117712-65-9; **8**, 117712-66-0; *dl*-**9**, 20007-99-2; **10**, 117712-67-1; **11**, 504-20-1; **12**, 117712-68-2; **13**, 78-59-1; (*E*)-**14**, 117712-69-3; (*Z*)-**14**, 117712-86-4; **15**, 765-43-5; *meso*-**16**, 117712-70-6; *dl*-**16**, 117712-90-0; (*E*)-**17**, 117712-71-7; (*Z*)-**17**, 117712-87-5; **18**, 6485-40-1; **19**, 117712-72-8; **20**, 117773-77-0; **21**, 117712-73-9; **22a**, 13747-73-4; **22b**, 89-82-7; *dl*-**23a**, 64870-43-5; **23b**, 117773-78-1; **24**, 20489-87-6; **25** (isomer 1), 40285-80-1; **25** (isomer 2), 40285-62-9; **26**, 43108-69-6; *dl*-**27**, 117712-74-0; *dl*-**28**, 117712-75-1; **29**, 2758-17-0; *dl*-**30**, 117712-76-2; **31**, 825-25-2; *dl*-**32**, 117712-77-3; *dl*-**33**, 3063-68-1; **34a**, 108762-96-5; **34b**, 117712-89-7; *cis*-**35**, 74310-83-1; *trans*-**35**, 74272-01-8; **36**, 117712-78-4; **37**, 117712-79-5; **38**, 117712-80-8; *dl*-**39** (isomer 1), 117712-81-9; *dl*-**39** (isomer 2), 117712-92-2; *dl*-**40**, 117712-82-0; **41** (isomer 1), 117712-83-1; **41** (isomer 2), 117712-93-3; **41** (isomer 3), 117712-94-4; **41** (isomer 4), 117712-95-5; *cis*-**42**, 117712-91-1; *trans*-**42**, 117712-84-2; $TiCl_4$, 7550-45-0; Mg, 7439-95-4; *t*-BuOH, 75-65-0; CH_2=$CHCH_2Br$, 106-95-6; CH_3CH=$CHCH_2Cl$, 591-97-9; $C_6H_5CH_2Br$, 100-39-0; mesitylene, 108-67-8; diethyl mesoxalate, 609-09-6.

Acetoxyselenenylation of Olefins for the Preparation of Vinylic and Allylic Acetates

Lars Engman

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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Terminal and 1,2-disubstituted olefins were irreversibly acetoxyselenenylated by treatment with PhSeBr in an acetate buffer solution. Styrene derivatives yielded only Markovnikov adducts whereas simple terminal olefins and olefins containing an allylic oxygen substituent (acyloxy or aryloxy group) afforded significant amounts (50–85%) of the anti-Markovnikov isomer. The product mixtures were isomerized to contain 90–97% of the Markovnikov product by treatment with a catalytic amount (6–41%) of BF_3·OEt_2 in chloroform. Oxidation (SO_2Cl_2/hydrolysis or MCPBA) of the isomerized products and selenoxide elimination at elevated temperature toward the acetoxy group afforded enol acetates in fair yields. The selenoxides of the anti-Markovnikov isomers (unisomerized mixtures) spontaneously eliminated, in the presence of the selenoxides of the Markovnikov isomer, to give allylic acetates in good yields at ambient temperature.

Introduction

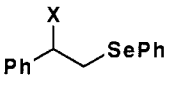
The oxyselenenylation reaction is a very useful procedure for the anti-1,2-addition of an organylseleno group and an oxygen substituent (HO, RO, RCO_2) to an olefin.[1] In general, Markovnikov addition to the olefin predominates (trisubstituted olefins, styrene derivatives), but anti-Markovnikov products are sometimes formed in substantial amounts (monosubstituted olefins). Since the adducts undergo facile selenoxide elimination regiospecifically *away* from the oxygen substituent, they have proven very useful for the preparation of allylic alcohols, ethers, and esters.

Much less attention has been directed to reactions where the selenoxide elimination occurs *toward* an oxygen substituent. Oxyselenenylation/selenoxide elimination would in this case convert olefins to ketones, enol ethers, or enol esters. This type of reaction would occur only if no other β-hydrogens are available for elimination, or, for steric reasons, the selenoxide function is unable to orient itself *syn* to the other β-hydrogens in the molecule. The first example of an elimination reaction toward oxygen was reported by Ho and Hall[2] in a deprotection procedure for alcohols protected as 2-(phenylseleno)ethyl ethers (enol ether involved). More recently the reaction was applied to the preparation of ketene acetals,[3] enol ethers,[4] enol acetates,[5,6] ketones,[6] an enol carbonate,[7] and an enol phosphate.[8]

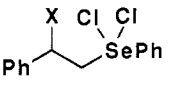
In this paper we report the acetoxyselenenylation of terminal and 1,2-disubstituted olefins and, after proper manipulations, the conversion of the products into synthetically useful[9] vinylic or allylic acetates.

Results

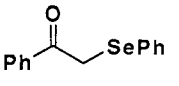
Initially, in order to study the influence of the β-substituent in a selenoxide elimination reaction toward oxygen, we prepared the hydroxy-, methoxy-, and acetoxyselenenylation products **1a–c** from styrene. After SO_2Cl_2



1 a X=OH
b X=OMe
c X=OAc



2 a X=OH
b X=OMe
c X=OAc



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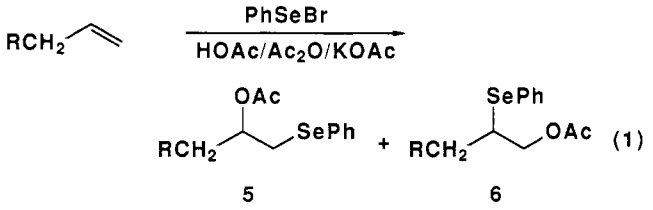
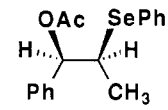
chlorination and hydrolysis of the resulting selenium(IV) dichlorides **2a–c** to the corresponding selenoxides, the eliminations were thermally induced in a two-phase system (aqueous $NaHCO_3$/benzene) at 100 °C analogously to a known procedure.[10] The reaction of the hydroxy compound **2a** yielded acetophenone in modest yield (32%) in addition to phenacyl phenyl selenide (**3**) (33% yield). A similar elimination reaction of the β-methoxy compound **2b** produced acetophenone and phenacyl phenyl selenide as well as the selenide **1b** (relative amounts = 12:56:32). Only the β-acetoxy compound **2c** produced the desired elimination product, α-acetoxystyrene (**4**), in fair yield (66%), together with selenide **1c** (23%). The failure of the selenoxide elimination reaction for enol ether synthesis has been previously noted[11] and tentatively explained by assuming a secondary reaction of the enol ether with PhSeOH (a byproduct of the selenoxide elimination reaction). A similar reaction could also account for the formation of compound **3** in the ketone synthesis. Out of the three oxygen substituents tried, only the acetoxy group seems to be compatible, in the product, with the forcing reaction conditions often needed to carry out a selenoxide elimination reaction toward an oxygen substituent.

Acetoxyselenenylation is most conveniently performed by treatment of an olefin with a benzeneselenenyl halide in an acetic acid/acetate buffer solution.[12] Other methods involve the generation of PhSeOAc from benzeneseleninic acid[13] or diphenyl diselenide[14,15] by chemical or electrochemical methods. MeSeOAc, generated from dimethyl selenoxide, has also been added to olefins.[16]

Regiochemistry. Concerning the regiochemistry of addition, early observations indicated that terminal olefins were acetoxyselenenylated[12] (or trifluoroacetoxyselenenylated[17]) with poor regiocontrol. We have treated a number of terminal olefins with PhSeBr in acetic acid/acetic anhydride containing KOAc and studied the regiochemistry of addition by using ^1H NMR spectroscopy (eq 1).



As shown in Table I, simple terminal olefins were acetoxyselenenylated with almost no regiocontrol whereas olefins containing an oxygen substituent (acyloxy or aryloxy group) in the allylic or homoallylic position showed a marked preference for anti-Markovnikov addition. On the other hand, styrene was acetoxyselenenylated to give the Markovnikov adduct **1c** (90% yield), free of its regioisomer. (*E*)- and (*Z*)-1-phenyl-1-propene were functionalized with similar regiocontrol to give adducts **7** (97%)



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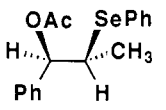

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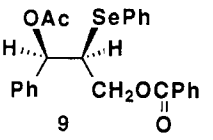

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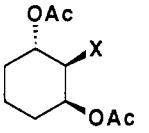
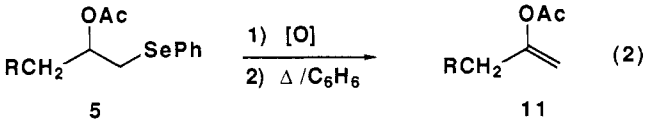


10 a X=SePh
b X=$SeCl_2Ph$

and **8** (99%), respectively. Another styrene derivative, cinnamyl benzoate, when submitted to the usual reaction conditions, yielded selenide **9** (95%) as the only regioisomer. As another example of an unsymmetrical 1,2-disubstituted olefin, 2-cyclohexen-1-ol acetate yielded adduct **10a**, isolated as its crystalline *Se,Se*-dichloride **10b** in 58% overall yield.

Isomerization Reactions. The addition of benzeneselenenyl halides to terminal olefins is known to occur preferentially anti-Markovnikov at low temperature (−78 °C). However, at elevated temperature the thermodynamically more stable, terminally phenylselenenylated products are formed by spontaneous isomerization of the former.[18] We envisaged a similar isomerization also for acetoxyselenenylation products. When a 50:50 mixture of selenides **5a** + **6a** was heated at reflux in acetic acid containing potassium acetate,[19] the slow isomerization to the Markovnikov product was observed (**5a**:**6a** = 92:8 after 72 h). It was also found that the isomerization occurred in chloroform solution at ambient temperature in the presence of a catalytic amount of boron trifluoride etherate (**5a**:**6a** = 96:4 after 24 h). By using 0.05–0.41 equiv of the catalyst, all but one[20] of the product mixtures **5** + **6** could be isomerized to contain 90–97% of the Markovnikov product (see Table I). The isomerizations were always accompanied by some loss of material due to decomposition of the selenides.

Elimination Reactions. With the β-acetoxyalkyl phenyl selenides **5** in hand, the eliminations to give vinylic acetates (eq 2) were attempted as described above (SO_2Cl_2 chlorination, with or without isolation of a selenium(IV) dichloride and hydrolytic selenoxide elimination in a two-phase system at 100 °C; method A). In an alternative



procedure, the selenides were oxidized with *m*-chloroperbenzoic acid and the resulting selenoxides thermolyzed in refluxing benzene (method B). As observed in the preparation of compound **4**, the enol acetate formed was always contaminated with a small amount of its corresponding selenide precursor **5**. However, this was efficiently removed as a residue by Kugelrohr distillation. Fair yields of the desired vinylic acetates **11**, contaminated only by traces of allylic acetates (from the eliminations of the small amounts of anti-Markovnikov isomers **6**), were usually obtained (Table II, entries 1–7).

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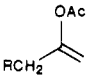
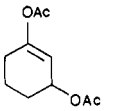
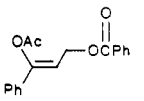
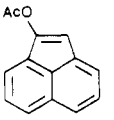
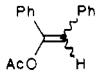
(18) Raucher, S. *J. Org. Chem.* **1977**, *42*, 2950.
(19) In the absence of KOAc the selenides were rapidly decomposed if heated at reflux in acetic acid.
(20) The isomerization of selenides **5e** + **6e** produced a complex product mixture due to migration of the benzoyloxy group from the 1- to the 2-position.

Table I. Acetoxyselenenylation of Terminal Olefins. BF_3-Catalyzed Isomerization of the Adducts

olefin	product	yield, %	isomer distribution 5:6 initially	isomer distribution 5:6 after isomerization	isomerization yield, %
1-octene	**5a** + **6a** (R = C_5H_{11})	97	50:50	96:4	81
1-dodecene	**5b** + **6b** (R = C_9H_{19})	98	51:49	96:4	86
allylbenzene	**5c** + **6c** (R = C_6H_5)	77	31:69	96:4	76[a]
allyl acetate	**5d** + **6d** (R = $CH_3C(O)O$)	67	20:80	97:3	75
allyl benzoate	**5e** + **6e** (R = $C_6H_5C(O)O$)	86	16:84	–	–
allyl phenyl ether	**5f** + **6f** (R = C_6H_5O)	98	15:85	90:10	56
3-buten-1-ol benzoate	**5g** + **6g** (R = $C_6H_5C(O)OCH_2$)	99	35:65	93:7	*b*

[a] Overall yield after isomerization + SO_2Cl_2 chlorination. [b] Not determined.

Table II. Preparation of Vinylic and Allylic Acetates by Using the Selenoxide Elimination Reaction

entry	starting material	elimination[a] method	product	yield, %
				
1	**5a**:**6a** = 96:4	A	**11a**, R = C_5H_{11}	71
2	**5b**:**6b** = 96:4	A	**11b**, R = C_9H_{19}	59
3	**5b**:**6b** = 96:4	B	**11b**, R = C_9H_{19}	76
4	**5c**:**6c** = 96:4	A	**11c**, R = C_6H_5	68[b]
5	**5d**:**6d** = 97:3	A	**11d**, R = $CH_3C(O)O$	64[b]
6	**5f**:**6f** = 90:10	B	**11e**, R = C_6H_5O	74
7	**5g**:**6g** = 93:7	A	**11f**, R = $C_6H_5C(O)OCH_2$	48[c]
8	**10a**	A	 **12**	43[b]
9	**10a**	B	**12**	29
10	**9**	C	 **13**	44[b]
11	**14**	B[d]	 **16**	69
12	**17**	B[d]	 **18**	96
13	**7**	C	 **19**	82
14	**8**	C	**19**	82
			$RCH{=}CHCH_2OAc$	
15	**5a**:**6a** = 50:50	C	**20a**, R = C_5H_{11}, *E*:*Z* = 4:1	89[e]
16	**5c**:**6c** = 31:69	C	**20b**, R = C_6H_5, *E* isomer only	100[e]
17	**5g**:**6g** = 35:65	C	**20c**, R = $C_6H_5C(O)OCH_2$, *E*:*Z* = 83:17	86[e]
18	**5d**:**6d** = 20:80	C	**20d**, R = $CH_3C(O)O$, *E*:*Z* = 38:62	24[e]
19	**5d**:**6d** = 20:80	B[d]	**20d**, R = $CH_3C(O)O$, *E*:*Z* = 40:60	86[e]

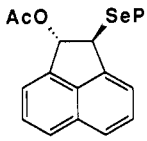
[a] For details, see text. [b] Yield based on *Se*,*Se*-dichloride (see Experimental Section). [c] Overall yield after isomerization, chlorination, and elimination. [d] Elimination at ambient temperature in CH_2Cl_2. [e] Yield based on the amount of anti-Markovnikov isomer present in the selenide mixture.

The elimination of selenide **10a** could also occur only toward an oxygen substituent. However, the yield of compound **12** was modest when either of the elimination procedures was used (Table II, entries 8, 9).

According to ^1H NMR analysis of the crude reaction product, the selenoxide elimination of selenide **9** occurred regiospecifically toward the acetoxy group when the reaction was carried out at ambient temperature (SO_2Cl_2 chlorination in CH_2Cl_2 and treatment with aqueous $NaHCO_3$ at ambient temperature; method C). The pure compound **13** was isolated in 44% yield after flash chromatography and recrystallization.

In principle, olefins containing no allylic hydrogens would only give rise to vinylic acetates when submitted to the acetoxyselenenylation–selenoxide elimination reaction sequence. To confirm this hypothesis, acenaphthylene was

acetoxyselenenylated to give selenide **14** in 72% yield. However, upon treatment with SO_2Cl_2 in chloroform, *trans*-1-acetoxy-2-chloroacenaphthene (**15**) was formed in



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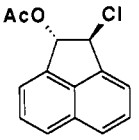

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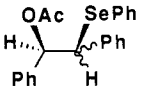

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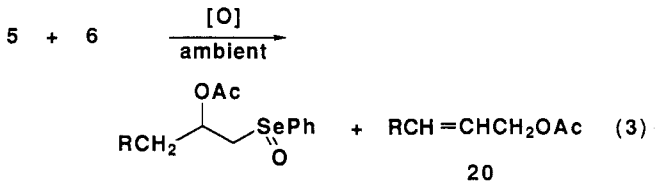
78% yield (due to 1,2-migration of chlorine from selenium to carbon) instead of the expected selenium(IV) dichloride. When *m*-chloroperbenzoic acid was used for the oxidation (elimination at ambient temperature), the desired vinylic acetate **16** was obtained in 69% yield. When acetoxyselenenylated, (*Z*)-1,2-diphenylethylene produced a 39:61 mixture (86% yield) of the two possible stereoisomers **17** (syn + anti addition). Selenoxide elimination of the mixture (method B; ambient temperature) produced the two enol acetates **18** as a mixture. Alkaline hydrolysis to give benzyl phenyl ketone provided additional support for the proposed structures. (*E*)-1,2-Diphenylethylene failed to react under the usual acetoxyselenenylation conditions.

In general, allylic acetates are formed in the selenoxide elimination reaction by using milder conditions than those required for the preparation of vinylic acetates. For example, when compounds **7** and **8** were submitted to the mild elimination conditions of method C, the allylic acetate **19** was isolated in 82% yield from both reaction mixtures (Table II, entries 13, 14). Therefore, by selective elimination of the anti-Markovnikov isomer **6** away from the acetoxy group, it should be possible to obtain an allylic acetate **20** from the elimination of a mixture of selenides **5** + **6** (eq 3).



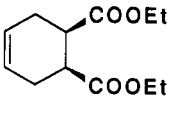
(3)

20

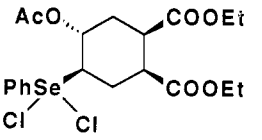
In fact, by using the mild conditions already described (method C), several allylic acetates **20** could be prepared in good yields, free of their corresponding vinylic acetates **11** (Table II, entries 15–17). The workup procedure included flash chromatography (to remove any selenoxide present) and Kugelrohr distillation. As seen from Table II, an *E*/*Z* mixture of allylic acetates was usually isolated.

It was also found that compound **6d** could be oxidatively eliminated under mild conditions in the presence of its regioisomer **5d** to give a vinylic acetate **20d** as an *E*/*Z* mixture. The poor product yield obtained by using method C was significantly improved when *m*-chloroperbenzoic acid was used for the oxidation step (Table II, entries 18, 19).

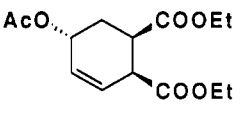
It is obvious from our results that allylic oxygen substituents have a strong influence on the regiochemistry of the acetoxyselenenylation reaction, thus favoring anti-Markovnikov addition to terminal olefins. We were curious to see if this effect could be synthetically useful in other systems with other directing groups. To this end, *cis*-4-cyclohexene-1,2-dicarboxylic acid diethyl diester (**21**) was submitted to the usual acetoxyselenenylation conditions and the product SO_2Cl_2 chlorinated to give an isomerically pure,[21] crystalline, selenium(IV) dichloride **22** in 77% overall yield. Hydrolytic selenoxide elimination (method C) slowly produced compound **23**, free of any regioisomers (96% yield after 21 days). The ^1H NMR data



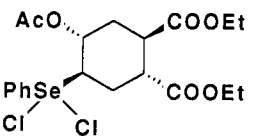
21



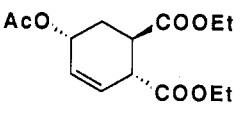
22



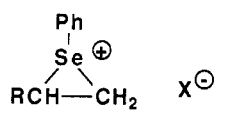
23



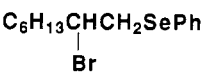
24



25



26



27

of the material suggest a conformation of the molecule where the acetoxy group and the allylic ethoxycarbonyl group are trans to each other, and pseudoaxial, with the remaining ethoxycarbonyl group occupying a pseudoequatorial position. According to a crude molecular mechanics calculation,[22] this conformation is energetically slightly favored over the other possible pseudochair form.

Compound **23** would result, after chlorination and elimination away from the acetoxy group, if the pseudoaxial ethoxycarbonyl group of diester **21** is directing the attack of the selenium electrophile to occur syn to itself with acetate attacking from the opposite side of the double bond.

For reference purposes (only one product possible for symmetry reasons), *trans*-4-cyclohexene-1,2-dicarboxylic acid diethyl diester was also carried through the elimination sequence (91% yield of selenium(IV) dichloride **24** and 98% yield of allylic acetate **25**). According to ^1H NMR analysis, the acetoxy group of compound **25** occupied a pseudoaxial position whereas the two ethoxycarbonyl groups were pseudoequatorially arranged.

Discussion

It is generally accepted that selenium electrophiles PhSeX react with olefins to produce seleniranium ions **26**. Nucleophilic attack at the terminal, sterically less hindered carbon then gives the anti-Markovnikov adduct, whereas attack at the nonterminal, sterically more hindered but more positively charged, carbon provides the Markovnikov product.

By using the system PhSeBr/HOAc/Ac_2O/KOAc for acetoxyselenenylation it is not clear whether the addition involves a direct reaction of PhSeOAc or solvolysis of a preformed PhSeBr adduct. We observed that treatment of 2-bromooctyl phenyl selenide (**27**) with HOAc/Ac_2O/KOAc produced the same isomeric mixture of selenides

(21) *cis*-4-Cyclohexene-1,2-dicarboxylic acid dimethyl diester has been reported to produce a mixture of regioisomers when treated with PhSeCl: Garratt, D. G.; Ryan, M. D.; Kabo, A. *Can. J. Chem.* **1980**, *58*, 2329.

(22) Software: SYBYL from Tripos Associates, Inc., St. Louis, MO, running on a Micro VAX system under VMS. Hardware: Evans & Sutherland PS 390 graphics system.

5a/**6a** as was obtained in the original acetoxyselenenylation experiment. This result seems to favor a solvolysis mechanism of the acetoxyselenenylation reaction. For an addition of PhSeX, if the nucleophile X is chlorine or bromine, the reaction becomes reversible even at low temperature. However, if X is an oxygen substituent (OH, OR, OAc), product isomerization does not occur even at ambient temperature.[23] Hydroxy-[24] and methoxyselenenylation[23] reactions of 1-hexene have been reported to produce 89 and 83% (relative yields), respectively, of the Markovnikov isomer. This shows that the thermodynamic product in these cases is also kinetically favored. On the other hand, our results with 1-octene and 1-dodecene indicate a similar energy barrier for both pathways in the acetoxyselenenylation reaction. The directing effect of an allylic oxygen substituent in electrophilic addition reactions has previously been observed with reagents like PhSeCl[25] and $PhSeCl_3$[26] (anti-Markovnikov products favored). As seen from Table I (allyl benzoate and homoallyl benzoate), the effect of a benzoyloxy group is markedly reduced as the substituent is shifted from an allylic to a homoallylic position.

The role of boron trifluoride etherate in the isomerization reaction is probably to assist in the removal of the acetoxy group, thus lowering the energy barrier for seleniranium ion formation. Due to decomposition of the selenides in long-time isomerization experiments, we can only say that the reported isomer ratios of Table I must be close to those of the thermodynamic mixture, if not identical with them.

The lack of regiospecificity has previously imposed serious restrictions on the applicability of the acetoxyselenenylation reaction in synthesis. Via the BF_3-catalyzed isomerization reaction, Markovnikov adducts are now easily accessible from a variety of terminal olefins. Their ready conversions to 2-acetoxy 1-olefins were also demonstrated by using the selenoxide elimination reaction at elevated temperature.

As compared with other oxyselenenylation reactions, the acetoxyselenenylation process gives significantly larger amounts of the *anti*-Markovnikov isomer. Its selenoxide elimination, selectively away from the acetoxy substituent, in the presence of the Markovnikov isomer, is therefore a synthetically useful process for the preparation of allylic acetates. Unfortunately, the acetoxyselenenylation reaction of simple olefins does not lend itself to much manipulation to increase the amount of anti-Markovnikov isomer. However, after introduction of an allylic oxygen substituent, the anti-Markovnikov isomer usually predominates with a ratio of at least 8:2 over its regioisomer.

Finally, our results with *cis*-4-cyclohexene-1,2-dicarboxylic acid diethyl diester demonstrate that it is also possible to efficiently control the regiochemistry of acetoxyselenenylation reactions by using other directing substituents than allylic alcohols, ethers, and esters. This finding should hopefully prove useful for future synthetic applications.

Experimental Section

Melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus. NMR spectra were obtained with Bruker WP 200 and AM 400 (indicated) instruments (operating at 200 and 400 MHz, respectively) and were recorded for $CDCl_3$ solutions containing tetramethylsilane as the internal standard. IR spectra were obtained by using a Perkin-Elmer 1710 FT infrared spectrometer. GLC analyses were carried out by using a Varian 3700 gas chromatograph equipped with a 30-m SE-30 capillary column. Elemental analyses were performed by Novo Microanalytical Laboratory, Bagsvaerd, Denmark. Chloroform was washed with water to remove ethanol and dried over $CaCl_2$. Sulfuryl chloride was freshly distilled. The different allyl and homoallyl alcohol benzoic acid esters as well as the allylic acetates were prepared as previously described.[27] Allyl phenyl ether was prepared by analogy with the preparation of allyl 4-chlorophenyl ether.[28] 1-Phenyl-2-(phenylseleno)ethanol[24] and *cis*-[29] and *trans*-4-cyclohexene-1,2-dicarboxylic acid diethyl diester[30] were prepared according to literature methods.

Acetoxyselenenylation of Olefins. Typical Procedure. 2-Acetoxy-2-phenylethyl Phenyl Selenide (1c). To a stirred suspension of PhSeBr (1.0 g, 4.2 mmol) in an acetate buffer solution (5 mL of HOAc, 0.5 mL of Ac_2O, and 0.7 g of KOAc) at ambient temperature was added styrene (0.44 g, 4.2 mmol). After disappearance of the solid (≈0.5 h), the resulting yellowish homogeneous solution was stirred for 15 h and the solvent evaporated at reduced pressure. The product was then extracted into CH_2Cl_2 (KBr filtered off) and purified by flash chromatography (SiO_2/CH_2Cl_2:hexane = 1:1) from traces of diphenyl diselenide to give 1.22 g (90%) of compound **1c** as an oil: ^1H NMR δ 2.01 (s, 3 H), 3.21 (dd, 1 H), 3.37 (dd, 1 H), 5.92 (dd, 1 H), 7.22–7.33 (several peaks, 8 H), 7.49 (m, 2 H). The material was analyzed as its *Se*,*Se*-dichloride **2c** (vide infra).

Products **5** + **6**, **7**, **8**, **9**, **10a**, **14**, and **17** were similarly prepared. ^1H NMR data and yields are reported as follows (selected peaks for compounds **5** and **6**; for yields see Table I).

5a: δ 1.94 (s, OAc), 3.06 (d, CH_2SePh), 5.02 (m, C*H*OAc).
6a: δ 1.99 (s, OAc), 3.31 (d, C*H*SePh), 4.21 (m, CH_2OAc).
5b: δ 1.94 (s, OAc), 3.07 (d, CH_2SePh), 5.01 (m, C*H*OAc).
6b: δ 2.00 (s, OAc), 3.31 (m, C*H*SePh), 4.23 (m, CH_2OAc).
5c: δ 1.88 (s, OAc), 5.23 (m, C*H*OAc).
6c: δ 1.99 (s, OAc), 3.59 (m, C*H*SePh).
5d: δ 1.98 (s, OAc), 2.03 (s, OAc), 3.09 (d, CH_2SePh).
6d: δ 2.05 (s, OAc), 3.53 (m, C*H*SePh).
5e: δ 1.99 (s, OAc), 3.18 (d, CH_2SePh).
6e: δ 2.03 (s, OAc), 3.68 (m, C*H*SePh).
5f: δ 1.98 (s, OAc), 3.27 (m, CH_2SePh).
6f: δ 2.03 (s, OAc), 3.65 (m, C*H*SePh).
5g: δ 1.92 (s, OAc), 3.15 (m, CH_2SePh).
6g: δ 2.01 (s, OAc), 3.48 (m, C*H*SePh).

7: δ 1.38 (d, 3 H), 2.07 (s, 3 H), 3.59 (m, 1 H), 5.92 (d, 1 H, J = 5.1 Hz), 7.25–7.31 (several peaks, 8 H), 7.53 (m, 2 H); yield 97%.

8: δ 1.23 (d, 3 H), 2.00 (s, 3 H), 3.63 (m, 1 H), 5.81 (d, 1 H, J = 8.1 Hz), 7.26–7.37 (several peaks, 8 H), 7.56 (m, 2 H); yield 99%.

9: δ 2.05 (s, 3 H), 3.89 (m, 1 H), 4.50 (dd, 1 H), 4.69 (dd, 1 H), 6.18 (d, 1 H, J = 6.2 Hz), 7.17–7.55 (several peaks, 13 H), 7.94 (m, 2 H); yield 95%; mp 80–1 °C.

10a: δ 1.50–1.75 (several peaks, 4 H), 1.96–2.05 (several peaks, 2 H), 1.99 (s, 3 H), 2.01 (s, 3 H), 3.45 (m, 1 H), 5.20–5.38 (several peaks, 2 H), 7.25–7.30 (several peaks, 3 H), 7.58 (m, 2 H); yield 75%.

14: δ 1.99 (s, 3 H), 5.13 (s, 1 H), 6.71 (s, 1 H), 7.16–7.77 (several peaks, 11 H); yield 72%.

17: (selected peaks) isomer A δ 1.86 (s, OAc), 4.55 (d, 1 H), isomer B δ 1.98 (s, OAc), 4.66 (d, 1 H); yield 86%; relative amounts A:B = 39:61.

Typical Isomerization Procedure. 2-Acetoxy-1-(phenylseleno)dodecane (5b). To a stirred 51:49 mixture of compounds **5b**/**6b** (2.1 g, 5.5 mmol) in $CHCl_3$ (25 mL) at ambient temperature was added boron trifluoride etherate (0.05 g, 0.35 mmol). After 24 h, the reaction mixture was shaken with water and the organic phase separated, dried, and evaporated. Flash chromatography (SiO_2/CH_2Cl_2:hexane = 1:1) afforded 1.83 g (86%) of a selenide mixture **5b**/**6b** containing 96% of isomer **5b**.

(23) The reversibility of the methoxyselenenylation reaction has previously been reported at elevated temperature: Toshimitsu, A.; Aoai, T.; Uemura, S.; Okano, M. *J. Org. Chem.* **1980**, *45*, 1953.
(24) Toshimitsu, A.; Aoai, T.; Owada, H.; Uemura, S.; Okano, M. *Tetrahedron* **1985**, *41*, 5301.
(25) Liotta, D.; Zima, G.; Saindane, M. *J. Org. Chem.* **1982**, *47*, 1258.
(26) Engman, L. *J. Org. Chem.* **1987**, *52*, 4086.
(27) Engman, L. *J. Am. Chem. Soc.* **1984**, *106*, 3977.
(28) White, W. N.; Gwynn, D.; Schlitt, R.; Girard, C.; Fife, W. *J. Am. Chem. Soc.* **1958**, *80*, 3271.
(29) Cope, A. C.; Herrick, E. C. *J. Am. Chem. Soc.* **1950**, *72*, 983.
(30) Sample, T. E., Jr.; Hatch, L. F. *Org. Synth.* **1970**, *50*, 43.

The isomerizations of compounds **5a + 6a** and **5c + 6c** were similarly performed. All other isomerizations were carried out by using a larger amount of catalyst (mol % catalyst shown in parantheses): **5d + 6d** (41%); **5e + 6e** (26%); **5f + 6f** (25%); **5g + 6g** (13%). For yields and isomer distributions after isomerization, see Table I.

Representative Preparation of a *Se,Se*-Dichloride. (2-Acetoxy-2-phenylethyl)phenylselenium Dichloride (2c). To a stirred solution of selenide **1c** (0.90 g, 2.8 mmol) in $CHCl_3$ (10 mL) at ambient temperature was added SO_2Cl_2 (0.38 g, 2.8 mmol). After 15 min, the solvent was evaporated and the crystalline residue recrystallized from CH_2Cl_2/hexane to give 0.97 g (88%) of compound **2c**: mp 120–1 °C dec; ^{1}H NMR δ 2.23 (s, 3 H), 4.37 (dd, 1 H), 4.62 (dd, 1 H), 6.75 (dd, 1 H), 7.39–7.54 (several peaks, 8 H), 7.92 (m, 2 H). Anal. Calcd for $C_{16}H_{16}Cl_2O_2Se$: C, 49.25; H, 4.13. Found: C, 49.45; H, 4.21.

Compounds **2a**, **10b**, **22**, and **24** were similarly prepared. Selenides **9**, **5c**, and **5d** (the latter two after BF_3-catalyzed isomerization) were also converted to their respective crystalline *Se,Se*-dichlorides by using the above procedure. ^{1}H NMR data, yields, and melting points for selenium(IV) compounds are reported as follows.

2a: ^{1}H NMR δ 3.19 (s, 1 H), 4.39 (dd, 1 H), 4.62 (dd, 1 H), 5.84 (dd, 1 H), 7.39–7.54 (several peaks, 8 H), 7.92 (m, 2 H); yield 99%; mp 97–9 °C dec. Anal. Calcd for $C_{14}H_{14}Cl_2OSe$: C, 48.30; H, 4.05. Found: C, 48.77; H, 4.15.

10b: ^{1}H NMR δ 1.12 (s, 3 H), 1.35–1.95 (several peaks, 4 H), 2.18 (m, 1 H), 2.19 (s, 3 H), 2.45 (m, 1 H), 4.71 (dd, 1 H, J = 2.2 and 10.9 Hz), 5.78 (ddd, 1 H, J = 4.8, 10.9, and 10.9 Hz), 6.26 (m, 1 H), 7.47–7.53 (several peaks, 3 H), 8.13 (m, 2 H); yield 77%; mp 146–7 °C dec; IR 1736 cm^{-1}.

22: ^{1}H NMR 1.23 (t, 3 H), 1.29 (t, 3 H), 1.65–1.88 (several peaks, 4 H), 2.65–2.86 (several peaks, 4 H), 3.40 (s, 1 H), 4.10–4.32 (several peaks, 4 H), 4.73 (m, 1 H), 5.60 (ddd, 1 H, J = 4.5, 11.0, and 11.0 Hz), 7.49–7.55 (several peaks, 3 H), 8.17 (m, 2 H); yield 77%; mp 134–5 °C dec; IR 1737 cm^{-1}.

24: ^{1}H NMR δ 1.32 (t, 3 H), 1.39 (t, 3 H), 1.81 (m, 1 H), 1.98 (s, 3 H), 2.48–2.80 (several peaks, 3 H), 3.39 (m, 2 H), 4.14–4.37 (several peaks, 4 H), 4.91 (ddd, 1 H, J = 4.1, 10.8, and 12.5 Hz), 5.60 (ddd, 1 H, J = 4.7, 10.8, and 10.8 Hz), 7.51–7.54 (several peaks, 3 H), 8.16 (m, 2 H); yield 91%; mp 130–1 °C dec; IR 1723 cm^{-1}.

[1-Acetoxy-3-(benzoyloxy)-1-phenyl-2-propyl]phenylselenium dichloride: ^{1}H NMR δ 2.29 (s, 3 H), 5.05–5.17 (several peaks, 3 H), 7.16–7.59 (several peaks, 14 H), 8.15 (m, 2 H); yield 96%; mp 92–4 °C dec. Anal. Calcd for $C_{24}H_{22}Cl_2O_4Se$: C, 54.98; H, 4.23. Found: C, 55.23; H, 4.29.

(2-Acetoxy-3-phenylpropyl)phenylselenium dichloride: ^{1}H NMR δ 2.13 (s, 3 H), 3.04 (dd, 1 H), 3.22 (dd, 1 H), 4.25 (dd, 1 H), 4.36 (dd, 1 H), 6.00 (m, 1 H), 7.24–7.34 (several peaks, 5 H), 7.47–7.53 (several peaks, 3 H), 7.86 (m, 2 H); yield (for isomerization + chlorination) 76%; mp 119–20 °C.

(2,3-Diacetoxypropyl)phenylselenium dichloride: ^{1}H NMR δ 2.14 (s, 3 H), 2.20 (s, 3 H), 4.37–4.50 (several peaks, 4 H), 5.95 (m, 1 H), 7.53–7.56 (several peaks, 3 H), 7.95 (m, 2 H); yield 92%; mp 108–9 °C dec. Anal. Calcd for $C_{13}H_{16}Cl_2O_4Se$: C, 40.44; H, 4.18. Found: C, 40.92; H, 4.31.

Compound **2b** was similarly prepared by SO_2Cl_2 chlorination of selenide **1b**. The selenide was prepared in 93% yield by treatment of styrene in anhydrous MeOH with PhSeCl. This material has previously been synthesized by using a more sophisticated selenium reagent.[23]

2b: ^{1}H NMR δ 3.39 (s, 3 H), 4.33 (dd, 1 H), 4.58 (dd, 1 H), 5.29 (dd, 1 H), 7.40–7.50 (several peaks, 8 H), 7.91 (m, 2 H); yield 92%; mp 139–40 °C dec. Anal. Calcd for $C_{15}H_{16}Cl_2OSe$: C, 49.75; H, 4.45. Found: C, 49.95; H, 4.55.

Typical Elimination Procedures. Method A. 2-Acetoxy-1-dodecene (11b). To a stirred solution of selenides **5b:6b** = 96:4 (0.55 g, 1.4 mmol) in dry benzene (20 mL) was added SO_2Cl_2 (0.20 g, 1.5 mmol). After 15 min, water (20 mL) containing $NaHCO_3$ (0.50 g, 6.0 mmol) was added and the two-phase system heated at 100 °C for 4 h. The yellow organic phase was then separated, dried, and evaporated and the residue Kugelrohr-distilled to give 0.19 g (59%) of compound **11b**: ^{1}H NMR δ 0.88 (t, 3 H), 1.27 (s, 14 H), 1.45 (m, 2 H), 2.14 (s, 3 H), 2.20 (t, 2 H), 4.72 (m, 2 H). Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 74.01; H, 12.07.

The isolated crystalline selenium(IV) dichlorides (vide supra) were dissolved in benzene and heated with aqueous $NaHCO_3$ as described above to effect elimination.

Diphenyl diselenide was removed from compound **11f** by using flash chromatography (SiO_2/CH_2Cl_2) before Kugelrohr distillation. According to GLC analysis, all compounds **11** contained ≤5% of their corresponding allylic acetates **20**. For yields, see Table II. ^{1}H NMR and analytical data for new compounds are reported as follows.

11d: δ 2.10 (s, 3 H), 2.17 (s, 3 H), 4.62 (s, 2 H), 5.02 (m, 1 H), 5.09 (m, 1 H). Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 52.75; H, 6.34.

11f: δ 2.14 (s, 3 H), 2.71 (t, 2 H), 4.44 (t, 2 H), 4.88 (s, 2 H), 7.39–7.59 (several peaks, 3 H), 8.03 (m, 2 H). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.56; H, 6.19.

12: δ 1.60–1.95 (several peaks, 4 H), 2.04 (s, 3 H), 2.13 (s, 3 H), 2.14–2.21 (several peaks, 2 H), 5.40 (m, 1 H), 5.51 (m, 1 H). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.28; H, 7.36.

The spectroscopic and/or physical data of the known compounds **11a**[31] and **11c**[32] showed good agreement with reported data.

Compounds **2a–c** were eliminated according to method A. The reaction of compound **2a** produced acetophenone (32%) and phenacyl phenyl selenide (**3**)[33] (33%), both compared with authentic samples. Compound **2b** similarly produced a 12:56:32 mixture of acetophenone, phenacyl phenyl selenide, and selenide **1b**, respectively (no total yield determined). Compound **3b** afforded α-acetoxystyrene[34] in 66% yield together with selenide **1c** (23%).

Method B. 2-Acetoxy-1-dodecene (11b). To a stirred solution of selenides **5b:6b** = 96:4 (1.0 g, 2.6 mmol) in dry benzene was added MCPBA (0.56 g; 80% by weight, 2.6 mmol) in small portions. After 15 min, the homogeneous, colorless solution was extracted with aqueous $NaHCO_3$ (to remove *m*-chlorobenzoic acid) and heated at reflux for 4 h. Workup according to method A afforded 0.45 g (76%) of compound **11b**.

Compounds **16**, **18**, and **20d** were prepared by using CH_2Cl_2 as solvent instead of benzene. After extraction with $NaHCO_3$ (aqueous), the organic phase was separated and kept at ambient temperature for 1, 2, and 5 days, respectively, to complete the elimination. Products were isolated by using flash chromatography. For yields of compounds prepared according to method B, see Table II.

Compound **11e** (isolated by flash chromatography) was only ca. 92% pure according to GLC analysis. The analytical sample was obtained by using preparative GLC: ^{1}H NMR δ 2.14 (s, 3 H), 4.57 (s, 2 H), 5.03 (m, 1 H), 5.13 (m, 1 H), 6.93–7.01 (several peaks, 3 H), 7.25–7.33 (several peaks, 2 H). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.85; H, 6.44.

Compound **16** melted at 45–7 °C, and its ^{1}H NMR spectrum was in good agreement with reported data.[35]

Compound **18** was obtained as a mixture of two isomers A and B: relative amounts A:B = 56:44; ^{1}H NMR (selected peaks) isomer A δ 2.19 (s, 3 H), 6.46 (s, 1 H), isomer B δ 2.31 (s, 3 H), 6.71 (s, 1 H). When the mixture (0.05 g, 0.21 mmol) was stirred in water (1 mL) and dimethoxyethane (5 mL) containing KOH (0.20 g, 3.6 mmol) for 18 h, 0.039 g (95%) of phenyl benzyl ketone, mp 54–5 °C (lit.[36] mp 55–6 °C), was isolated.

Compound **20d** was obtained as an *E*/*Z* mixture (Table II). Both isomers were previously described.[37] *E* isomer: ^{1}H NMR δ 2.06 (s, 3 H), 2.15 (s, 3 H), 4.55 (d, 2 H), 5.56 (dt, 1 H, J = 7.4 and 12.6 Hz), 7.38 (d, 1 H, J = 12.6 Hz). *Z* isomer: ^{1}H NMR δ 2.07 (s, 3 H), 2.17 (s, 3 H), 4.73 (d, 2 H), 5.06 (dt, 1 H, J = 7.0 and 6.4 Hz), 7.21 (d, 1 H, J = 6.4 Hz).

Method C. 1-Acetoxy-2-octene (20a). To a stirred solution of selenides **5a:6a** = 50:50 (1.35 g, 4.1 mmol) in CH_2Cl_2 (40 mL) was added SO_2Cl_2 (0.56 g, 4.1 mmol). After 15 min, the reaction

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mixture was shaken in a separatory funnel with water (40 mL) containing $NaHCO_3$ (1.4 g, 16.7 mmol). When the initial gas evolution had ceased, the two-phase system was left for 3 days to complete the elimination. Flash chromatography (SiO_2/CH_2Cl_2:hexane = 1:1) and Kugelrohr distillation afforded 0.31 g (89%) of compound **20a** as an isomeric mixture (*E*:*Z* = 4:1). The *Z* isomer was separated by using HPLC (Waters M-45 instrument; μ-Porasil column; EtOAc:hexane = 1:99) from the well-characterized[38] *E* isomer. *Z* isomer: ^1H NMR (400 MHz) δ 0.89 (t, 3 H), 1.29–1.39 (several peaks, 6 H), 2.06 (s, 3 H), 2.09 (m, 2 H), 4.62 (d, 2 H), 5.54 (m, 1 H), 5.64 (m, 1 H); J_{H-H} olefinic = 10.9 Hz.

Compounds **19**[39] and **20b**[39] were similarly prepared. For the preparation of compounds **13**, **20c**, and **20d**, the two-phase system was left for 24 h, 24 h, and 4 days, respectively, to complete the elimination. ^1H NMR and/or analytical data for new compounds prepared according to method C are as follows. For yields and *E*:*Z* ratios, see Table II.

13: δ 2.33 (s, 3 H), 4.96 (d, 2 H), 6.11 (t, 1 H), 7.34–7.57 (several peaks, 8 H), 8.06 (m, 2 H); mp 57–8 °C. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.98; H, 5.57.

20c. The *Z* isomer was previously described.[40] *E* isomer: ^1H NMR (selected peaks) δ 2.08 (s, 3 H), 4.61 (d, 2 H), 4.84 (d, 2 H).

In the preparation of compound **20d** according to method C, the selenide mixture **5d** + **6d** was isolated in 58% yield.

Compounds **22** and **24** were dissolved in CH_2Cl_2 and treated with aqueous $NaHCO_3$ as described in method C (elimination time 21 and 5 days, respectively) to give compounds **23** and **25** in 96 and 98% yields, respectively.

23: ^{13}C NMR (400 MHz) δ 14.08, 21.18, 27.27, 37.10, 42.21, 60.74, 60.97, 65.99, 126.97, 128.99, 170.30, 170.80, 172.72; ^1H NMR (400 MHz) δ 1.24 (t, 3 H), 1.25 (t, 3 H), 2.04 (s, 3 H), 2.24 (ddd, 1 H, J = 2.4, 3.5, and 14.7 Hz), 2.35 (ddd, 1 H, J = 4.4, 11.8, and 14.7 Hz), 2.97 (ddd, 1 H, J = 3.5, 5.1, and 11.8 Hz), 3.60 (dd, 1 H, J = 5.1 and 5.1 Hz), 4.11–4.20 (several peaks, 4 H), 5.31 (m, 1 H), 5.95 (dd, 1 H, J = 4.6 and 9.8 Hz), 6.10 (dd, 1 H, J = 5.1 and 9.8 Hz). Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.15; H, 7.09. Found: C, 58.74; H, 7.21.

25: ^{13}C NMR (400 MHz) δ 14.09, 21.18, 30.26, 37.42, 44.02, 60.92, 61.22, 64.78, 125.65, 129.43, 170.38, 171.78, 174.09; ^1H NMR (400 MHz) δ 1.27 (t, 3 H), 1.28 (t, 3 H), 1.86 (ddd, 1 H, J = 4.3, 12.7, and 14.2 Hz), 2.07 (s, 3 H), 2.20 (ddd, 1 H, J = 3.0, 3.0, and 14.2 Hz), 3.10 (ddd, 1 H, J = 3.0, 10.1, and 12.6 Hz), 3.50 (dd, 1 H, J = 1.5 and 10.1 Hz), 4.14–4.23 (several peaks, 4 H), 5.25 (m, 1 H), 5.91 (dd, 1 H, J = 4.8 and 10.0 Hz), 6.07 (dd, 1 H, J = 1.5 and 10.0 Hz). Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.15; H, 7.09. Found: C, 59.12; H, 7.15.

***trans*-1-Acetoxy-2-chloroacenaphthene (15).** To a stirred solution of selenide **14** (1.13 g, 3.1 mmol) in $CHCl_3$ (10 mL) at ambient temperature was added SO_2Cl_2 (0.42 g, 3.1 mmol). The orange-red solution was then left for 4 days. Evaporation and flash chromatography (SiO_2; CH_2Cl_2:hexane = 1:1) of the residue afforded 0.59 g (78%) of compound **15**, mp 99 °C (lit.[41] mp 94–5 °C).

2-Bromooctyl phenyl selenide was prepared by treatment of PhSeBr (0.54 g, 2.2 mmol) with 1-octene (0.25 g, 2.2 mmol) in $CHCl_3$ (2 mL) for 24 h by analogy with a literature procedure.[10] The reaction mixture was then poured into 5 mL of the acetate buffer solution used in the typical acetoxyselenenylation procedure (vide supra). Workup afforded a 48:52 mixture of compounds **5a** and **6a** (yield not determined).

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Registry No. **1a**, 51558-95-3; **1b**, 63603-28-1; **1c**, 67007-25-4; **2a**, 118270-70-5; **2b**, 116117-96-5; **2c**, 118270-69-2; **5a**, 67007-28-7; **5a** (olefin), 111-66-0; **5b**, 118270-52-3; **5b** (olefin), 112-41-4; **5c**, 118270-54-5; **5c** (olefin), 300-57-2; **5d**, 118270-56-7; **5d** (olefin), 591-87-7; **5e**, 118270-57-8; **5e** (olefin), 583-04-0; **5f**, 118270-59-0; **5f** (olefin), 1746-13-0; **5g**, 118270-61-4; **5g** (olefin), 18203-32-2; **6a**, 67007-29-8; **6b**, 118270-53-4; **6c**, 118270-55-6; **6d**, 99018-35-6; **6e**, 118270-58-9; **6f**, 118270-60-3; **6g**, 118270-62-5; **7**, 118270-63-6; **7** (olefin), 766-90-5; **8**, 118270-64-7; **8** (olefin), 873-66-5; **9**, 118270-65-8; **9** (olefin), 5320-75-2; **10a**, 118270-66-9; **10a** (olefin), 14447-34-8; **10b**, 118270-71-6; **11a**, 26735-84-2; **11b**, 118270-77-2; **11c**, 25522-54-7; **11d**, 97146-99-1; **11e**, 118270-80-7; **11f**, 118270-78-3; **12**, 118270-79-4; **13**, 118270-81-8; **14**, 118270-67-0; **14** (olefin), 208-96-8; **15**, 50499-75-7; **16**, 33033-36-2; **17**, 118270-68-1; **17** (olefin), 645-49-8; (*E*)-**18**, 24647-07-2; (*Z*)-**18**, 13892-81-4; **19**, 7217-71-2; (*E*)-**20a**, 3913-80-2; (*Z*)-**20a**, 26806-12-2; (*E*)-**20b**, 21040-45-9; (*E*)-**20c**, 118270-82-9; (*Z*)-**20c**, 118270-83-0; (*E*)-**20d**, 31447-25-3; (*Z*)-**20d**, 31447-24-2; **22**, 118270-73-8; **22** (selenide), 118270-72-7; **23**, 118270-84-1; **24**, 118374-49-5; **24** (selenide), 118374-48-4; **25**, 118270-85-2; styrene, 100-42-5; [1-acetoxy-3-(benzoyloxy)-1-phenyl-2-propyl]phenylselenium dichloride, 118270-74-9; (2-acetoxy-3-phenylpropyl)phenylselenium dichloride, 118270-75-0; (2,3-diacetoxypropyl)phenylseleniumdichloride, 118270-76-1; acetophenone, 98-86-2; phenacyl phenyl selenide, 35050-01-2; 2-bromooctyl phenyl selenide, 66221-85-0; α-acetoxystyrene, 2206-94-2.

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4-(Phenylsulfonyl)butanoic Acid. Preparation, Dianion Generation, and Application to Four-Carbon Chain Extension[1]

Charles M. Thompson* and Jeffrey A. Frick

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

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The bishomoenolate dianion of 4-(phenylsulfonyl)butanoic acid was investigated. It was observed that the dianion could be generated in greater than 95% yield with 200 mol % of *n*-BuLi at certain concentrations. The dianion was reacted with a variety of aldehydes to afford, after cyclization, substituted tetrahydropyran-2-ones (lactones). These derivatives were reductively eliminated to afford methyl 4-butenoates in yields of 56–85%.

Carboxylic acid dianions have emerged as valuable tools in carbon–carbon bond formation.[2] This is due, in part, to their ready availability and reluctance to self condense. As a result, they are frequently desirable reagents or

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