Novel Preparation of α,β-Unsaturated Aldehydes. Benzeneselenolate Promotes Elimination of HBr from α-Bromoacetals

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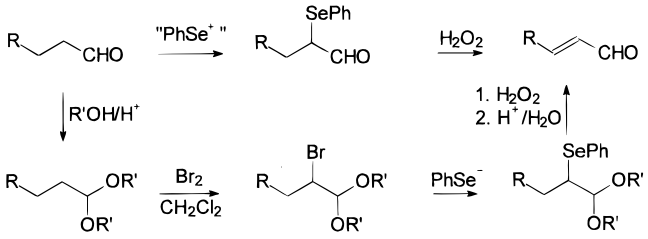
Acetalization, α-bromination, nucleophilic phenylselenenylation, oxidative elimination/hydrolysis was investigated as a novel protocol for the α,β-dehydrogenation of aldehydes. Treatment of acetals with bromine in methylene chloride afforded the corresponding α-bromoacetals in 80−90% yields. Nucleophilic phenylselenenylation was then conveniently effected by treatment with benzeneselenolate generated in situ in dimethyl sulfoxide from diphenyl diselenide, hydrazine and potassium carbonate. Unbranched α-bromoacetals cleanly afforded substitution products whereas β- and γ-branched ones gave substantial amounts of α,β-unsaturated acetals via formal loss of hydrogen bromide. Oxidative elimination/hydrolysis of these mixtures afforded α,β-unsaturated aldehydes in 50−80% overall yields. In the case of tertiary α-bromoacetals, treatment with benzeneselenolate afforded only dehydrobromination products as mixtures of isomers. The presence of at least a catalytic amount of the organoselenium reagent was found to be crucial for olefin formation. A SET-mechanism, involving benzeneselenolate-induced electron transfer to the halide, loss of bromide ion, and hydrogen atom or proton/electron was proposed for the benzenselenolate-promoted elimination reaction. Experiments designed to trap carbon-centered radicals in intramolecular cyclization or ring-opening reactions failed to provide any evidence for free-radical intermediates.

Introduction

The discovery that selenium substituents could be easily introduced α to a variety of acidifying functional groups and that these derivatives could be converted to olefins by selenoxide syn elimination under mild conditions greatly broadened the range of α,β-unsaturated carbonyl compounds that could be prepared from their saturated analogues.[1] However, for the preparation of α,β-unsaturated aldehydes the electrophilic introduction of selenium into the α-position is often troublesome. Aldehyde enolates are not routinely available by α-deprotonation. Aldehyde enols, enol ethers, or enamines are therefore often used for their preparation. Direct phenylselenenylation of aldehydes[2,3] often gives moderate product yields or requires unstable selenium reagents[4] (Scheme 1, upper pathway). In fact, phenylseleninylation using phenylselenium trichloride and reduction seems to be one of the most efficient methods for the preparation of α-phenylselenoaldehydes.[5,6] Phenylselenenylation of aldehyde derivatives[7] such as enol ethers or enamines is also not unproblematic. We therefore decided to investigate another route for the dehydrogenation of aldehydes, taking advantage of the strongly nucleophilic properties of selenium reagents (Scheme 1, lower pathway). α-Haloesters undergo smooth substitution when treated with selenolate reagents.[8] However, nucleophilic attack at halogen,[9] resulting in overall reduction of the α-halo compound, is often a disturbing side reaction when more stable enolates (ketone or aldehyde) can serve as leaving groups. Reduction can be completely suppressed, though, if the α-haloaldehyde is protected as an acetal. α-Bromoacetals are most conveniently prepared by treatment of the corresponding acetals with bromine. Although secondary bromides of this type are known to react sluggishly or not at all with benzeneselenolate generated by the sodium borohydride method,[10,11] we

Scheme 1



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(3) Toshimitsu, A.; Owada, H.; Terao, K.; Uemura, S.; Okano, M. *J. Org. Chem*. **1984**, *49*, 3796.
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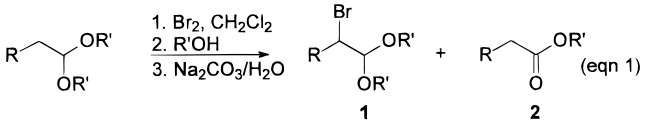
thought it would be possible to effect substitution by using a polar aprotic solvent for the reaction.[12,13] Since selenoxide syn elimination is known to occur preferentially *away* from an oxygen substituent, oxidation of the selenide, followed by hydrolysis, would furnish the desired α,*β*-unsaturated aldehyde (Scheme 1, lower pathway). In this paper, we demonstrate the successful application of this protocol to enal synthesis. Interestingly, it was found that nucleophilic substitution of bromide was often accompanied by selenolate promoted elimination of HBr to furnish the corresponding α,*β*-unsaturated acetals. Although mechanistically intriguing, this reaction is by no means disturbing since the products could be readily hydrolyzed to the desired α,*β*-unsaturaded aldehydes.

Results

In contrast to Br_2-induced α-bromination of ketals,[14,15] bromination has only been rarely used for the introduction of bromide into the α-position of acetals.[16,17] Previous studies by one of us[18] have indicated that the outcome of the reaction critically depends on the conditions used. The desired α-bromoacetal **1** (eq 1) is formed via addition of bromine to an enol ether intermediate, followed by alcoholysis of the terminal bromide. Varying amounts of

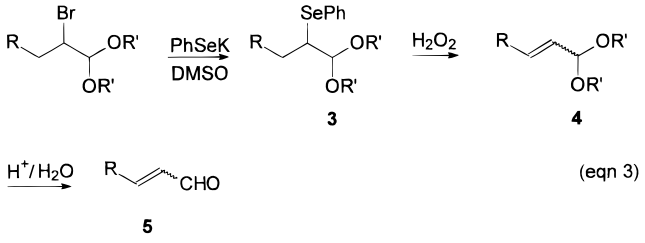


1 **2**

ester byproduct **2** are also formed in the reaction, probably via competing radical bromination/loss of alkyl bromide R′Br from the acetal. In the procedure for α-bromination reported in this paper, bromine in methylene chloride was slowly titrated into a solution of the acetal in the same solvent at 25−30 °C until the orange color did not fade away. At this point, excess alcohol was added and the reaction mixture rapidly neutralized. The crude product usually contains 90−95% of α-bromoacetal **1**, small amounts of the corresponding ester (Table 1), and traces of unreacted starting material. After basic hydrolysis of the ester byproduct and distillation/column chromatography, α-bromoacetals **1a**−**n** were isolated in good to excellent (60−90%) yields. As shown in Table 1, a large variety of acetals could be used, including straight-chain, α, *β*-, *γ*- and *β*,*β*-branched and cyclic compounds as well as cyclopropane derivatives.

Nucleophilic displacement of bromide in α-bromacetals was effected in DMSO at 70 °C with potassium benzeneselenolate. This reagent was conveniently generated by hydrazine reduction of diphenyl diselenide in the presence of potassium carbonate (eq 2).[13] Sodium benzene-

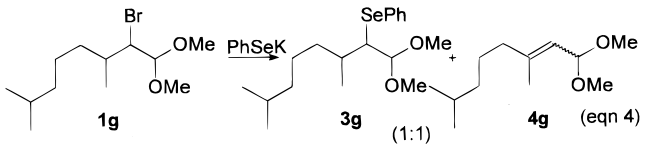
selenolate generated by sodium borohydride reduction of the diselenide in ethanol left the bromide essentially untouched under reflux conditions. Simple unbranched α-bromoacetals cleanly afforded the desired α-phenylselenenylated acetals **3** in good yields (eq 3; Table 2, entries 1−6). Areneselenolates of varying nucleophilicity



3 **4** **5**

(4-Cl-$C_6H_4Se^-$, $PhSe^-$, and 4-MeO-$C_6H_4Se^-$) caused complete consumption of bromacetal **1c** with the two latter reagents, whereas the least nucleophilic 4-chlorobenzeneselenolate left some (11%) of the starting material untouched (Table 2, entries 2−4). Attempted direct α-phenylselenenation of acetals using PhSeCl resulted in the formation of α-chloroacetals and diphenyl diselenide. α-Phenylselenenyl acetals and ketals are known to undergo hydrogen peroxide induced selenoxide elimination away from the oxygen substituents to give α,*β*-unsaturated acetals and ketals.[19,20] It was therefore not surprising to find that selenides **3** afforded the corresponding α,*β*-unsaturated acetals **4** when treated with hydrogen peroxide in tetrahydrofuran (eq 3). Some of these compounds were isolated (Table 2, entries 1, 6, and 9) but most of them were subjected to acidic hydrolysis to give the corresponding α,*β*-unsaturated aldehydes **5**, predominantely as *E*-isomers.

Surprisingly, when *β*- or *γ*-branched or cyclic α-bromoacetals were subjected to the reaction conditions for nucleophilic substitution, varying amounts of α,*β*-unsaturated acetals **4** were always formed in addition to the substitution products. For example, *β*-branched acetal **1g** afforded a 1/1 mixture of substitution and elimination products (eq 4). Other branched or cyclic compounds gave



1g **3g** **4g**

similar results (Table 2, entries 7−12). Oxidation/hydrolysis of these mixtures afforded the corresponding α,*β*-unsaturated aldehydes **5** in 50−80% yields (Table 2). Control experiments showed that the α,*β*-unsaturated

(10) See ref 8, p 1068, entry 10.
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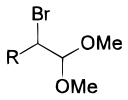
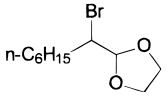
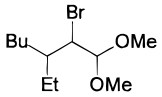
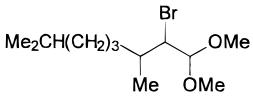
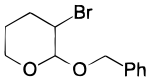
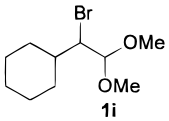
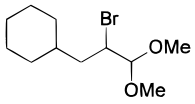
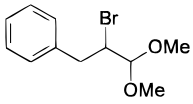
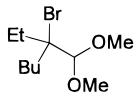
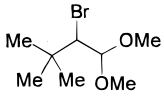
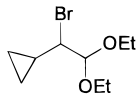
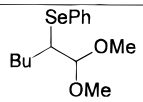
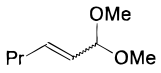
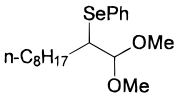
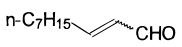
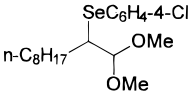
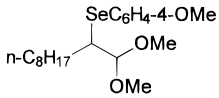
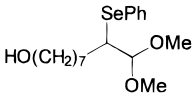
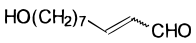
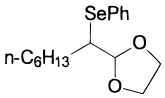
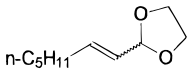
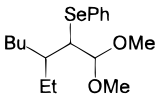
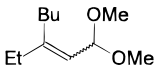
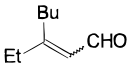
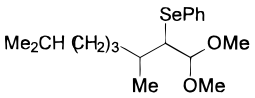
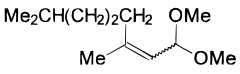
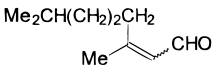
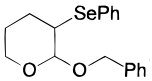
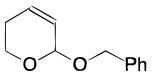
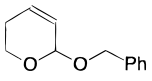
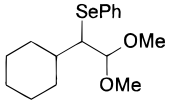
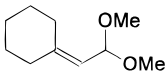
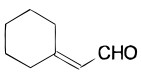
Table 1. α-Bromination of Acetals

Acetal	α-Bromoacetal	Yield (%)[a]	Ester **2** (%)[c]
			
1,1-Dimethoxyhexane	**1a** R=n-Bu	83	2
1,1-Dimethoxyoctane	**1b** R=n-C_6H_{13}	79[d]	4
1,1-Dimethoxydecane	**1c** R=n-C_8H_{17}	69[d]	5
10-Acetoxy-1,1-dimethoxydecane	**1d** R=$HO(CH_2)_8$	82	1
			
2-Heptyl-1,3-dioxolane	**1e**	56[d]	13[d]
			
1,1-Dimethoxy-3-ethylheptane	**1f**	86	3
			
1,1-Dimethoxy-3,7-dimethyloctane	**1g**	76	12
			
2-Benzyloxytetrahydropyran	**1h**	62	-
			
2-Cyclohexyl-1,1-dimethoxyethane	**1i**	94[b]	3
			
3-Cyclohexyl-1,1-dimethoxypropane	**1j**	70	-
			
1,1-Dimethoxy-3-phenylpropane	**1k**	89	7
			
1,1-Dimethoxy-2-ethylhexane	**1l**	86[b]	3
			
1,1-Dimethoxy-3,3-dimethylbutane	**1m**	72	5
			
2-Cyclopropyl-1,1-dimethoxyethane	**1n**	75	10

[a] Isolated yield after distillation or chromatography. [b] Yield as determined by ^{1}H NMR or GC analysis of the crude reaction product. The material was used without further purification in the next step. [c] Percent of ester in the crude product as determined by ^{1}H NMR. [d] From ref 18.

Table 2. Preparation of α-Phenylselenenylacetals and Their Conversion to α,β-Unsaturated Acetals/Enals by Selenoxide Elimination/Hydrolysis

Entry	α-Bromo-acetal	α-Phenylselenenyl-acetal	α,β-Unsaturated acetal formed in the substitution reaction	Selenide yield (%)[a]	**3**/**4**-ratio in the substitution reaction	α,β-Unsaturated acetal **4** or enal **5** prepared.	yield (%)
							
1	**1a**	**3a**	-	84	100/0	**4a**	70[b]
							
2	**1c**	**3c**	-	85	100/0	**5c**	73[b]
							
3	**1c**		-	64	100/0	-	-
							
4	**1c**		-	82	100/0	-	-
							
5	**1d**	**3d**	-	87	100/0	**5d**	97[b]
							
6	**1e**	**3e**	-	93	100/0	**4e**	74[c]
							
7	**1f**	**3f**	**4f**	d	30/70	**5f**	51[c]
							
8	**1g**	**3g**	**4g**	d	50/50	**5g**	59[c]
							
9	**1h**	**3h**	**4h**	d	25/75	**4h**	56[c]
							
10	**1i**	**3i**	**4i**	88	96/4	**5i**	78[b]

[a] Isolated yield. [b] Yield of acetal. [c] Yield of enal. [d] Not determined.

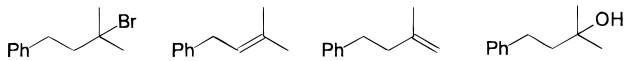
Table 2. (Continued)

Entry	α-Bromo-acetal	α-Phenylselenenyl-acetal	α,β-Unsaturated acetal formed in the substitution reaction	Selenide yield (%)[a]	**3**/**4**-ratio in the substitution reaction	α,β-Unsaturated acetal **4** or enal **5** prepared.	yield (%)
11	**1j**	**3j**	**4j**	78	88/12	**5j**	65[c]
12	**1k**	**3k**	**4k**	d	50/50	**5k**	59[c]
13	**1l**	**3l**	**4l** **4l'**	d	0/100	**5l** **5l'**	64[e]
14	**1m**	**3m**	-	46	100/0	-	-

[a] Isolated yield. [b] Isolated yield based on selenide **3**. [c] Isolated yield based on bromide **1**. [d] The crude mixture of selenide **3** and α,β-unsaturated acetal **4** was subjected to selenoxide elimination/hydrolysis. [e] ^{1}H NMR yield based on bromide **1** as determined using an internal standard.

acetals **4** were not formed as a result of competing base-induced elimination of hydrogen bromide from α-bromoacetals **1** during attempted nucleophilic substitution with benzeneselenolate. Thus, bromides **1a**, **1g**, and **1i** were essentially unchanged when submitted to the reaction conditions for nucleophilic substitution (diphenyl diselenide omitted), whereas cyclic bromide **1h** afforded the corresponding elimination product **4h** in low (8%) yield. Bromide **1k**, though, carrying benzylic hydrogens, was more prone to undergo base-induced elimination. Heating in DMSO containing potassium carbonate produced a 1/1 mixture of unreacted starting material and elimination product **4k**. α-Phenylselenenyl acetals **3** were also shown not to be precursors of α,β-unsaturated acetals **4**. Thus, selenide **3k** was unchanged when treated with PhSeK under the standard conditions for nucleophilic substitution. Attempted nucleophilic substitution of tertiary bromide **1l** afforded only elimination products as a mixture of α,β-unsaturated acetals **4l** and **4l′** (Table 2, entry 13). In fact, the reaction was complete within 3 h. In the absence of diphenyl diselenide, only 30% conversion into the same olefin mixture was observed under similar conditions. Sterically hindered bromide **1m**, lacking hydrogens in the γ-position, afforded a substitution product **3m** in low (42%) yield when the substitution reaction was carried out at slightly elevated temperature (120 °C). Acidification of the aqueous phase obtained during workup of the reaction gave 3,3-dimethylbutyric acid. This seems to indicate that elimination of HBr had occurred to some extent to produce a ketene acetal.

Tertiary bromide **6** (lacking an acetal function) afforded mainly elimination products **7** and **8** (2/1 mixture, 82% yield) when subjected to the reaction conditions for nucleophilic substitution (2 h at 20 or 70 °C). The only identifiable byproduct was alcohol **9**. Under similar



6 **7** **8** **9**

reaction conditions, but in the absence of diphenyl diselenide, elimination was considerably slower. Thus, after 2 h at 20 °C, the product consisted of 39% unreacted starting material, 47% of olefins **7**/**8**, and 14% of carbinol **9**. It was also found that a *catalytic* amount of diphenyl diselenide (10 mol %) was sufficient to give a complete conversion of bromide into olefins after 2 h at 20 °C. Likewise, tertiary bromide **1l** was found to undergo smooth dehydrobromination to give olefins **4l**/**4l′** under the standard reaction conditions using a catalytic amount of diphenyl diselenide or, in the absence of hydrazine, by using a catalytic amount (20%) of potassium benzeneselenolate. However, bromides that afforded mixtures of selenides and elimination products under stoichiometric conditions (e.g., compound **1h**) showed incomplete conversion of starting material in the catalytic process due to trapping of the catalyst. Phenolates, thiophenolates, and tellurophenolates were also examined for their ability to act as nucleophiles/elimination promotors toward α-bromoacetals. α-Bromoacetal **1l** was recovered essentially unchanged after treatment with potassium

phenolate in DMSO at 70 °C for 7 h. Potassium benzenethiolate and the sterically more demanding potassium 2,6-dimethylbenzenethiolate afforded substitution products **10a** (83% yield) and **10b** (70% yield), respectively, when treated with bromide **1a** under similar conditions. Secondary α-bromoacetal **1f** predominantely

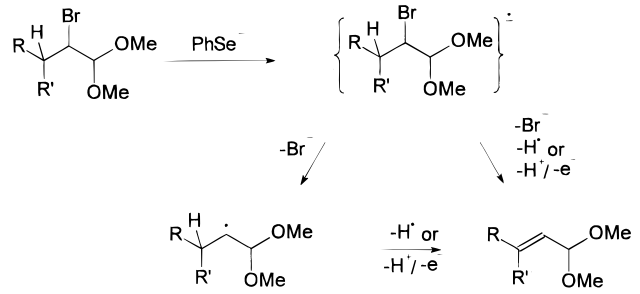
10 a Ar=Ph
b Ar=2,6-C_6H_3 **11**

(90%) and tertiary α-bromoacetal **1l** exclusively underwent elimination when heated with potassium benzenethiolate to give olefins **4f** and **4l**/**4l′**, respectively. In the latter case, catalytic amounts of disulfide (10%) or potassium benzenethiolate (20% in the absence of hydrazine) were also found to cause complete elimination of HBr from the starting material. Dehydrobromination was the only reaction observed when bromide **1f** was treated with a stoichiometric amount of 2,6-dimethylbenzenthiolate. Hydrazine in DMSO containing potassium carbonate failed to reduce diphenyl ditelluride to potassium benzenetellurolate. Sodium benzenetellurolate was therefore generated by sodium borohydride reduction of the ditelluride in ethanol. However, this reagent was only nucleophilic enough to give a 50% conversion of bromide **1a** to telluride **11** under reflux conditions. A more nucleophilic organotellurium reagent was produced from sodium borohydride and diphenyl ditelluride in DMF. After the mixture was heated with bromide **1a** at 70 °C for 7 h, unstable telluride **11** was isolated in 82% yield. The reagent was inappropriate for dehydrobromination reactions, though. Thus, bromide **1f** afforded mainly unreacted starting material (64%) in addition to some olefin (20%) and an unidentified organotellurium compound.

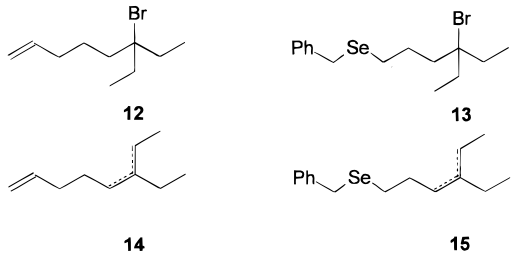
Discussion

Although the acetalization/bromination/nucleophilic selenenylation/oxidation/hydrolysis sequence for dehydrogenation of aldehydes proposed in the lower part of Scheme 1 involves one or two steps more than procedures commonly used, it is a general and versatile method that could find synthetic use for the preparation of a variety of α,β-unsaturated aldehydes. The competing elimination reaction observed in the substitution of branched or tertiary bromoacetals with benzeneselenolate (resulting in the formation of α,β-unsaturated acetals) is by no means disturbing since the product can be readily hydrolyzed to the desired enal.[21] Olefin formation is intriguing from a mechanistic point of view, though. The substitution reaction is carried out under slightly basic conditions in DMSO containing hydrazine and potassium carbonate. Control experiments showed that branched secondary bromoacetals did not undergo elimination to any appreciable extent in the absence of benzeneselenolate and that dehydrobromination of tertiary bromides was significantly accelerated in the presence of the

Scheme 2



organoselenium species. Benzeneselenolate itself is approximately as weak as a base as acetate ion.[22] The substitution products (selenides) were shown not to give rise to olefins when resubjected to the reaction conditions for substitution. Also, since 18-crown-6 did not promote dehydrobromination of bromide **1f** under selenium free conditions in a control experiment, phase-transfer catalysis by benzeneselenolate seems unlikely to be operative. Reports in the literature indicate that benzeneselenolate ion can sometimes act as an electron-transfer agent.[23] If this mechanism is operative, the formation of elimination product could occur according to a SET-mechanism as shown in Scheme 2. After electron transfer to the α-bromoacetal, the radical anion could give rise to olefin either by more or less concerted loss of bromide ion and hydrogen atom/proton plus electron, or by loss of bromide followed by loss of a hydrogen atom/proton plus electron from the resulting carbon centered radical. From Table 2, it is clear that the amount of elimination product increases as the steric hindrance around the bromine is increased (unbranched secondary bromide < branched secondary bromide < tertiary bromide). Thus, the SET mechanism becomes predominating only with tertiary bromides or with sterically hindered secondary bromides. To find evidence for radical intermediates, tertiary bromides **12** and **13** were subjected to the usual reaction conditions for nucleophilic substitution. If radical



intermediates are involved, these could be expected to undergo 5-exo radical cyclization and intramolecular substitution at chalcogen, respectively, to give cyclopentane and tetrahydroselenophene derivatives. However, when submitted to the reaction conditions for nucleophilic substitution, both substrates afforded only elimination products as mixtures of olefins **14** and **15**, respectively. The rate of 5-exo cyclization in the above system could be estimated to 3×10^5.[24] The few rate data available for intramolecular homolytic substitution at selenium suggest that cyclization of the radical derived from

(21) The base-induced conversion of α-bromoacetals to enals via α,β-unsaturated acetals has previously been explored.[21a] However, dehydrobromination towards the acetal to give a ketene acetal serves to reduce overall enal yields in the process (see ref 18). Bedoukian, P. Z. *J. Am. Chem. Soc.* **1957**, *79*, 889.

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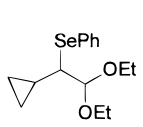
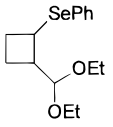
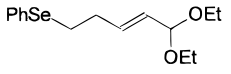
bromide **13** would proceed at least as fast.[25] α-Bromo-α-cyclopropylacetal **1n** (Table 1) when subjected to the conditions for nucleophilic substitution afforded a 59/11/30 mixture of cyclopropyl carbinyl (**16**), cyclobutyl (**17**), and homoallyl (**18**) selenides in 62% yield. The ring



16



17

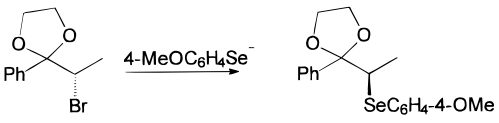


18

opening of the cyclopropylmethyl radical to give a homoallyl radical is a well-known, rapid, radical clock ($k = 2 \times 10^8$ s^{-1}).[26] Thus, the high proportion of substitution product **16** in this reaction again testify against the involvement of a free radical as proposed in the lower left part of Scheme 2. Products **17** and **18** are more likely to be formed by rearrangement of a cyclopropylcarbinyl cation prior to nucleophilic attack[27] or by direct attack on the cyclopropane ring.[28]

To probe the involvement of a carbocation intermediate in the elimination process, bromide **1l** was treated with silver tetrafluoroborate in acetonitrile. After heating at reflux, the starting material was recovered largely unchanged. This reluctance of the bromide to react suggests carbocations as less likely to be involved in the benzeneselenolate promoted dehydrobromination of α-bromoacetals. At present, we propose that the elimination reaction is more or less concerted as outlined in the lower right part of Scheme 2.

Secondary bromide displacement by selenolate ion is commonly believed to occur via an S_N2 reaction.[29] However, a SET-mechanism is also conceivable for formation of the substitution product. To the best of our knowledge, the stereochemical outcome of nucleophilic substitution in α-bromo acetals or ketals has never been studied. Therefore, an enantiomerically enriched α-bromoketal **19** (40% ee) was prepared[15] and subjected to the usual conditions for substitution, using bis(4-methoxyphenyl) diselenide as a source of selenolate ion (a similar approach to enantiomerically enriched α-bromacetals failed; see the Experimental Section). As determined by HPLC using a chiral column, substitution of the bromide occurs with clean inversion of configuration to give selenide **20** (40% ee; eq 5). This result seems to preclude any involvement of a radical intermediate in the substitution process.



19 **20** (eqn 5)

Conclusions

This work has demonstrated a new general approach for aldehyde dehydration based on acetalization, α-bromination, nucleophilic substitution with benzeneselenolate, selenoxide elimination, and hydrolysis. In the substitution reaction, substantial amounts of elimination products were formed when the α-bromoacetals were sterically hindered or tertiary. It is proposed that these products are formed via a SET-mechanism involving electron transfer from selenolate, followed by a more or less concerted dissociation of bromide and loss of a hydrogen atom or a proton/electron.

Experimental Section

NMR spectra were recorded in $CDCl_3$ at 299.903 MHz (^1H), 75.419 MHz (^{13}C) and 57.213 (^{77}Se). ^{77}Se chemical shifts are given in ppm relative to neat Me_2Se and were measured relative to neat Me_2Se_2 (δ 275 ppm), which was inserted into the NMR tube in a sealed capillary. Enantiomeric purity was assessed by GC (bromide **19**) using a commercial Chirasel Dex-CB column at 140 °C and nitrogen (15 psi) as a carrier gas or by HPLC (selenide **20**) on a Chiralpack AD column, using a 254 nm UV detector, 1% *i*-PrOH in hexane as eluent (flow rate of 0.5 mL/min). Elemental analyses were performed by Analytical Laboratories, Lindlar, Germany. Starting aldehydes, if not commercially available, were prepared by PCC oxidation of the corresponding primary alcohols. 1,1-Dimethoxyhexane,[30] 1,1-dimethoxy-3,7-dimethyloctane,[31] 2-benzyloxytetrahydropyran,[32] 2-cyclohexyl-1,1-dimethoxyethane,[33] 1,1-dimethoxy-3-phenylpropane,[34] 1,1-dimethoxy-2-ethylhexane,[35] 1,1-dimethoxy-3,3-dimethylbutane,[36] and 2-cyclopropyl-1,1-diethoxyethane[37] were prepared according to the literature. New acetals 10-acetoxy-1,1-dimethoxydecane, 3-cyclohexyl-1,1-dimethoxypropane, and 1,1-dimethoxy-3-ethyl-heptane were prepared by acetalization of the correspondimg aldehydes with excess MeOH or $CH(OMe)_3$ in the presence of *p*-toluenesulfonic acid (^1H and/or ^{13}C NMR spectra are included in the Supporting Information). 2-Bromo-1,1-dimethoxyoctane (**1b**),[18] 2-bromo-1,1-dimethoxydecane (**1c**),[18] and 2-(1-bromoheptyl)-1,3-dioxolane (**1d**)[18] were prepared as previously described. 2-Bromo-2-methyl-4-phenylylbutane (**6**) was prepared by treatment of the corresponding alcohol with concentrated HBr at rt for 3 h. ^1H NMR data were in good agreement with the literature.[38] DMSO was used as purchased; CH_2Cl_2 was distilled from CaH_2.

Bromination of Acetals. General Procedure. Bromine (4.0−4.2 g, 1.29−1.36 mL, 25−26.3 mmol) in CH_2Cl_2 (5 mL) was added dropwise during 30 min into a stirred solution of the acetal (25 mmol) in CH_2Cl_2 (20 mL). During the addition, the temperature was kept at 25−30 °C until the orange color did not fade away. The corresponding alcohol (e.g., methanol in the case of dimethyl acetals) (15 mL) was added, and after 3 min the mixture was poured into a stirred solution of Na_2CO_3 (5 g) and Na_2SO_3 (1 g) in water (50 mL). The organic layer was separated, the aqueous phase was extracted with ether, and the combined extracts were dried ($CaCl_2$) and concen-

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trated. If, according to ^{1}H NMR, much ester **2** had been formed during bromination (>ca. 10%), the residue was dissolved in a mixture of methanol (20 mL), water (8 mL), and KOH (4 g) and stirred at ambient temperateure for 4−5 h. Methanol was then distilled off, and the residue was treated with water, extracted with ether, dried ($CaCl_2$), and concentrated in vacuo. The material thus obtained was purified by column chromatography or vacuum distillation. In some cases (see Table 1), the crude product was used for further transformations. The following compounds were prepared according to the general procedure in a scale ranging from 3 to 50 mmol.

2-Bromo-1,1-dimethoxyhexane (1a): bp 90 °C (1 Torr); yield 83% in 37.5 mmol scale; ^{1}H NMR data were in good agreement with the literature;[16] ^{13}C NMR δ 13.9 q, 22.1 t, 29.4 t, 32.5 t, 54.9 q, 55.0 q, 55.4 d, 106.2 d. Anal. Calcd for $C_8H_{17}BrO_2$: C, 42.68; H, 7.61. Found: C, 42.93; H, 7.62.

9-Bromo-10,10-dimethoxydecanol (1d) was prepared by bromination of 10-acetoxy-1,1-dimethoxydecane (0.866 g, 3.33 mmol) according to the general procedure. The crude material was dissolved in methanol (20 mL), solid K_2CO_3 (1 g) was added, and the mixture was stirred at room temperature (TLC monitoring) until transesterification was complete (ca. 4 h). Methanol was distilled off, and the residue was treated with water and extracted with ether. After drying (Na_2SO_4) and concentration in vacuo, the crude material was purified by column chromatography (5, 20, and finally 30% EtOAc in pentane as an eluent) to afford 0.812 g (82%) of the title compound as a colorless oil: ^{1}H NMR δ 1.22−1.41 (several peaks, 10H), 1.48−1.60 (several peaks, 3H), 1.74 (m, 1H), 1.92 (m, 1H), 3.44 (s, 6H), 3.63 (t, 2H, J = 6.7 Hz), 3.96 (ddd, 1H, J = 10.1, 5.6, 3.2 Hz), 4.37 (d, 1H, J = 5.7 Hz); ^{13}C NMR δ 25.7 t, 27.2 t, 28.9 t, 29.2 t, 29.3 t, 32.7 t, 32.8 t, 54.9 q, 55.0 q, 55.5 d, 63.0 t, 106.3 d. Anal. Calcd for $C_{12}H_{25}BrO_3$: C, 48.49; H, 8.48. Found: C, 48.44; H, 8.41.

2-Bromo-1,1-dimethoxy-3-ethylheptane (1f) was purified by column chromatography (eluent 1% EtOAc in pentane): yield 83% of two diastereomers (1:1) in 10.3 mmol scale; ^{1}H NMR δ 0.83−0.96 (several peaks, 6H), 1.13−1.60 (several peaks, 9H), 3.34, 3.35, 3.42 and 3.43 (all s, Σ 6H), 4.13 and 4.16 (both dd, Σ 1H, J = 7.9, 2.6 Hz and 7.9, 2.2 Hz), 4.54 and 4.55 (both d, Σ 1H, J = 7.9 Hz); ^{13}C NMR δ 11.5 q, 11.9 q, 14.0 q, 22.7 t, 22.9 t, 23.5 t, 24.7 t, 29.2 t, 29.5 t, 30.3 t, 31.1 t, 40.7 d, 40.8 d, 53.3 q, 53.4 q, 54.5 q, 59.3 d, 59.7 d, 104.2 d, 104.3 d. Anal. Calcd for $C_{11}H_{23}BrO_2$: C, 49.45; H, 8.68. Found: C, 49.27; H, 8.63.

2-Bromo-1,1-dimethoxy-3,7-dimethyloctane (1g): bp 108−112 °C (5 Torr); yield 76% of two diastereomers (3:2) in 25.5 mmol scale. Ester byproduct was removed by saponification prior to distillation. The analytically pure sample was obtained by further column chromatography (1% EtOAc in pentane): ^{1}H NMR δ 0.85 and 0.86 (both d, Σ 6H, J = 6.3 Hz), 0.91 and 1.00 (both d, Σ 3H, J = 6.3 Hz), 1.10−1.45 (several peaks, 6H), 1.52 (m, 1H), 1.82 and 1.90 (both m, Σ 1H), 3.35, 3.36 and 3.42 (all s, Σ 6H), 3.98 and 4.10 (both dd, Σ 1H, J = 7.6, 3.0 Hz and 8.1, 2.5 Hz), 4.47 and 4.49 (both d, Σ 1H, J = 7.9, 7.6 Hz); ^{13}C NMR δ 15.1 q, 18.4 q, 22.4 q, 22.5 q, 22.6 q, 22.7 q, 24.5 t, 24.7 t, 27.8 d, 32.0 t, 33.9 d, 34.6 d, 35.9 t, 38.9 t, 39.0 t, 53.6 q, 54.0 q, 54.2 q, 54.3 q, 61.2 d, 62.7 d, 104.2 d, 104.4 d; HRMS *m/e* calcd for $(M - OMe)^+$ 249.08545, found 249.0821.

2-Benzyloxy-3-bromotetrahydropyran (1h). Purified by column chromatography (2% EtOAc in pentane): yield 62% in 30 mmol scale (general procedure: benzyl alcohol was used instead of methanol to quench the reaction); ^{1}H NMR δ 1.56 (m, 1H), 1.87−2.00 (several peaks, 4H), 2.43 (m, 1H), 3.62 (m, 1H), 3.96 (m, 1H), 4.06 (m, 1H), 4.56 (d, 1H, J = 11.6 Hz), 4.73 (d, 1H, J = 4.2 Hz), 4.82 (d, 1H, J = 11.6 Hz), 7.28−7.41 (several peaks, 5H); ^{13}C NMR δ 23.1 t, 29.9 t, 49.2 d, 62.4 t, 69.6 t, 100.0 d, 127.9 d, 128.3 d, 128.4 d, 137.3 s; HRMS *m/e* calcd for $(M - CH_2Ph)^+$ 178.97081, found 178.9711.

2-Bromo-2-cyclohexyl-1,1-dimethoxyethane (1i): crude yield 98% in 18.5 mmol scale. The analytical sample was purified by column chromatography (eluent 1.5% EtOAc in pentane): ^{1}H NMR δ 1.04−1.42 (several peaks, 5H), 1.50−1.81 (several peaks, 6H), 3.38 (s, 3H), 3.41 (s, 3H), 3.92 (dd, 1H, J = 7.4, 3.1 Hz), 4.47 (d, 1H, J = 7.4 Hz); ^{13}C NMR δ 25.7 t, 26.1 t, 28.0 t, 31.8 t, 39.3 d, 54.3 q, 61.8 d, 104.0 d. Anal. Calcd for $C_{10}H_{19}BrO_2$: C, 47.82; H, 7.62. Found: C, 47.92; H, 7.80.

2-Bromo-3-cyclohexyl-1,1-dimethoxypropane (1j): yield 70% in 16.1 mmol scale; bp 115−8 °C (2 Torr); n^{20}_D 1.4850; ^{1}H NMR δ 0.78 (m, 1H), 0.99 (m, 1H), 1.10−1.35 (several peaks, 3H), 1.50−1.82 (several peaks, 8H), 3.42 (s, 3H), 3.43 (s, 3H), 4.05 (dt, 1H, J = 8.0 and 5.4 Hz), 4.35 (d, 1H, J = 5.4 Hz); ^{13}C NMR δ 25.8 t, 26.2 t, 26.5 t, 31.3 t, 34.0 t, 34.9 d, 39.9 t, 52.5 d, 55.1 q, 55.4 q, 106.6 d. Anal. Calcd for $C_{11}H_{21}BrO_2$: C, 49.82; H, 7.98. Found: C, 50.00; H, 8.07.

2-Bromo-1,1-dimethoxy-3-phenylpropane (1k). yield of crude material 89% in 44 mmol scale. Attempts to further purify the product by vacuum distillation led to decomposition. The crude material was found suitable for further transformations. ^{1}H NMR data were in good agreement with literature.[16] ^{13}C NMR: δ 39.1 t, 54.8 q, 55.2 q, 55.7 d, 105.5 d, 126.7 d, 128.3 d, 129.3 d, 138.0 s.

2-Bromo-1,1-dimethoxy-2-ethylhexane (1l): yield 86% of crude material in 25 mmol scale, which was used without further purification; ^{1}H NMR δ 0.90 (t, 3H, J = 7.1 Hz), 0.99 (t, 3H, J = 7.2 Hz), 1.22−1.46 (several peaks, 4H), 1.78−2.00 (several peaks, 4H), 3.55 (s, 3H), 3.57 (s, 3H), 4.32 (s, 1H); ^{13}C NMR δ 9.6 q, 14.0 q, 23.0 t, 27.2 t, 30.6 t, 37.0 t, 58.7 q, 58.9 q, 78.5 s, 109.6 d. Anal. Calcd for $C_{10}H_{21}BrO_2$: C, 47.44; H, 8.36. Found: C, 47.79; H, 8.46.

2-Bromo-1,1-dimethoxy-3,3-dimethylbutane (1m): bp 61−64 °C (1 Torr); yield 72% in 36.4 mmol scale; ^{1}H NMR δ 1.11 (s, 9H), 3.42 (s, 3H), 3.47 (s, 3H), 3.89 (d, 1H, J = 3.5 Hz), 4.35 (d, 1H, J = 3.5 Hz); ^{13}C NMR δ 28.5 q, 35.0 s, 55.2 q, 55.5 q, 67.0 d, 104.3 d. Anal. Calcd for $C_8H_{17}BrO_2$: C, 42.68; H, 7.61. Found: C, 42.47; H, 7.48.

2-Bromo-2-cyclopropyl-1,1-diethoxyethane (1n): bp 80−82 °C (1 Torr); yield 75% in 19.3 mmol scale; ^{1}H NMR δ 0.34 (m, 1H), 0.56 (m, 1H), 0.69 (m, 1H), 0.84 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.0 Hz, 3H), 1.32 (m, 1H), 3.38 (dd, J = 10.0, 4.7 Hz, 1H), 3.61 (m, 2H), 3.75 (m, 2H), 4.55 (d, J = 4.7 Hz, 1H); ^{13}C NMR δ 5.7 t, 9.5 t, 15.1 d, 15.2 q, 61.6 d, 63.7 t, 64.2 t, 104.4 d. Anal. Calcd for $C_9H_{17}BrO_2$: C, 45.59; H, 7.23. Found: C, 45.37; H, 7.38.

Reaction of α-Bromoacetals with Areneselenolates. General Procedure. A mixture of α-bromoacetal **1** (1 mmol), diaryl diselenide (0.55 mmol), freshly powdered K_2CO_3 (0.5 g), and DMSO (2.5 mL) in a 10 mL flask equipped with a stirring bar and a rubber septum was degassed using a manifold connected to vacuum and nitrogen lines. Hydrazine hydrate (0.15 mL, 2.78 mmol) was then injected, and the mixture was heated to 70 °C. During heating, the color of diselenide gradually disappeared. The reaction mixture was stirred for 7 h, cooled, diluted with water (15 mL), and extracted with ether. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was subjected to column chromatography to afford α-arylselenoacetals **3**. If a mixture of selenide **3** and α,β-unsaturated acetal **4** was formed, it was subjected to oxidative elimination without further purification. The following compounds were prepared according to the general procedure:

1,1-Dimethoxy-2-phenylselenenylhexane (3a). Purified by column chromatography (eluent 1.5% EtOAc in pentane): yield 84%; ^{1}H NMR δ 0.87 (t, 3H, J = 7.4 Hz), 1.20−1.63 (several peaks, 5H), 1.79 (m, 1H), 3.23 (m, 1H), 3.38 (s, 3H), 3.42 (s, 3H), 4.38 (d, 1H, J = 5.0 Hz), 7.20−7.30 (several peaks, 3H), 7.60 (m, 2H); ^{13}C NMR δ 13.9 q, 22.5 t, 29.8 t (two peaks), 48.7 d, 55.2 q, 55.3 q, 107.4 d, 127.3 d, 128.8 d, 129.7 s, 134.6 d; ^{77}Se NMR δ 338.4. Anal. Calcd for $C_{14}H_{22}O_2Se$: C, 55.85; H, 7.37. Found: C, 55.94; H, 7.47.

1,1-Dimethoxy-2-phenylselenenyldecane (3c). Purified by column chromatography (eluent 2% EtOAc in pentane): yield 85%; ^{1}H NMR δ 0.87 (t, 3H), 1.17−1.33 (several peaks, 10H), 1.41 (m, 1H), 1.57 (m, 2H), 1.79 (m, 1H), 3.24 (ddd, 1H, J = 8.7, 4.9, 4.5 Hz), 3.38 (s, 3H), 3.42 (s, 3H), 4.38 (d, 1H, J = 4.9 Hz), 7.22−7.28 (several peaks, 3H), 7.60 (m, 2H); ^{13}C NMR δ 14.0 q, 22.5 t, 27.6 t, 29.1 t, 29.2 t, 29.3 t, 30.1 t, 31.7

t, 48.7 d, 55.2 q, 107.5 d, 127.3 d, 128.8, 129.9 s, 134.8 d. Anal. Calcd for $C_{18}H_{30}O_2Se$: C, 60.49; H, 8.46. Found: C, 60.38; H, 8.49.

2-(4-Chlorophenylselenenyl)-1,1-dimethoxydecane was prepared from compound **1c** (0.665 mmol) and bis(4-chlorophenyl) diselenide according to the general procedure (9 h at 70 °C). The crude material contained 11% of unreacted α-bromoacetal. Column chromatography (eluent 1.5% EtOAc in pentane) afforded 0.168 g (64%) of the title compound: ^{1}H NMR δ 0.87 (t, 3H), 1.18−1.31 (several peaks, 10H), 1.39 (m, 1H), 1.55 (m, 2H), 1.77 (m, 1H), 3.19 (dd, 1H, J = 7.8, 5.0 Hz), 3.38 (s, 3H). 3.40 (s, 3H), 4.36 (d, 1H, J = 5.0 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.52 (d, 2H, J = 8.4 Hz); ^{13}C NMR δ 14.1 q, 22.6 t, 27.6 t, 29.2 t, 29.4 t (two peaks), 30.3 t, 31.8 t, 49.3 d, 55.2 q, 55.5 q, 107.4 d, 128.0 s, 129.0 d, 133.6 s, 136.1 d. Anal. Calcd for $C_{18}H_{29}ClO_2Se$: C, 55.17; H, 7.46. Found: C, 54.94; H, 7.35.

1,1-Dimethoxy-2-(4-methoxyphenylselenenyl)decane was prepared from compound **1c** (1 mmol) and bis(4-methoxyphenyl) diselenide according to the general procedure (9 h at 75 °C gave complete consumption of **1c**). Column chromatography (1−4% ether in pentane) afforded 0.318 g (82%) of the title compound as a colorless oil: ^{1}H NMR δ 0.87 (t, 3H, J = 6.8 Hz), 1.18−1.33 (several peaks, 10H), 1.36−1.58 (several peaks, 3H), 1.72 (m, 1H), 3.10 (m, 1H), 3.37 (s, 3H), 3.39 (s, 3H), 3.80 (s, 3H), 4.34 (d, 1H, J = 5.3 Hz), 6.80 (d, 2H, J = 8.8 Hz), 7.54 (d, 2H, J = 8.8 Hz); ^{13}C NMR δ 14.1 q, 22.7 t, 27.6 t, 29.3 t, 29.4 t (two peaks), 29.9 t, 31.9 t, 48.7 d, 55.0 q, 55.1 q, 55.2 q, 107.2 d, 114.5 d, 119.2 s, 137.4 d, 159.5 s. Anal. Calcd for $C_{19}H_{32}O_3Se$: C, 58.90; H, 8.33. Found: C, 58.81, H, 8.47.

10,10-Dimethoxy-9-phenylselenenyldecanol (3d) was prepared from bromoacetal **1d** (0.202 g, 0.68 mmol), diphenyl diselenide (0.125 g, 0.4 mmol), freshly powdered K_2CO_3 (0.5 g), and DMSO (1.5 mL) according to the general procedure (90 °C, 8 h). Column chromatography (5, 20, and 35% EtOAc in pentane) afforded 0.221 g (87%) of the title compound as a colorless oil: ^{1}H NMR δ?1.20−1.45 (several peaks, 10H), 1.48−1.53 (several peaks, 4H), 1.79 (m, 1H), 3.22 (m, 1H), 3.38 (s, 3H), 3.41 (s, 3H), 3.62 (t, 2H, J = 6.7 Hz), 4.38 (d, 1H, J = 4.8 Hz), 7.22−7.28 (several peaks, 3H), 7.59 (m, 2H); ^{13}C NMR δ 25.7 t, 27.6 t, 29.2 t, 29.3 t, 30.1 t, 32.8 t, 48.8 d, 55.4 q, 63.0 t, 107.5 d, 127.3 d, 128.8 d, 129.8 s, 134.7 d. Anal. Calcd for $C_{18}H_{30}O_3Se$: C, 57.90; H, 8.10. Found: C, 57.64; H, 7.96.

2-(1-Phenylselenenylheptyl)-1,3-dioxolane (3e). Purified by column chromatography (eluent 2% EtOAc in pentane): yield 93%; ^{1}H NMR δ 0.88 (t, 3H), 1.19−1.32 (several peaks, 6H), 1.42 (m, 1H), 1.63 (m, 2H), 1.82 (m, 1H), 3.25 (m, 1H), 3.91 (m, 2H), 4.08 (m, 2H), 5.08 (d, 1H, J = 5.0 Hz), 7.21−7.31 (m, 3H), 7.60 (m, 2H); ^{13}C NMR δ 13.9 q, 22.4 t, 27.6 t, 28.9 t, 30.4 t, 31.5 t, 49.6 d, 65.4 t, 65.6 t, 105.6 d, 127.2 t, 128.8 t, 129.9 s, 134.4 d. Anal. Calcd for $C_{16}H_{24}O_2Se$: C, 58.75; H, 7.40. Found: C, 59.02; H, 7.88.

1,1-Dimethoxy-3-ethyl-2-phenylselenenylheptane (3f). The crude product was an inseparable mixture of the title compound and acetal **4f**. Hydrolysis in an acetone−water mixture (3:1, 4 mL) in the presence of oxalic acid (0.1 g) for 2 h at ambient temperature, extractive workup, and column chromatography (0.5% EtOAc in pentane) allowed separation of the corresponding aldehydes. 3-Ethyl-2-phenylselenoheptanal thus obtained was acetalized with $CH(OMe)_3$ and subjected to column chromatography to afford a purer (ca. 90%) title compound as a mixture of two diastereomers (1:1): ^{1}H NMR δ 0.80−0.95 (several peaks, 6H), 1.12−1.70 (several peaks, 9H), 3.35 (m, 1H), 3.34 and 3.35 (both s, Σ 6H), 4.55 and 4.57 (both d, Σ 1H, J = 6.9 and 7.0 Hz), 7.19−7.28 (several peaks, 3H), 7.62 (m, 2H); ^{13}C NMR δ 12.1 q, 12.3 q, 14.0 q, 22.8 t, 24.6 t, 24.7 t, 29.7 t, 29.9 t, 31.0 t, 31.4 t, 40.7 d, 40.8 d, 53.3 q, 53.5 q, 53.9 q, 54.2 q, 55.5 d, 106.9 d, 107.0 d, 127.0 d, 128.7 d, 131.2 s, 134.3 d; ^{77}Se NMR δ 290.7 and 291.9.

1,1-Dimethoxy-3,7-dimethyl-2-phenylselenenyloctane (3g). The crude product was an inseparable 1:1 mixture of the title compound and acetal **4g**. A purer (ca. 90%) sample of compound **3g** was prepared as described for compound **3f** (acidic hydrolysis of acetals **3g** and **4g**, separation of aldehydes by column chromatography, and reacetalization of 2-phenylselenenyl-3,7-dimethyloctanal thus obtained). Final column chromatography (0.5% EtOAc in pentane) afforded the title compound as a mixture of two diastereomers (3:2): ^{1}H NMR δ 0.82 and 0.85 (both d, Σ 6H, J = 6.6 Hz), 0.95 and 1.08 (both d, Σ 3H, J = 6.5 and 6.9 Hz), 1.08−1.55 (several peaks, 8H), 3.22 and 3.29 (both dd, Σ 1H, J = 6.2, 3.2 Hz and 7.1, 2.8 Hz), 3.34, 3.35, 3.36 and 3.37 (all s, Σ 6H), 4.52 and 4.53 (both d, Σ 1H, J = 6.2 and 7.1 Hz), 7.18−7.26 (several peaks, 3H), 7.62 (m, 2H); ^{13}C NMR δ 17.1 q, 18.1 q, 22.5 q, 22.6 q, 22.7 q, 24.9 t, 25.2 t, 27.9 d, 33.7 d, 33.9 t, 34.3 d, 35.9 t, 38.9 t, 39.0 t, 53.7 q, 54.1 q, 55.3 q, 55.6 q, 56.4 d, 57.2 d, 106.5 d, 107.2 d, 127.0 d, 128.8 d, 131.0 s, 131.2 s, 134.2 d, 134.4 d; ^{77}Se NMR δ 290.7 and 281.9.

2-Benzyloxy-3-phenylselenenyltetrahydropyran (3h). The crude product was an inseparable 1:3 mixture of the title compound and acetal **4h**. ^{1}H NMR data for the selenide were in good agreement with literature.[20]

2-Cyclohexyl-1,1-dimethoxy-2-phenylselenenylethane (3i). The crude material was a 96:4 mixture of the title compound and unsaturated acetal **4i**. Column chromatography (eluent 1% EtOAc in pentane) afforded 0.288 g (88%) of the selenide **3i** as a colorless oil: ^{1}H NMR δ 1.04−1.36 (several peaks, 4H), 1.45−1.95 (several peaks, 7H), 3.13 (dd, 1H, J = 6.1, 3.4 Hz), 3.34 (s, 3H), 3.38 (s, 3H), 4.51 (d, 1H, J = 6.1 Hz), 7.19−7.28 (several peaks, 3H), 7.61 (m, 2H); ^{13}C NMR δ 26.2 t, 26.3 t, 26.4 t, 30.3 t, 31.8 t, 39.2 d, 54.6 q, 55.4 q, 57.3 d, 106.8 d, 126.9 d, 128.8 d, 131.5 s, 134.0 d. Anal. Calcd for $C_{16}H_{24}O_2Se$: C, 58.71; H, 7.39. Found: C, 58.56; H, 7.33.

3-Cyclohexyl-1,1-dimethoxy-2-phenylselenenylpropane (3j) was prepared essentially (0.78 mmol of Ph_2Se_2 was used at 90 °C and 9 h) according to the general procedure. The crude material was an 88:12 mixture of the title compound and 3-cyclohexyl-1,1-dimethoxy-2-propene **(4j)**. Column chromatography (1% EtOAc in pentane) afforded the pure title compound: yield 78% in 1 mmol scale; ^{1}H NMR δ 0.90 (m, 2H), 1.06−1.29 (several peaks, 4H), 1.48 (m, 1H), 1.53−1.78 (several peaks, 6H), 3.30 (m, 1H), 3.37 (s, 3H), 3.41 (s, 3H), 4.32 (d, 1H, J = 5.0 Hz), 7.21−7.28 (several peaks, 3H), 7.60 (m, 2H); ^{13}C NMR δ 26.0 t, 26.3 t, 26.5 t, 32.2 t, 34.0 t, 35.2 d, 37.4 t, 46.1 d, 55.4 q, 55.5 q, 107.9 d, 127.4 d, 128.8 d, 129.6 s, 134.9 d. Anal. Calcd for $C_{17}H_{26}O_2Se$: C, 59.82; H, 7.68. Found: C, 59.80; H, 7.81.

1,1-Dimethoxy-3-phenyl-2-phenylselenenylpropane (3k). The reaction of 2-bromo-1,1-dimethoxy-3-phenylpropane **(1k)** with PhSeK according to the general procedure afforded an inseparable 1:1 mixture of the title compound and cinnamic aldehyde dimethyl acetal **(4k)**. The crude product was hydrolyzed in an acetone−water mixture (3:1, 4 mL) in the presence of oxalic acid (0.1 g) for 2 h at ambient temperature. Extractive workup and column chromatography (1% EtOAc in pentane) afforded the known 2-phenylselenenyl-3-phenylpropanal (NMR data were in close agreement with literature[6]). Acetalization with MeOH in the presence of *p*-toluenesulfonic acid afforded the title product **4f** (90% purity, the major contaminant was 1,1-dimethoxy-3-phenylpropane): ^{1}H NMR δ 2.92 (dd, 1H, J = 14.2, 8.2 Hz), 3.23 (dd, 1H, J = 14.2, 6.1 Hz), 3.41 (s, 6H), 3.48 (m, 1H), 4.34 (d, 1H, J = 4.0 Hz), 7.20−7.35 (several peaks, 8H), 7.45 (m, 2H); ^{13}C NMR δ 37.0 t, 50.2 d, 55.8 q, 106.8 d, 126.3 d, 127.3 d, 128.2 d, 129.0 d, 129.3 d, 129.7 s, 134.7 d, 139.6 d; ^{77}Se NMR δ 343.3.

1,1-Dimethoxy-2-phenylselenenyl-3,3-dimethylbutane (3m) was prepared in 46% yield essentially according to the general procedure (120 °C for 8 h; at 70 °C the compound is not formed) and purified by column chromatography (eluent 1% Et_2O and 1% Et_3N in pentane): ^{1}H NMR δ 1.09 (s, 9H), 2.97 (d, J = 1.6 Hz, 1H), 3.41 (s, 3H), 3.47 (s, 3H), 4.47 (d, J = 1.6 Hz, 1H), 7.18−7.23 (several peaks, 3H), 7.63 (m, 2H); ^{13}C NMR δ 29.0 q, 35.0 s, 56.2 q, 56.3 q, 64.4 d, 106.6 d, 126.7 d, 128.7 d, 132.9 s, 134.1 d; ^{77}Se NMR δ 284.5. Anal. Calcd for $C_{14}H_{22}O_2Se$: C, 55.81; H, 7.36. Found: C, 55.56; H, 7.28.

The aqueous phase obtained during workup was acidified with HCl (pH = 1), extracted with ether, dried, and concentrated in vacuo. NMR analysis of the residue showed, except for Ph_2Se_2, the presence of 3,3-dimethylbutyric acid: ^{1}H NMR

δ 1.09 (s,9H), 2.26 (s, 2H) (cf. ref 39); ^{13}C NMR δ 29.6 q, 30.6 s, 47.6 t, 178.0 s.

Selenoxide elimination in phenylselenenylacetals was performed by stirring of the selenide **3** (1 mmol), THF (2 mL), 30% H_2O_2 (0.2 mL), and triethylamine (0.2 mL) at ambient temperature (in a larger scale cooling was needed) for 5 h. During this time the solution became opaque. Hexane (10 mL) was then added, and the mixture was washed with a saturated solution of $NaHCO_3$. The organic phase was dried (Na_2SO_4) and concentrated in vacuo. The crude material could either be distilled in vacuo, affording unsaturated acetal **4**, or subjected to acidic hydrolysis (acetone−water 3:1, oxalic acid, rt, 1 h, see the procedure for compound **5c**) to give conjugated enal **5**.

1,1-Dimethoxy-2-hexene (4a). A 9:1 mixture of *E* and *Z* isomers was obtained from 1.856 g of selenide **3a**. Distillation afforded 0.635 g (70%) of the title compound: bp 80 °C (15 Torr) [lit.[40] bp 164 °C (760 Torr)]. *E* Isomer: ^{1}H NMR δ 0.91 (t, J = 7.4 Hz, 3H), 1.40 (sextet, J = 7.4 Hz, 2H), 2.03 (q, J = 7.4 Hz, 2H), 3.31 (s, 6H), 4.69 (d, J = 5.6 Hz, 1H), 5.42 (dd, J = 15.7, 5.6 Hz, 1H), 5.81 (dt, J = 15.7, 6.9 Hz, 1H); ^{13}C NMR δ 13.5 q, 21.9 t, 34.1 t, 52.5 q, 103.4 d, 126.5 d, 135.6 d. Characteristic ^{1}H NMR peaks of the *Z* isomer were found at δ 2.05 (q, J = 7.4 Hz, 2H), 5.05 (d, J = 6.8 Hz, 1H), 5.64 (dt, J = 10.9, 7.7 Hz); ^{13}C NMR δ 13.5 q, 22.4 t, 29.9 t, 52.2 q, 99.4 d, 126.4 d, 135.4d.

2-(1-Hepten-1-yl)-1,3-dioxolane (4e). A 9:1 mixture *E* and *Z* isomers was obtained; yield 74%. ^{1}H NMR data were in close agreement with the literatue.[18]

2-Benzyloxy-5,6-dihydro-2*H*-pyran (4h). Oxidative elimination and column chromatography (1% EtOAc in pentane) afforded the title compound in 56% yield. ^{1}H NMR data were in close agreement with the literature.[20] ^{13}C NMR δ 24.7 t, 57.4 t, 69.2 t, 92.9 d, 125.7 d, 127.5 d, 128.0 d, 128.3 d, 129.2 d, 138.1 s.

2-Decenal (5c). Selenide **4c** (0.155 g, 0.43 mmol), THF (2 mL), triethylamine (0.2 mL), and 30% H_2O_2 (0.2 mL) were stirred at ambient temperature for 5 h. Hexane (5 mL) was then added, and the mixture was treated with saturated $NaHCO_3$ (aq). The organic layer was washed with aqueous NaCl, dried, and concentrated in vacuo. The residue was dissolved in 75% acetone (4 mL) containing oxalic acid (0.1 g) and was stirred at ambient temperature for 1 h. Acetone was distilled off, and the remaining slurry was treated with $NaHCO_3$ (aq) and extracted with ether. The extracts were washed with aqueous NaCl, dried (Na_2SO_4), and concentrated in vacuo. Column chromatography (1.5% EtOAc in pentane) afforded a 9:1 mixture of *E* and *Z* isomers of the title compound as a colorless oil: yield 0.049 g (73%); n^{20}_D 1.4560; ^{1}H NMR data of the *E* isomer were in close agreement with the literature;[41] ^{13}C NMR δ 14.1 q, 22.6 t, 27.8 t, 29.0 t, 29.1 t, 31.7 t, 32.7 t, 132.9 d, 159.1 d, 194.2 d; Characteristic peaks of the *Z* isomer in the ^{1}H NMR spectrum were found at δ 2.60 (q, J = 8.1 Hz, 2H), 5.95 (ddt, J = 11.3, 8.2, 1.6 Hz, 1H), 6.63 (dt, J = 11.3, 8.2 Hz, 1H), 10.08 (d, J = 8.3 Hz, 1H).

10-Hydroxy-2-decenal (5d). A 9:1 mixture of *E* and *Z* isomers was obtained: yield 97% in 5.5 mmol scale; ^{1}H NMR data for the *E* isomer were in close agreement with the literature;[42] ^{13}C NMR δ 25.5 t, 27.6 t, 28.9 t, 29.0 t, 32.5 t, 32.6 t, 62.8 t, 132.9 d, 159.1 d, 194.2 s; characteristic signals in the ^{1}H NMR spectrum of the *Z* isomer were found at δ 2.58 (q, 2H, J = 7.8 Hz), 5.93 (ddt, 1H, J = 11.2, 8.0, 1.6 Hz), 6.61 (dt, 1H, J = 11.2, 8.3 Hz), 10.0 (d, 1H, J = 8.1 Hz).

3-Ethyl-2-heptenal (5f). The crude mixture of selenide **3f** and unsaturated acetal **4f** obtained during selenation of bromide **1f** (1 mmol) was treated with hydrogen peroxide and then subjected to acidic hydrolysis (see the preparation of compound **5c**). Purification by column chromatography (1.5% EtOAc in pentane) afforded 0.070 g (51%) of the title compound as a 1:1 mixture of *E* and *Z* isomers. ^{1}H and ^{13}C NMR data were in close agreement with the literature.[43]

3,7-Dimethyl-2-octenal (5g). The crude mixture of selenide **3g** and unsaturated acetal **4g** obtained during selenation of bromide **1g** was treated with hydrogen peroxide and then subjected to acidic hydrolysis (see the preparation of compound **5c**). Purification by column chromatography (2% EtOAc in pentane) afforded the title compound as a 3:2 mixture of *E* and *Z* isomers: yield 51%; n^{20}_D 1.4652 (lit.[44] n^{20}_D 1.4643). Column chromatography using 1% EtOAc in pentane allowed separation of the isomers (the *Z*-isomer was eluted first). ^{1}H NMR data of both isomers were in close agreement with the literature.[45] *Z* Isomer: ^{13}C NMR δ 22.5 q, 25.0 q, 26.6 t, 27.8 d, 32.7 t, 38.5 t, 128.4 d, 164.8 s, 190.7 s. *E* Isomer: ^{13}C NMR δ 17.5 q, 22.5 q, 24.9 t, 27.8 d, 38.4 t, 40.8 t, 127.3 d, 164.3 s, 191.3 s.

Cyclohexylideneacetaldehyde (5i) was obtained by oxidation/hydrolysis of selenide **3i** (0.5 mmol), following the procedure for the preparation of compound **5c**. Purification by column chromatography (5% ether in pentane) afforded 0.048 g (78%) of the title compound. NMR data were in close agreement with the literature.[46]

***(E)*-3-Cyclohexyl-2-propenal (5j).** The crude mixture of selenide **3j** and unsaturated acetal **4j** obtained during selenation of bromide **1j** was treated with hydrogen peroxide and then subjected to acidic hydrolysis (see the preparation of compound **5c**). Purification by column chromatography (2% EtOAc in pentane) afforded the title compound in 65% yield. NMR data were in close agreement with the literature.[47]

Cinnamic Aldehyde (5k). The crude mixture of selenide **3k** and unsaturated acetal **4k** obtained during selenation of bromide **1k** was treated with hydrogen peroxide and then subjected to acidic hydrolysis (see the preparation of compound **5c**). Purification by column chromatography (3% EtOAc in pentane) afforded the title compound, identical to an authentic sample, in 59% yield.

2-Butyl-2-butenal (5l) and 2-Ethyl-2-hexenal (5l′). The crude mixture of unsaturated acetals **4l** and **4l′** obtained during selenation of bromide **1l** was subjected to acidic hydrolysis as described for the preparation of compound **5c**. A 68:32 mixture of compounds **5l** (9:1 mixture of *E* and *Z* isomers) and **5l′** (2:1 mixture of *E* and *Z* isomers) was formed in 64% yield as determined by ^{1}H NMR using 1,4-dibromobenzene as an internal standard. Column chromatography (1% EtOAc in pentane) afforded a mixture of purified aldehydes in 32% yield. NMR data of the components were in close agreement with literature.[48]

2-Methyl-4-phenyl-2-butene (7) and 2-methyl-4-phenyl-1-butene (8) were obtained as a 2:1 mixture by treatment of bromide **6** with PhSeK according to the general procedure for nucleophilic substitution (20 or 70 °C). Yield of crude material: 82%. ^{1}H NMR data were in close agreement with the literature.[49]

Catalytic Procedure for HBr Elimination from Tertiary Bromides. These experiments were performed as described in the general procedure for nucleophilic substitution with areneselenolates. A catalytic amount (10%) of diphenyl diselenide was used.

1,1-Dimethoxy-2-phenylthiohexane (10a) was prepared in 83% yield from bromoacetal **1b** according to the general procedure for nucleophilic substitution (diphenyl disulfide instead of diselenide). It was purified by column chromatography (1% EtOAc in pentane): ^{1}H NMR δ 0.89 (t, J = 7.3 Hz, 3H), 1.25−1.64 (several peaks, 5H), 1.80 (m, 1H), 3.17 (m, 1H),

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3.37 (s, 3H), 3.43 (s, 3H), 4.31 (d, J = 4.9 Hz, 1H), 7.19−7.31 (several peaks, 3H), 7.46 (d, J = 7.4 Hz, 2H); ^{13}C NMR δ 14.0 q, 22.6 t, 29.1 t, 29.2 t, 52.1 d, 55.3 q, 55.7 q, 107.1 d, 126.7 d, 128.7 d, 131.9 d, 135.7 s. Anal. Calcd for $C_{14}H_{22}O_2S$: C, 66.10; H, 8.72. Found: C, 65.95; H, 8.80. The product could also be prepared by treatment of compound **1b** with thiophenol and K_2CO_3 in DMSO at 70 °C for 7 h.

1,1-Dimethoxy-2-(2,6-dimethylphenylthio)hexane (10b). A mixture of bromoacetal **1b** (0.113 g, 0.5 mmol), 2,6-dimethylthiophenol (0.083 g, 0.6 mmol), K_2CO_3 (0.6 g), and DMSO (2 mL) was degassed and stirred under nitrogen at 80 °C for 7 h. Usual workup followed by column chromatography (eluent 0.5−1% EtOAc and 0.5% Et_3N in pentane) afforded 0.99 g (70%) of the title compound as a colorless oil: ^{1}H NMR δ 0.88 (t, J = 7.1 Hz, 3H), 1.29 (sextet, J = 7.4 Hz, 2H), 1.39−1.60 (several peaks, 3H), 1.76 (m, 1H), 2.56 (s, 6H), 3.03 (m, 1H), 3.15 (s, 3H), 3.36 (s, 3H), 4.19 (d, J = 4.8 Hz, 1H), 7.09 (br s, 3H); ^{13}C NMR δ 13.9 q, 22.2 q, 22.9 t, 29.2 t, 29.3 t, 50.1 d, 54.5 q, 55.2 q, 107.0 d, 128.0 d (two peaks), 133.2 s, 143.1 s. Anal. Calcd for $C_{16}H_{26}O_2S$: C, 68.04; H, 9.28. Found: C, 67.94; H, 9.42.

1,1-Dimethoxy-2-phenyltellurenylhexane (11). A solution of sodium borohydride (0.028 g, 0.75 mmol) in DMF (0.5 mL) was injected dropwise under argon into a degassed solution of diphenyl ditelluride (0.154 g, 0.375 mmol) and ethanol (0.104 g, 2.25 mmol) in DMF (1 mL) until the red color of ditelluride faded away. Bromide **1a** (0.113 g, 0.5 mmol) was added, and the mixture was stirred at 70 °C for 7 h. Aqueous workup followed by column chromatography (1.5% EtOAc in pentane) afforded 0.144 g (82%) of the unstable (solutions of the compound rapidly turned opaque on exposure to the atmosphere) title compound. ^{1}H NMR analysis of freshly evaporated samples indicated ca. 90% purity of the title compound: ^{1}H NMR δ 0.82 (t, J = 7.3 Hz, 3H), 1.21 (sextet, J = 7.5 Hz, 2H), 1.34 (m, 1H), 1.45 (m, 1H), 1.64 (m, 1H), 1.76 (m, 1H), 3.39 (s, 3H), 3.40 (s, 3H), 3.45 (m, 1H), 4.37 (d, J = 4.9 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1h), 7.83 (d, J = 6.8 Hz, 2H); ^{13}C NMR δ 13.9 q, 22.4 t, 31.4 t, 31.7 t, 35.1 d, 54.6 q, 55.6 q, 108.3 d, 112.1 s, 127.8 d, 128.9 d, 140.1 d.

3-Bromo-3-ethyl-7-octene (12). The reaction of ethylmagnesium bromide (21 mmol) with ethyl 5-hexenoate (8.7 mmol) in diethyl ether afforded after aqueous workup 3-ethyl-7-octen-3-ol (1.35 g, 98%): ^{1}H NMR δ 0.84 (t, 6H, J = 7.6 Hz), 1.18 (br s, 1H), 1.36−1.48 (several peaks, 4H), 1.45 (q, J = 7.6 Hz, 4H), 2.04 (m, 2H), 4.97 (m, 2H), 5.80 (m, 1H); ^{13}C NMR δ 7.7q, 22.7 t, 30.9 t, 34.2 t, 37.6 t, 74.5 s, 114.5 t, 138.8 d. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.94; H, 12.95. The tertiary alcohol (0.3 g) was vigorously stirred with concentrated HBr (2 mL) for 0.5 h, and the mixture was then diluted with water and extracted with pentane. The extracts were washed with water, dried (Na_2SO_4), and concentrated in vacuo to afford the title compound (the amount of byproducts increases considerably with a longer reaction time): yield 0.282 g (67%); ^{1}H NMR δ 0.97 (t, J = 7.2 Hz, 6H), 1.25 (m, 2H), 1.53 (m, 2H), 1.87 (q, J = 7.2 Hz, 4H), 2.07 (q, J = 7.1 Hz, 2H), 5.00 (m, 2H), 5.80 (m, 1H); ^{13}C NMR δ 9.8 q, 24.4 t, 33.7 t, 34.6 t, 40.9 t, 80.6 s, 114.9 t, 138.3 d.

1-Benzyselenenyl-4-bromo-4-ethylhexane (13). Dibenzyl diselenide (0.893 g, 2.625 mmol) was titrated in absolute ethanol (40 mL) under nitrogen with sodium borohydride (ca. 0.3 g) until the yellow color of diselenide had disappeared. Ethyl 4-bromobutanoate (0.975 g, 5 mmol) was then added, and the mixture was left overnight. Ethanol was distilled off, and the residue was treated with $NaHCO_3$ (aq) and extracted with ether. After drying ($CaCl_2$) and concentration in vacuo, column chromatography (1−3% EtOAc in pentane) afforded 1.160 g (81%) of ethyl 4-benzylselenenylbutanoate as a yellowish oil: ^{1}H NMR δ 1.25 (t, J = 7.2 Hz, 3H), 1.94 (m, 2H), 2.38 (t, J = 7.3 Hz, 2H), 2.53 (t, J = 7.2 Hz, 2H), 3.77 (s, 2H), 4.12 (q, J = 7.2 Hz, 2H), 7.15−7.30 (several peaks, 5H); ^{77}Se NMR δ 250.7. A solution of this ester (0.844 g, 2.96 mmol) in ether (2 mL) was added dropwise to freshly prepared ethylmagnesium bromide (6 mmol) in ether (10 mL) and stirred for 3 h at ambient temperature. After workup with aqueous NH_4Cl, extraction, drying ($MgSO_4$), evaporation of the solvents in vacuo and column chromatography (3−10% EtOAc in pentane), 0.763 g (86%) of 1-benzylselenenyl-4-ethyl-4-hexanol was isolated as a colorless oil: ^{1}H NMR δ 0.83 (t, J = 7.5 Hz, 6H), 1.09 (br s, 1H), 1.42 (q, J = 7.5 Hz, 4H), 1.46 (m, 2H), 1.59 (m, 2H), 2.49 (t, J = 7.2 Hz, 2H), 3.78 (s, $^2J_{Se-H}$=12.9 Hz, 2H), 7.21 (m, 1H), 7.26−7.32 (several peaks, 4H); ^{13}C NMR δ 7.7 q, 24.2 t, 24.6 t, 27.0 t, 30.9 t, 38.4 t, 74.4 s, 126.6 d, 128.4 d, 128.8 d, 139.5 s; ^{77}Se NMR δ 255.3. Anal. Calcd for $C_{15}H_{24}OSe$: C, 60.19; H, 8.08. Found: C, 60.02; H, 8.22. The tertiary alcohol thus prepared (0.599 g, 2 mmol) was vigorously stirred with 48% HBr (6 mL) at ambient temperature for 3 h. Water (10 mL) was added, and the product was extracted with pentane. The extracts were washed with NaBr (aq), dried ($MgSO_4$), and concentrated in vacuo to leave the title compound: yield 0.522 g (72%); ^{1}H NMR δ 0.90 (t, J = 7.5 Hz, 6H), 1.76 (m, 2H), 1.83 (q, J = 7.5 Hz, 4H), 1.85 (m, 2H), 2.48 (t, J = 7.2 Hz, 2H), 3.78 (s, $^2J_{Se-H}$=12.9 Hz, 2H), 7.21 (m, 1H), 7.24−7.31 (several peaks, 4H); .^{13}C NMR δ 9.7 q, 23.7 t, 25.9 t, 27.0 t, 34.6 t, 41.5 t, 79.8 s, 126.7 d, 128.5 d, 128.8 d, 139.3 s; ^{77}Se NMR δ 256.1. Anal. Calcd for $C_{15}H_{23}BrSe$: C, 49.74; H, 6.40. Found: C, 49.93; H, 6.56.

A mixture of 3-ethyl-3,7-octadiene and 3-ethyl-2,7-octadiene (14) was obtained by treatment of bromide **12** (1 mmol) with PhSeK according to the general procedure for nucleophilic substitution; yield 0.086 g (62%). The crude product showed characteristic peaks in the ^{1}H NMR at δ 0.95 (t, J = 7.7 Hz), 0.98 (t, J = 7.5 Hz), 1.28 (m), 1.46 (m), 1.58 (d, J = 6.7 Hz), 2.03 (m), 4.88−5.05 (m), 5.19 (m), 5.82 (m). Hydrogenation over 5% Pd/C in EtOH at 1 atm of H_2 and 50 °C for 3 h afforded the known[50] 3-ethyloctane as the only product: ^{1}H NMR δ 0.84 (t, J = 6.9 Hz, 6H), 0.89 (t, J = 6.3 Hz, 3H), 1.02−1.38 (several peaks, 13H); ^{13}C NMR δ 10.9 q, 14.2 q, 22.8 t, 25.5 t, 26.5 t, 32.4 t, 32.7 t, 40.4 d; MS (m/z) M^+ 142.

A mixture of 1-benzylselenenyl-4-ethyl-3-hexene and (*E,Z*)-1-benzylselenenyl-4-ethyl-4-hexene (15) was obtained as a 27/31/42 mixture by treatment of bromide **13** (1 mmol) with PhSeK according to the general procedure for nucleophilic substitution. The crude material was dissolved in absolute ethanol (3 mL) and titrated under nitrogen with sodium borohydride until the yellow color had disappeared. The mixture was cooled to −50 °C, treated with bromoacetic acid (0.3 g), and allowed to warm to ambient temperature. Ethanol was distilled off, and the residue was treated with $NaHCO_3$ (aq) and extracted with ether. The extracts were dried ($CaCl_2$), concentrated in vacuo, and subjected to column chromatography (0.5−2% EtOAc in pentane) to afford 0.227 g (81%) of the isomeric mixture of title compounds as a colorless oil: ^{1}H NMR δ 0.94−1.02 (several peaks), 1.59 (br d, J = 6.8 Hz), 1.71 (m), 1.95−2.06 (several peaks), 2.10 (t, J = 8.3 Hz), 2.36 (q, J = 7.5 Hz), 2.47−2.53 (several peaks), 3.79 (s), 3.80 (s), 3.81 (s), 5.08 (t, J = 6.6 Hz, 0.27 H), 5.17 (q, J = 6.6 Hz, 0.31 H), 5.24 (q, J = 6.6 Hz, 0.42 H), 7.23 (m), 7.28−7.33 (several peaks); ^{13}C NMR δ 12.7 q, 12.8 q, 12.9 q, 13.2 q, 13.3 q, 22.6 t, 23.2 t, 23.7 t, 23.8 t, 24.0 t, 26.8 t, 26.9 t, 27.0 t, 28.5 t, 28.6 t, 28.7 t, 29.0 t, 29.5 t, 30.0 t, 36.6 t, 117.8 d, 118.5 d, 121.2 d, 126.5 d, 128.4 d, 128.7 d, 139.4 s, 139.5 s, 140.6 s, 144.2 s; ^{77}Se NMR δ 253.9, 256.4, and 260.9. Anal. Calcd for $C_{15}H_{22}Se$: C, 64.05; H, 7.88. Found: C, 63.91; H, 8.00.

2-Cyclopropyl-1,1-diethoxy-2-phenylselenenylethane (16), 1-(Diethoxymethyl)-2-phenylselenenylcyclobutane (17), and 1,1-Diethoxy-5-phenylselenenyl-2-pentene (18). The reaction of 2-bromo-2-cyclopropyl-1,1-diethoxyethane **(1n)** (1 mmol) with PhSeK was performed according to the general procedure for nucleophilic substitution. The crude material (62% yield) was a 59:11:30 mixture of selenides **16**, **17**, and **18**. Column chromatography (1−4% EtOAc in pentane) gave an inseparable 85:15 mixture (35% total yield) of isomeric compounds **16** and **17**. Anal. Calcd for $C_{15}H_{22}O_2Se$: C, 57.51; H, 7.08. Found: C, 57.29; H, 7.15. 1,1-Diethoxy-5-phenylselenenyl-2-pentene during chromatography

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underwent hydrolysis to give the corresponding aldehyde (*E*)-5-phenylselenenyl-2-pentenal (15% isolated yield). Compound **16**: ^{1}H NMR δ 0.07 (m, 1H), 0.36 (m, 1H), 0.46 (m, 1H), 0.64 (m, 1H), 1.09 (m, 1H), 1.16 (t, J = 7.6 Hz, 3H), 1.21 (t, J = 7.6 Hz, 3H), 2.66 (dd, J = 10.1, 4.1 Hz, 1H), 3.54 (m, 2H), 3.74 (m, 2H), 4.58 (d, J = 4.1 Hz, 1H), 7.17−7.28 (several peaks, 3H), 7.65 (m, 2H); ^{13}C NMR δ 4.9 t, 7.1 t, 13.2 d, 15.2 q, 15.4 q, 54.8 d, 63.9 t, 64.0 t, 105.6 d, 127.3 d, 128.6 d, 129.8 s, 135.5 d; ^{77}Se NMR δ 362.1. Compound **17**: characteristic peaks in the ^{1}H NMR spectrum were found at δ 2.14 (m, 2H), 2.46 (m, 1H), 2.90 (m, 1H), 4.20 (q, J = 7.4 Hz, 1H), 4.83 (d, J = 7.9 Hz, 1H), 7.43 (m, 2H); ^{13}C NMR δ 15.2 q, 15.5 q, 21.8 t, 29.4 t, 38.2 d, 42.1 d, 60.7 t, 62.0 t, 103.8 d, 126.3 d, 128.8 d, 131.5 s, 132.1 d; ^{77}Se NMR δ 335.4. **(*E*)-5-Phenylselenenyl-2-pentenal:** ^{1}H NMR δ 2.72 (q, J = 7.1 Hz, 2H), 3.02 (t, J = 7.5 Hz, 2H), 6.12 (ddt, J = 15.7, 7.8, 1.6 Hz, 1H), 6.81 (dt, J = 15.7, 6.8 Hz, 1H), 7.22−7.31 (several peaks, 3H), 7.51 (m, 2H), 9.48 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 25.0 t, 33.1 t, 127.4 d, 129.0 s, 129.2 d, 133.3 d, 133.6 d, 156.1 d, 193.7 d; ^{77}Se NMR δ 304.9.

(*R,S*)-2-Phenyl-2-(1-bromoethyl)-1,3-dioxolane (19) was prepared from 2-ethyl-2-phenyl-1,3-dioxolane following the general procedure for bromination of acetals. ^{1}H NMR data were in accordance with the literature.[11]

(*S*)-2-Phenyl-2-(1-bromoethyl)-1,3-dioxolane ((*S*)-19). Propiophenone was ketalized with dimethyl L-tartarate, and (4*R*,5*R*)-2-ethyl-2-phenyl-1,3-dioxolane-4,5-dicarboxylic acid dimethyl ester thus obtained was α-brominated as described,[15] affording a 9:1 mixture of diastereomers, (4*R*,5*R*,1′*S*)-2-phenyl-2-(1′-bromoethyl)-1,3-dioxolane-4,5-dicarboxylic acid dimethyl ester being the major one. The product thus obtained (1 g) was heated at 80 °C in a mixture of methanesulfonic acid (3 mL), methanol (1 mL), and water (1 mL) for 3 h. NMR analysis at this point showed 22% conversion to ketone. Further heating did not improve conversion but rather increased racemization. The reaction mixture was poured onto crushed ice and extracted with ether. The extracts were washed with brine, dried, evaporated, and immediately subjected to column chromatography (eluent 3% EtOAc in pentane), affording the corresponding ketone (unreacted ketal could be recovered by further elution with 30% EtOAc in pentane). The ketone was heated (70 °C, 4 h) with trimethyl orthoformate (0.4 mL), ethylene glycol (0.5 mL), and methanesulfonic acid (0.1 mL). Aqueous workup and extraction afforded the title compound and its enantiomer ((*R*)-**19**) as a 7:3 mixture (GC analysis using a chiral column), corresponding to 40% ee: $[\alpha]^{25}_D$ = +5.9° ($CHCl_3$). Aldehydes acetalized with dimethyl L-tartarate were α-brominated with lower diastereoselectivity (typically 40% de). However, we were unable to remove the chiral auxiliary from these materials.

(*R,S*)-2-Phenyl-2-[1-(4-methoxyphenylselenenyl)ethyl]-1,3-dioxolane (20) was prepared from racemic bromoketal **19** (0.129 g, 0.5 mmol) according to the general procedure for nucleophilic substitution [bis(4-methoxyphenyl) diselenide was used]. NMR analysis of the crude material showed 40% conversion to the title compound, which was isolated (0.060 g, 33% yield) by column chromatography (2−4% EtOAc in pentane): ^{1}H NMR δ 1.27 (d, 3H, J = 7.2 Hz), 3.60 (q, 1H, J = 7.2 Hz), 3.78 (s, 3H), 3.83 (m, 2H), 4.14 (m, 2H), 6.77 (d, 2H, J = 8.8 Hz), 7.28−7.36 (several peaks, 3H), 7.43−7.53 (several peaks, 4H); ^{13}C NMR δ 17.7 q, 48.8 d, 55.2 q, 65.1 t, 65.3 t, 111.1 s, 114.4 d, 119.7 s, 126.4 d, 127.9 d, 128.1 d, 137.3 d, 140.6 s, 159.4 s. Anal. Calcd for $C_{18}H_{20}O_3Se$: C, 59.51; H, 5.55. Found: C, 59.37; H, 5.42.

(*R*)-2-Phenyl-2-[1-(4-methoxyphenylselenenyl)ethyl]-1,3-dioxolane ((*R*)-20) was similarly prepared from bromoketal (*S*)-**19**. NMR data were identical to those of the racemate **20**. HPLC analysis on a chiral column showed the same two peaks as was present in the racemate, but in a 3:7 ratio (corresponding to 40% ee): $[\alpha]^{25}_D$ = −13.5° ($CHCl_3$). In the assignment of the product as resulting from inversion of configuration, we assume that bromides and arylselenides of the same absolute configuration show the same sign of rotation.[51]

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Supporting Information Available: ^{1}H and/or ^{13}C spectra of 10-acetoxy-1,1-dimethoxydecane, 3-cyclohexyl-1,1-dimethoxypropane, 1,1-dimethoxy-3-ethyl-heptane, compounds **1g**,**h**, **11**, **12**, and (*E*)-5-phenylselenenyl-2-pentenal. This material is available free of charge via the Internet at http://pubs.acs.org.

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