagent is described in the experimental part.

Experimental Part

General remarks. All reactions were carried out under argon. The IR. spectra (CCl_4) are given in cm^{-1}. The chemical shifts in ^{1}H-NMR. spectra (100 MHz, $CDCl_3$) are given in ppm relative to tetramethylsilane as internal standard ($\delta = 0$). Multiplicities are expressed as singlet (*s*), doublet (*d*), triplet (*t*), quartet (*qa*), multiplet (*m*), doublet of doublet ($d \times d$), *etc.* Spin-spin coupling constants (J) are given in Hertz (Hz). Aluminium oxide 90 *Merck* (activity II-III) and silica gel PF_{254} *Merck* (0.05–0.20 mm) were used for preparative chromatography. Gas chromatography (GC.) on steel columns (3 mm, stationary phase on Chromosorb W, 2.5 atm. N_2; column A: 3% KOH, 15% Carbowax, 2 m; column B: 5% OV 225, 4 m); retention time in min. Abbreviation: br. broad, THF tetrahydrofuran.

Preparation of the starting materials. The allylic alcohols **5a–5d**, **5e** [14], **5g**, **5i** and **5k/5l**[8]) were obtained by $LiAlH_4$ reduction (ether, 0°) of 2-cyclohexen-1-one (*Fluka* pract.), 2-methyl-2-cyclohexen-1-one [15], 3-methyl-2-cyclohexen-1-one *(Aldrich)*, 1-cyclopentenylcarboxaldehyde [16], 2-carboethoxycyclopentanone (*Fluka* purum), ethyl cyclohexylideneacetate [17], $\Delta^{9,10}$-octal-1-one [18][9]) and 10-methyl-$\Delta^{1,9}$-2-octalone [20][9]), respectively. 1-Vinylcyclohexanol **5f** resulted from the addition of vinylmagnesium bromide [19] to cyclohexanone (THF, 10°).

Preparation of benzeneselenenyl bromide. To a vigorously stirred solution of 19.7 g (63 mmol) of diphenyldiselenide (*Fluka* pract.) in 120 ml of dry CCl_4 kept at 25° was added a solution of 2.95 ml (57 mmol) of bromine in 60 ml of dry CCl_4 over a period of 1 h. The dark red-orange reaction mixture was stirred for an additional hour before the solvent was carefully removed under reduced pressure. The remaining red solid (m.p. 50–54°) was subsequently sublimed (25°/0.001 mm) to afford 25.4 g (95%) of dark red crystals, m.p. 57–58°.

General procedure for the preparation of selenides **6**. To a vigorously stirred solution of benzeneselenenyl bromide (1.5 equiv.) in dry THF (7 ml/mmol of **5**) at 25° was added at once neat ethyl vinyl ether (1.65 equiv., *Fluka* purum) immediately followed by a solution of the appropriate allylic alcohol **5a–l** and diisopropylamine (1.65 equiv.) in dry THF (2 ml/mmol of **5**). During this operation the initially dark orange color turned to clear yellow and then a voluminous white precipitate was quickly formed. After stirring an additional 10 min the reaction mixture was poured into aq. $NaHCO_3$-solution and extracted with ether (3×). The organic layers were washed with water (1×) and brine (1×), dried over K_2CO_3 and concentrated *in vacuo*. The remaining yellow oil was chromatographed on alumina activity III (50–70 g/g of crude product) with hexane (*ca.* 34 mg of diphenyldiselenide recovered/mmol of **5**) and hexane/ether 8:1 to afford the pure selenides **6a–l** in the indicated yields (see also *Tables*). For the following transformations (**6**→**7**→**9**) this last purification step may be conveniently omitted if no analytically pure samples of the selenides **6** are required.

Selenide **6a** *from 2-cyclohexen-1-ol* **5a**. Yield 91%. – IR.: 3050, 3020, 1480, 1115, 1050, 1025, 698, 675. – ^{1}H-NMR.: 1.19 (*t*, $J = 7$, 3 H); 1.41–2.16 (br. *m*, 6 H); 3.14 (*d*, $J = 6$, 2 H); 3.43–3.82 (br. *m*, 2 H); 4.04–4.30 (*m*, 1H); 4.88 (*t*, $J = 6$, 1H); 5.62–6.02 (*m*, 2 H); 7.16–7.72 (*m*, 5 H). – MS.: 326 and 324 (M^+), 274, 252, 229, 200, 183, 171, 157, 103 (100%), 95, 91, 81, 75 ($C_{16}H_{22}O_2Se$).

Selenide **6b** *from 2-methyl-2-cyclohexen-1-ol* **5b**. Yield 95%. – IR.: 3050, 1480, 1380, 1440, 1190, 1105, 950, 687, 668. – ^{1}H-NMR.: 1.20 (*t*, $J = 7$, 3 H); 1.38–2.18 (br. *m* with *s* at 1.78, 9 H); 3.04–3.30 (*m*, 2 H); 3.40–4.08 (br. *m*, 3 H); 4.72–4.98 (*m*, 1H); 5.52–5.73 (*m*, 1H). – MS.: 340 and 338 (M^+), 274, 229, 183, 171, 157, 103 (100%), 95, 91, 75 ($C_{17}H_{24}O_2Se$).

Selenide **6c** *from 3-methyl-2-cyclohexen-1-ol* **5c**. Yield 92%. – IR.: 3060, 1675, 1580, 1480, 1440, 1380, 1340, 1105, 1020, 950, 910, 689. – ^{1}H-NMR.: 1.19 (*t*, $J = 7$, 3 H); 1.45–2.20 (*m* with *s* at 1.70, 9 H); 3.14 (*d*, $J = 6$, 2 H); 3.44–3.80 (*m*, 2 H); 4.02–4.28 (*m*, 1H); 4.88 (*t*, $J = 6$, 1H); 5.42–5.62 (*m*, 1H); 7.18–7.72 (*m*, 5 H). – MS.: 340 and 338 (M^+), 274, 266, 229, 200, 183, 172, 157, 109, 103, 95 (100%), 91, 75 ($C_{17}H_{24}O_2Se$).

Selenide **6d** *from 1-cyclopentenylmethanol* **5d**. Yield 98%. – IR.: 3050, 1580, 1480, 1440, 1370, 1340, 1115, 1050, 688. – ^{1}H-NMR.: 1.20 (*t*, $J = 7$, 3 H); 1.70–2.06 (*m*, 2 H); 2.20–2.48 (tripletoid *m*, 4 H); 3.15 (*d*, $J = 6$, 2 H); 3.38–3.86 (*m*, 2 H); 4.15 (br. *s*, 2 H); 4.80 (*t*, $J = 6$, 1H); 5.67 (br. *s*, 1H); 7.18–7.66 (*m*, 5 H). – MS.: 326 and 324 (M^+), 281, 252, 229, 200, 183, 171, 157, 103, 95, 91, 81 (100%) ($C_{16}H_{22}O_2Se$).

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[8]) GC. analysis (column A/170°) showed 91% β-alcohol (retention time 11.2) and 9% α-alcohol (retention time 9.6).

[9]) We thank Dr. *F. Näf* and Dr. *S. Escher, Firmenich SA*, for a generous supply of 1-decalone and 10-methyl-$\Delta^{1,9}$-2-octalone, respectively.

Selenide **6e** *from 2-methylidenecyclopentanol* **5e**. Yield 98%. – IR.: 3060, 1580, 1480, 1440, 1380, 1345, 1115, 910, 698. – ^{1}H-NMR.: 1.20 (*t* with fine splitting, $J=7$, 3 H); 1.44–2.66 (br. *m*, 6 H); 3.14 (*d* with fine splitting, $J=6$, 2 H); 3.42–3.82 (*m*, 2 H); 4.22–4.48 (*m*, 1H); 4.78–4.98 (*m*, 1H); 4.98–5.22 (doubletoid *m*, 2 H); 7.12–7.70 (*m*, 5 H). – MS.: 326 and 324 (M^+), 274, 252, 229, 200, 183, 171, 157, 103, 95, 91, 81 (100%) ($C_{16}H_{22}O_2Se$).

Selenide **6f** *from 1-vinylcyclohexanol* **5f**[10]. Yield 86%. – IR.: 3050, 1480, 1105, 1008, 955, 930, 698. – ^{1}H-NMR.[11]): 1.02–2.04 (br. *m*, 10 H); 1.14 (*t*, $J=7$, 3 H); 3.05 (δ_B), 3.13 (δ_A) and 4.80 (δ_M) (*ABM*-system, $J_{AB}=12.19$, $J_{AM}=5.59$, $J_{BM}=5.59$, 3 H of the acetal unit); 3.51 (*qa*, $J=7$, 2 H); 5.18 (δ_B), 5.20 (δ_A) and 5.83 (δ_M) (complex *ABM*-system, $J_{AB}=1.19$, $J_{AM}=11.59$, $J_{BM}=17.00$, 3 H of the vinyl group); 7.16–7.72 (*m*, 5 H). – MS.: 354 and 352 (M^+), 280, 229, 183, 172, 157, 123, 109 (100%), 91, 81, 67, 55 ($C_{18}H_{26}O_2Se$).

Selenide **6g** *from 2-cyclohexylidene-ethanol* **5g**. Yield 90%. – IR.: 3050, 1668, 1580, 1480, 1440, 1370, 1338, 1110, 1025, 688. – ^{1}H-NMR.: 1.20 (*t*, $J=7$, 3 H); 1.42–1.72 (br. *s*, 6 H); 2.00–2.34 (*m*, 4 H); 3.14 (*d*, $J=6$, 2 H); 3.40–3.86 (*m*, 2 H); 4.12 (*d*, $J=7$, 2 H); 4.78 (*t*, $J=6$, 1H); 5.20–5.42 (tripletoid *m*, 1H); 7.18–7.70 (*m*, 5 H). – MS.: 354 and 352 (M^+), 314, 280, 274, 229, 183, 171, 157, 123, 109, 103 (100%), 91, 81, 75, 67 ($C_{18}H_{26}O_2Se$).

Selenide **6h** *from benzyl alcohol* **5h**. Yield 98%. – IR.: 3050, 3020, 1480, 1345, 1120, 1050, 1025, 698. – ^{1}H-NMR.: 1.13 (*t*, $J=7$, 3 H); 3.06 (*d*, $J=6$, 2 H); 3.37–3.74 (*m*, 2 H); 4.40–4.67 (*AB*-system, $J_{AB}=11.5$, 2 H); 4.76 (*t*, $J=6$, 1H); 7.06–7.60 (*m*, 5 H). – MS.: 336 and 334 (M^+), 291, 262, 229, 183, 171, 165, 105, 91 (100%) ($C_{17}H_{20}O_2Se$).

Selenide **6i** *from* $\Delta^{9,10}$*-octal-1-ol* (**5i**). Yield 93%. – IR.: 3050, 1580, 1480, 1445, 1350, 1325, 1105, 950, 699, 678. – ^{1}H-NMR.: 1.19 (*t*, $J=7$, 3 H); 1.36–2.60 (br. *m*, 14 H); 3.04–3.28 (doubletoid *m*, 2 H); 3.52–3.80 (quartetoid *m*, 2 H); 3.90 (br. *s*, 1H); 4.72–4.94 (*m*, 1H); 7.16–7.70 (*m*, 5 H). – MS.: 380 and 378 (M^+), 306, 274, 229, 200, 183, 171, 149, 135 (100%), 103, 91, 75 ($C_{20}H_{28}O_2Se$).

Selenides **6k/6l** *from 10-methyl-*$\Delta^{1,9}$*-octal-2-ol* (**5k/5l**)[12]. Yield 99%. – IR.: 3060, 1660, 1580, 1480, 1440, 1055, 689. – ^{1}H-NMR.: 0.80–2.42 (br. *m*, 12 H); 1.03 and 1.11 (2 *s*, 3 H, methyl group of **6l** and **6k**, respectively); 1.19 (*t*, $J=7$, 3 H); 3.14 (*d*, $J=6$, 2 H); 3.42–3.80 (*m*, 2 H); 3.96–4.32 (br. *m*, 1H); 4.65–4.99 (2 tripletoid *m*, 1H); 5.25–5.50 (*m*, 1H); 7.08–7.74 (*m*, 5 H). – MS.: 394 and 392 (M^+), 274, 229, 228, 214, 183, 171, 163, 157, 155, 149, 103, 91 (100%), 75 ($C_{21}H_{30}O_2Se$).

General procedure for the preparation of the γ,δ*-unsaturated esters* **9**. To a well stirred solution of the selenides **6a–l** in MeOH/H_2O 6:1 (30 ml/mmol of **6**) was added solid $NaHCO_3$ (1.1 equiv.) and sodium metaperiodate (1.5 equiv.). A thick white precipitate was rapidly formed. After stirring for 1 h the reaction mixture was poured into water and extracted with CH_2Cl_2 (3×). The organic layers were washed with brine (1×), dried over K_2CO_3 and concentrated *in vacuo* to give the selenoxides **7a–l** as colorless viscous oils in almost quantitative yields. A mixture of crude **7a–l** and hexylamine (3 equiv.) in dry toluene (10 ml/mmol of **7**) was heated under reflux for 18 h. During this time the formation of diphenyldiselenide results in a dark yellow color[13]. The solvent and excess hexylamine was removed at reduced pressure and the remaining oil was chromatographed on silica gel (15 g/300 mg of crude product) with benzene or toluene to afford diphenyldiselenide (*ca.* 90 mg/mmol of **7**)[14] and the pure γ,δ-unsaturated ethyl esters **9a–l**[15] in the indicated yields (see also *Tables*).

Ethyl 2-cyclohexenylacetate **9a** *from* **6a**. Yield 86%. – IR.: 3010, 1738, 1370, 1160, 1032. – ^{1}H-NMR.: 1.07–2.14 (br. *m*, 6 H); 1.26 (*t*, $J=7.5$, 3 H); 2.23–2.39 (*m*, 2 H); 2.43–2.80 (br. *m*, 1H); 4.17 (*qa*, $J=7.5$, 2 H); 5.48–5.88 (*m*, 2 H). – MS.: 168 (M^+), 139, 123, 122, 97, 95, 94, 93, 89, 88, 81, 80 (100%), 79, 67, 61 ($C_{10}H_{16}O_2$).

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[10]) The reaction was carried out in dry benzene instead of THF.

[11]) We are indebted to Dr. *U. Burger* for simulating this spectrum.

[12]) The reaction was carried out on an epimeric mixture (**5k/5l** ≅10:1, see footnote 8). According to ^{1}H-NMR. analysis a similar isomer distribution is found for **6k/6l**.

[13]) Disproportionation of benzeneselenenic acid to diphenyldiselenide and benzeneseleninic acid is a known process; for a leading reference see [9].

[14]) One third of the benzeneselenenic acid, which is oxidized to benzeneseleninic acid (see footnote 10), is presumably trapped by hexylamine.

[15]) Selenoxide **7h** does not give ethyl *o*-tolylacetate **9h** under these conditions; see theoretical part.

Ethyl 2-methyl-2-cyclohexenylacetate **9b** *from* **6b**. Yield 78%. – IR.: 1739, 1370, 1280, 1172, 1032. – ^{1}H-NMR.: 1.27 (*t*, *J*=7, 3 H); 1.38–2.70 (br. *m*, 12 H); 4.18 (*qa*, *J*=7, 2 H); 5.39–5.62 (*m*, 1H). – MS.: 182 (M^+), 153, 137, 136, 108, 94 (100%), 79, 67, 61, 55 ($C_{11}H_{18}O_2$).

Ethyl 1-methyl-2-cyclohexenylacetate **9c** *from* **6c**. Yield 80%. – IR.: 1735, 1370, 1320, 1240, 1160, 1096, 1037. – ^{1}H-NMR.: 1.10 (*s*, 3 H); 1.25 (*t*, *J*=7, 3 H); 1.48–2.12 (br. *m*, 6 H); 2.28 (*s*, 2 H); 4.14 (*qa*, *J*=7, 2 H); 5.44–5.78 (*m*, 2 H). – MS.: 182 (M^+), 167, 153, 136, 121, 108, 95 (100%), 94, 79, 67, 61, 55 ($C_{11}H_{18}O_2$).

Ethyl 2-methylidenecyclopentylacetate **9d** *from* **6d**. Yield 95%. – IR.: 3070, 1740, 1660, 1370, 1168, 1031, 880. – ^{1}H-NMR.: 1.10–3.04 (br. *m*, 9 H); 1.27 (*t*, *J*=7, 3 H); 4.17 (*qa*, *J*=7, 2 H); 4.81 (*qa*, *J*=2, 1 H); 4.92 (*qa*, *J*=2, 1 H). – MS.: 168 (M^+), 139, 123, 94 (100%), 81, 79 ($C_{10}H_{16}O_2$).

Ethyl 3-(1-cyclopentenyl)propionate **9e** *from* **6e**. Yield 97%. – IR.: 3040, 1730, 1655, 1378, 1340, 1305, 1043, 943, 861. – ^{1}H-NMR.: 1.26 (*t*, *J*=7, 3 H); 1.62–2.66 (br. *m*, 10 H); 4.16 (*qa*, *J*=7, 2 H); 5.38 (br. *s*, 1H). – MS.: 168 (M^+), 139, 122, 94, 81, 79 (100%), 67 ($C_{10}H_{16}O_2$).

Ethyl 4-cyclohexylidenebutyrate **9f** *from* **6f**. Yield 95%. – IR.: 1730, 1450, 1375, 1350, 1160, 1040, 940. – ^{1}H-NMR.: 1.08–1.76 (*m*, 6 H); 1.25 (*t*, *J*=7, 3 H); 1.90–2.50 (*m*, 8 H); 4.15 (*qa*, *J*=7, 2 H); 4.90–5.22 (*m*, 1H). – MS.: 196 (M^+), 150, 132, 122, 108 (100%), 101, 91, 81, 79, 67, 61, 55 ($C_{12}H_{20}O$).

Ethyl 1-vinylcyclohexylacetate **9g** *from* **6g**. Yield 91%. – IR.: 3070, 1735, 1640, 1370, 1215, 1155, 1130, 1035, 1000, 915. – ^{1}H-NMR.: 1.24 (*t*, *J*=7, 3 H); 1.20–1.82 (br. *m*, 10 H); 2.32 (*s*, 2 H); 4.12 (*qa*, *J*=7, 2 H); 5.04 (*d*×*d*, *J*=18 and 1.5, 1H); 5.13 (*d*×*d*, *J*=11 and 1.5, 1H); 5.84 (*d*×*d*, *J*=18 and 11, 1H). – MS.: 196 (M^+), 167, 150, 122, 109 (100%), 108, 93, 88, 81, 79, 67 ($C_{12}H_{20}O_2$).

Ethyl $\Delta^{4,10}$*-9-octalylacetate* **9i** *from* **6i**. Yield 92%. – IR.: 1720, 1370, 1315, 1290, 1090, 1000, 945. – ^{1}H-NMR.: 1.00–2.30 (br. *m*, 14 H); 1.26 (*t*, *J*=7, 3 H); 2.36–2.73 (*AB*-system, J_{AB}=14, 2 H); 4.14 (*qa*, *J*=7, 2 H); 5.32–5.50 (*m*, 1H). – MS.: 222 (M^+), 176, 134 (100%), 119, 105, 91, 79, 67 ($C_{14}H_{22}O_2$).

9-Carboethoxymethyl-10-methyl-Δ^1*-octalin* **9k/9l**[16] *from* **6k/6l**. Yield 74%. – IR.: 1718, 1440, 1370, 1325, 1290, 1165, 1095, 1030, 925. – ^{1}H-NMR.: 0.76–1.86 (br. *m*, 10 H); 0.91 and 1.02 (2 *s*, 3 H, CH_3 of **9k** and **9l**, respectively); 1.26 (*t*, *J*=7, 3 H); 1.94–2.20 (*m*, 2 H); 2.36 and 2.41 (2 *s*, 3 H, CH_2COOEt of **9k** and **9l**, respectively); 4.13 (*qa*, *J*=7, 2 H); 5.47–5.79 (*m*, 2 H). – MS.: 236 (M^+), 221, 190, 148, 133, 119, 105, 93, 91, 81, 67 ($C_{15}H_{24}O_2$).

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[16] GC. analysis (column B/200°) showed 91.5% of β-isomer **9k** (retention time 8.7) and 8.5% of α-isomer **9l** (retention time 21.5).