Phenylselenium Trichloride in Organic Synthesis. Reaction with Unsaturated Compounds. Preparation of Vinylic Chlorides via Selenoxide Elimination

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Phenylselenium trichloride, $PhSeCl_3$, was reacted with a number of olefinic compounds to produce (β-chloroalkyl)phenylselenium dichlorides. The addition was anti stereospecific and irreversible. The presence of an oxygen substituent (acyloxy or aryloxy group) in the allylic position of the olefin directed the attack of $PhSeCl_3$ to occur regiospecifically anti-Markovnikov to give a (β-acyloxy/aryloxy-β'-chloroalkyl)phenylselenium dichloride. When the (β-chloroalkyl)phenylselenium dichlorides were treated in methylene chloride with aqueous sodium hydrogen carbonate, the selenium dichloride moiety was readily hydrolyzed to a selenoxide, which underwent the usual selenoxide elimination reaction to produce an allylic or a vinylic chloride. Symmetrical olefins containing no allylic hydrogens were converted to vinylic chlorides with retention of olefin geometry. Olefins containing a directing oxygen substituent in the allylic position afforded vinylic chlorides where the vinylic halogen atom was oriented 1,3 to the oxygen substituent (*E*/*Z* mixture). Other olefins afforded mixtures of allylic and vinylic halides in varying proportions. The reaction of phenylselenium tribromide, $PhSeBr_3$, with some olefinic compounds was also investigated. This material showed the same stereo- and regiochemical behavior as $PhSeCl_3$ in its addition reactions. However, the adducts were not useful for the preparation of vinylic or allylic bromides by using the hydrolytic selenoxide elimination reaction.

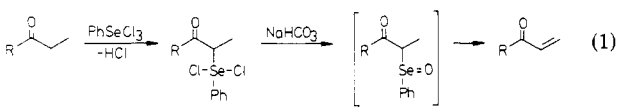
Introduction

Phenylselenium trichloride (**1a**) is a potentially useful substance for the introduction of selenium(IV) into organic molecules. However, the material has found very limited

$ArSeCl_3$

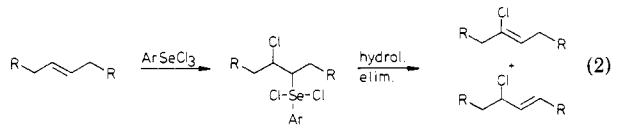
1 a Ar = phenyl
b Ar = 2,4-dinitrophenyl

use in organic synthesis, probably because it is reputed to be thermally unstable and hygroscopic. We recently reported the use of phenylselenium trichloide for the mild conversion of ketones to enones.[1] This process was based upon the facile introduction of a $PhSeCl_2$ group into the α-position of ketones (eq 1). Hydrolysis of the selenium dichloride moiety to a selenoxide resulted in rapid elimination to give the enone.



(1)

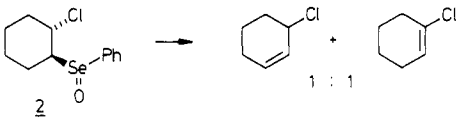
To the best of our knowledge, this simple variation of the selenoxide elimination reaction[2] has not previously been described. In order to extend the synthetic utility of the reaction, we have been looking for other constructive ways to introduce the $PhSeCl_2$ group into organic molecules. One such reaction is the little studied[3] addition of arylselenium trichlorides to alkenes to yield (β-chloroalkyl)arylselenium dichlorides. Subsequent hydrolysis/selenoxide elimination would in this case afford vinylic or allylic chlorides as shown in eq 2.



(2)

Obviously, there are several regio- and stereochemical problems associated with the suggested reaction sequence. Garratt and Schmid[4] have studied the addition (2,4-dinitrophenyl)selenium trichloride (**1b**) to (*E*)- and (*Z*)-1-phenylpropene. They reported only products of anti addition. However, the reactions were nonregiospecific, affording a mixture of Markovnikov and anti-Markovnikov (β-chloroalkyl)(2,4-dinitrophenyl)selenium dichlorides.

Concerning the direction of the selenoxide elimination step, Sharpless and co-workers[5] observed no selectivity in the elimination of the cyclohexane compound **2** (eq 3). On the other hand, when the elimination could occur in two directions, as for compound **3**, only the vinylic chloride product was observed (eq 4).[6]



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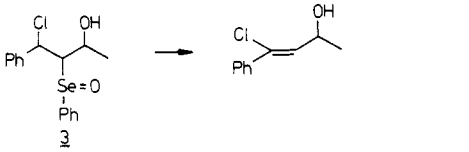

(4)

2 **3**

In the following we describe the addition of phenylselenium trichloride to a variety of unsaturated compounds. Whenever stereo- and regiochemistry could be controlled, the mild hydrolytic selenoxide elimination reaction has been carried out in order to obtain synthetically useful products like vinylic chlorides (equivalent to ketones after hydrolysis[7]) or allylic chlorides.

Results

Stereochemistry. Although phenylselenium trichloride is very easily prepared by chlorination of diphenyl diselenide, most of the chemistry concerning the class of arylselenium trichlorides has been carried out with the less available (2,4-dinitrophenyl)selenium trichloride (**1b**).[4,8] Since compound **1b** underwent a stereospecific anti addition to olefins, phenylselenium trichloride could be expected to behave similarly. In order to confirm this hypothesis, $PhSeCl_3$ was reacted in dry ether with (*E*)- and

(1) Engman, L. *Tetrahedron Lett.* **1985**, *26*, 6385.
(2) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.
(3) Schmid, G. H.; Garratt, D. G. In *The Chemistry of Double-Bonded Functional Groups* Patai, S., Ed.; Wiley: London, 1977; p 855.
(4) Garratt, D. G.; Schmid, G. H. *Can. J. Chem.* **1974**, *52*, 3599.
(5) Sharpless, K. B.; Lauer, R. F. *J. Org. Chem.* **1974**, *39*, 429.
(6) Liotta, D.; Zima, G.; Saindane, M. *J. Org. Chem.* **1982**, *47*, 1258.
(7) Martin, S. F.; Chou, T. *Tetrahedron Lett.* **1978**, *19*, 1943.
(8) Lawson, D. D.; Kharasch, N. *J. Org. Chem.* **1959**, *24*, 857.

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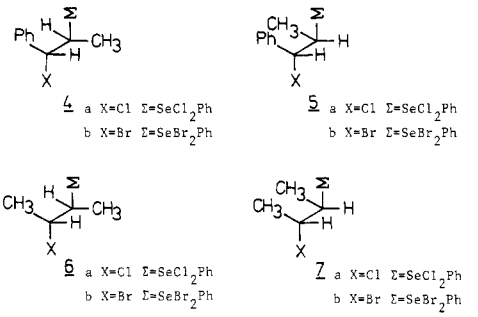
(*Z*)-1-phenylpropene at 0 °C. The isolated products, compounds **4a** and **5a**, respectively, were obtained in very good yields after precipitation with light petroleum.

Assignment of stereochemistry was arrived at by spectroscopic means and chemical reactions (vide infra). It is known that in the ^1H NMR spectra of a series of erythro and threo 1,2-disubstituted 1-arylpropanes, the β-methyl protons of the threo isomer always appear at higher field than those of the erythro isomer.[9] Since the β-methyl protons of compound **4a** resonated at 1.90 ppm and those of compound **5a** at 1.45 ppm, it was concluded that compound **4a** was an erythro isomer and compound **5a** a threo one.



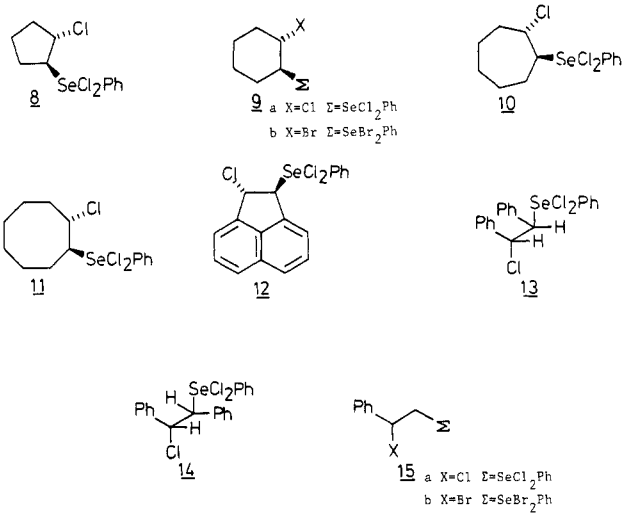
(*E*)- and (*Z*)-2-butene were similarly used for the assignment of stereochemistry. The (*E*)-olefin cleanly afforded adduct **6a**, whereas the (*Z*)-olefin gave adduct **7a**. The relative configurations of the two adducts were assigned by observing the variation of the vicinal proton–proton coupling constant of the methine protons with solvent dielectric constant. For the threo compound $^3J_{H,H}$ should increase with increasing solvent dielectric, whereas for the erythro compound a decrease should be observed.[10] From the observed values of $^3J_{H-H}$ in deuteriochloroform (ϵ = 4.70) and acetonitrile-d_3 ($\epsilon \approx$ 37.5) we have assigned compound **6a** as an erythro [$^3J_{H-H}$ = 6.3 ($CDCl_3$), 4.1 Hz (CD_3CN)] and compound **7a** as a threo isomer [$^3J_{H-H}$ = 7.7 ($CDCl_3$), 8.2 Hz (CD_3CN)]. In conclusion, the above results confirm the anticipated anti stereospecificity of the addition of phenylselenium trichloride to olefins.

When the cyclic olefins cyclopentene, cyclohexene, cycloheptene, and cyclooctene were reacted in dry ether at 0 °C with phenylselenium trichloride, the addition compounds **8**, **9a**, **10**, and **11**, respectively, were formed in almost quantitative yields. The products were assigned the trans configuration in analogy with previous results. Overlapping signals in the NMR spectrum prevented any conclusive determination of the stereochemistry.

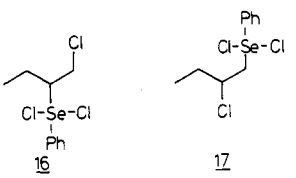
An attempt to carry out the addition of $PhSeCl_3$ to cyclohexene in methanol did not result in any incorporation of a methoxy group from the solvent. The β-chloro compound **9a** was again the only product formed.

Acenaphthylene and *cis*- and *trans*-stilbene also reacted readily with phenylselenium trichloride. The assignment of trans stereochemistry of the products **12–14**, respectively, was based on further chemical reactions of the adducts (vide infra).

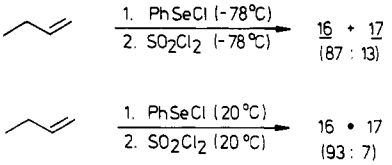
Regiochemistry. (2,4-Dinitrophenyl)selenium trichloride showed a very moderate regioselectivity in its reactions with (*E*)- and (*Z*)-1-phenylpropene.[4] On the other hand, phenylselenium trichloride added in a regiospecific way to these olefins, producing only the Markovnikov adducts **4a** and **5a**, respectively. This conclusion was arrived at by studying the products from the hydrolytic selenoxide elimination of the adducts (vide infra). Styrene regiospecifically yielded the Markovnikov adduct **15a** when treated with $PhSeCl_3$ in ether.



However, $PhSeCl_3$ showed only a moderate regioselectivity when treated with 1-butene in dry ether at 0 °C. The anti-Markovnikov adduct **16** was the main product in addition to the Markovnikov adduct **17** (ratio **16**/**17** = 81:19).



Benzeneselenenyl chloride, PhSeCl, is known to add reversibly to terminal olefins.[3] At low temperature (−78 °C) the anti-Markovnikov product predominates. At higher temperature (25 °C) this material is isomerized to the thermodynamically more stable Markovnikov adduct. By chlorinating the respective β-chloroalkyl phenyl selenide with sulfuryl chloride as shown in eq 5, compounds **16** and **17** were independently synthesized. The compounds did not interconvert at ambient temperature over a period of several days in deuteriochloroform. Obviously the addition of phenylselenium trichloride to the olefin is not a reversible process.

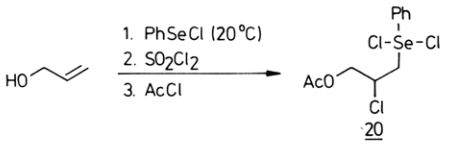


(5)

It was previously reported that certain oxygen substituents in the allylic position of olefins had a strongly directing influence on the addition of benzeneselenenyl chloride.[6] Phenylselenium trichloride was therefore reacted with a number of olefins carrying an allylic substituent and the regiochemistry of addition studied. Allyl alcohol yielded only one addition product **18** when treated with $PhSeCl_3$. A similar result was obtained with allyl acetate (compound **19**). However, at this point the regiochemistry of addition could not be unambiguously determined. Treatment of alcohol **18** in refluxing acetyl chloride/chloroform yielded acetate **19**. This shows that

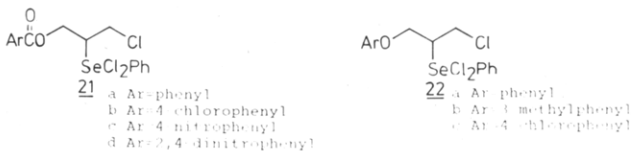
(9) Schmid, G. H. *Can. J. Chem.* **1968**, *46*, 3415.
(10) Garratt, D. G.; Ujjainwalla, M.; Schmid, G. H. *J. Org. Chem.* **1980**, *45*, 1206.

the two olefinic substrates were similarly attacked by the selenium reagent. The conclusive assignment of structures **18** and **19** as anti-Markovnikov adducts was arrived at by studying their chemical reactions (vide infa). Furthermore, the Markovnikov adduct **20** was independently synthesized from the addition of PhSeCl to allyl alcohol, followed by chlorination and acetylation (eq 6). The physical and spectroscopic properties of this material were distinctly different from those of compound **19**.

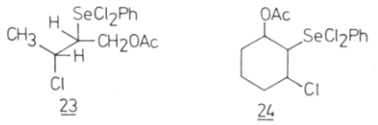


20 (6)

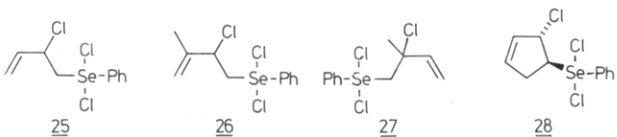
Allyl benzoate and a series of derivatives thereof (allyl 4-chlorobenzoate, allyl 4-nitrobenzoate, and allyl 2,4-dinitrobenzoate) yielded the Markovnikov adducts **21a–d**, respectively, with $PhSeCl_3$. The allyl aryl ethers, allyl phenyl ether, allyl 3-methylphenyl ether, and allyl 4-chlorophenyl ether, showed a similar directing effect in the addition reaction to yield compounds **22a–c**, respectively.

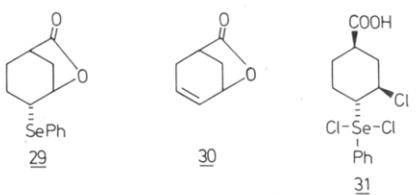


Crotyl acetate and 2-cyclohexen-1-yl acetate gave adducts **23** and **24**, respectively. These two examples show that the reaction is applicable also to more complex olefins than the simplest propenes.



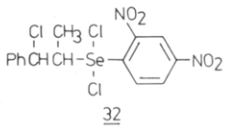
In order to further explore the possibility of introducing tetravalent selenium into organic molecules, phenylselenium trichloride was reacted with some dienic compounds. Butadiene yielded a low-melting solid in good yield. The facile conversion of the product into chloroprene via the hydrolytic selenoxide elimination reaction was consistent with a 1,2-addition structure **25** of the chloroselenation compound. Isoprene reacted similarly. According to ^1H NMR analysis there was formed a 1:1 mixture of isomers **26** and **27** in the addition. Cyclopentadiene gave only a single addition product according to NMR analysis. However, its structure could not be conclusively determined. We have tentatively assigned the unstable compound structure **28** in analogy with the results from the other dienes.

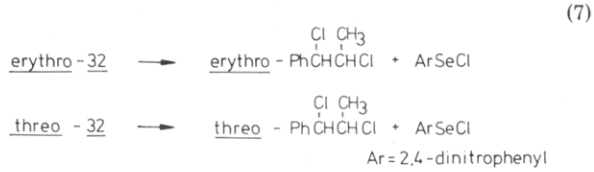




The unsaturated acid 3-cyclohexene-1-carboxylic acid is known to undergo a smooth regiospecific cyclofunctionalization reaction when treated with benzeneselenenyl chloride.[11] The product, compound **29**, can be oxidatively eliminated to yield the unsaturated lactone **30**. Since $PhSeCl_3$ addition/hydrolysis in principle could be expected to effect the same synthetic transformations, it was of interest to study the regiochemistry of $PhSeCl_3$ addition to the olefin. From inspection of the IR spectrum of the product (1685 and 2940 broad cm^{-1}) it was concluded that phenylselenium trichloride did not induce any lactonization. Instead, addition to the olefin occurred (97% yield). When the product was treated with thiourea in acetone[12] to reductively remove the two chlorine atoms bonded to selenium, the lactone **29** was isolated in 63% yield. From this result we have tentatively assigned structure **31** to the chloroselenation product. To account for the stereochemistry of the reduction product **29**, the lactonization process has to involve a selenium-assisted substitution of chlorine with retention of configuration.

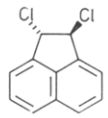
(β-Chloroalkyl)phenylselenium dichlorides represent a rather unstable class of compounds. Besides their sensitivity to hydrolysis/selenoxide elimination, they decompose via a 1,2-shift of chlorine from selenium to carbon.[13] Garratt and Schmid[4] reported the stereospecific decomposition of the two compounds **32** with retention of configuration as shown in eq 7.[14]





(7)

The decomposition of the corresponding adducts of $PhSeCl_3$, compounds **4a** and **5a**, respectively, was studied by recording the NMR spectra of their $CDCl_3$ solutions at intervals over a period of several weeks. It was found that *both* compounds stereoselectively yielded *erythro*-1,2-dichloro-1-phenylpropane (erythro/threo = 9:1) in addition to benzeneselenenyl chloride. Compound **12** also decomposed upon standing in chloroform. In this case *trans*-1,2-dichloroacenaphthene (**33**) was stereospecifically formed in 62% isolated yield.



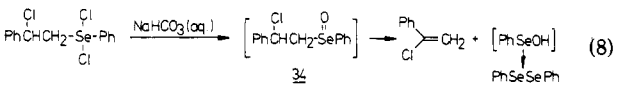
Some of the addition compounds were rather unstable and did not give a completely satisfying analysis. If kept in a freezer, however, the samples could be stored for

(11) Nicolaou, K. C.; Seitz, S. P.; Sipio, W.J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884.
(12) Appa Rao, G. V. N.; Seshasayee, M.; Aravamudan, G.; Sowrirajan, S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 620.
(13) Foster, D. G. *Recl. Trav. Chim. Pays-Bas* **1934**, *53*, 405.
(14) The reported[4] ^1H NMR parameters for the two compounds **32** are not in very close agreement with the value we observed for the similar compounds **4a** and **5a**. If the parameters for the corresponding dechlorinated compounds are taken into consideration,[4,15] this disagreement becomes even clearer. Unfortunately we could not prepare compounds **32** because the required (2,4-dinitrophenyl)selenium trichloride in our hands could not be prepared as described in the literature by SO_2Cl_2 chlorination of 2,4-dinitrophenyl selenocyanate.[8] Even when the reflux time was extended from the recommended 10 min to 3 h, unreacted 2,4-dinitrophenyl selenocyanate always crystallized out after filtration and cooling.
(15) Garratt, D. G. *Can. J. Chem.* **1979**, *57*, 2180.

several months without any visible decomposition.

Elimination Reactions. The regio- and stereospecificity of the addition of $PhSeCl_3$ to unsaturated systems would be of limited interest unless one could find ways to further elaborate the products in a constructive way. By use of the mild hydrolytic selenoxide elimination reaction, it should be possible to convert the adducts into synthetically useful vinylic or allylic chlorides. Although vinylic ethers or esters cannot be easily prepared by employing the selenoxide elimination reaction, the few experiments done indicate that vinylic chlorides are formed quite readily.[16] However, it has been reported that the elimination proceeds sluggishly when unactivated cyclohexane rings are involved.[6]

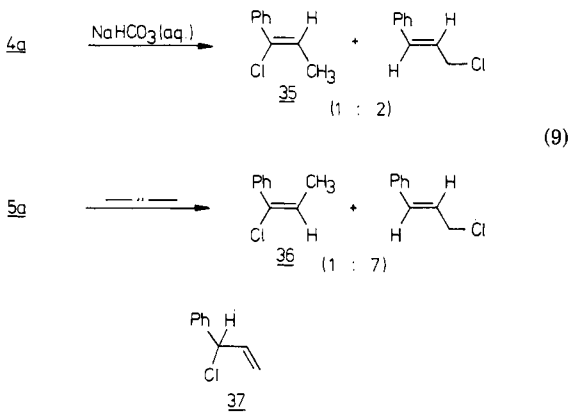
We have found that the hydrolytic variation of the selenoxide elimination reaction is well suited for the syntheses of vinylic as well as allylic halides. In a typical procedure compound **15a**, the adduct of styrene and $PhSeCl_3$, was dissolved in methylene chloride and shaken in a separatory funnel with a dilute aqueous solution of sodium hydrogen carbonate. After the initial gas evolution had ceased, the two-phase system was left for 24 h to complete the elimination of selenoxide **34** (eq 8). The



(8)

yellow organic phase was then separated and the product, α-chlorostyrene, Kugelrohr-distilled (78% yield) from some diphenyl diselenide, which was always formed in the elimination (as a secondary product of PhSeOH).

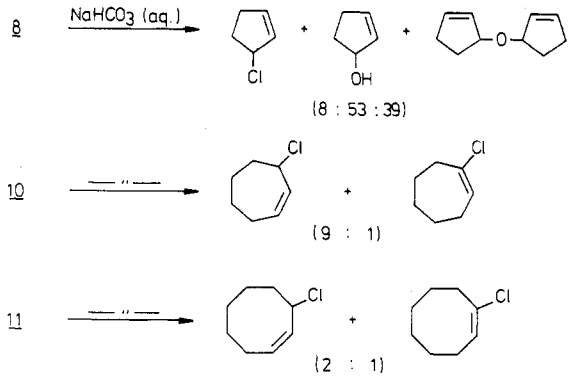
Compounds **4a** and **5a** yielded mixtures of vinylic and allylic chlorides in 88% and 93% overall yields, respectively, when treated in methylene chloride with aqueous $NaHCO_3$ (eq 9). Obviously, for these substrates the



(9)

elimination can proceed in either of two directions, producing the vinylic chlorides **35** and **36**, respectively (shown in eq 9) or the allylic chloride **37**. However, the latter substance isomerized during workup to the more stable terminal allylic chloride shown in the equation.

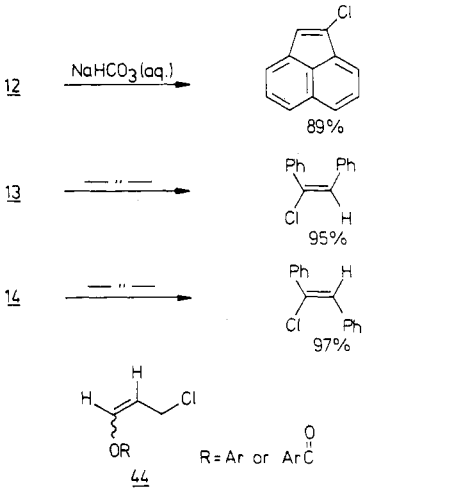
As already mentioned, the conventional selenoxide elimination of 2-chlorocyclohexyl phenyl selenoxide (**2**) produced a 1:1-mixture of allylic and vinylic chloride as shown in eq 3. We have studied the direction of elimination for the corresponding five-, seven-, and eight-membered selenoxides resulting from hydrolysis of the selenium dichlorides **8**, **10**, and **11**. The selenoxide **2**, hydrolytically derived from compound **9a**, eliminated only very slowly at ambient temperature as judged by the slow formation of diphenyl diselenide. The other three elimination reactions were completed within 15 min at ambient temperature by using the hydrolytic procedure described above (eq 10). 3-Chlorocyclopentene, 2-cyclopenten-1-ol,



(10)

and bis(2-cyclopenten-1-yl) ether were isolated (56% total yield) in the elimination of the cyclopentane compound. Since the two latter compounds are probably derived from the very reactive allylic chloride,[17] we conclude that the elimination has occurred exclusively *away* from chlorine. The cycloheptane and cyclooctane compounds both afforded mixtures of allylic and vinylic chlorides in 83% and 73% total yields, respectively.

The olefin–$PhSeCl_3$ addition compounds derived from acenaphthylene, *cis*- and *trans*-stilbene can only produce vinylic chlorides in the elimination reaction. As shown in eq 11 the expected products were formed in very good yields. The observed retention of olefin geometry among



(11)

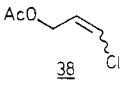
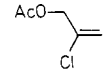
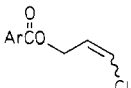
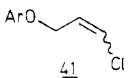
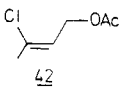
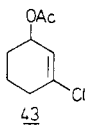
the stilbenes was used for the configurational assignment of compounds **13** and **14** as discussed above. As distillation could no longer be used for the separation of vinylic chloride products from diphenyl diselenide, a reductive workup procedure was developed, involving $NaBH_4$ reduction of the diselenide and alkaline extraction of the phenyl selenolate.

All addition products obtained from $PhSeCl_3$ and allylic esters and ethers (compounds **19–24**) underwent elimination reactions upon treatment with aqueous $NaHCO_3$. After Kugelrohr distillation vinylic chlorides **38–43** were isolated, usually as a mixture of *E* and *Z* isomers (see Table I). In some cases there was also formed a certain amount (0–35% yield) of another elimination product which we have assigned a vinyl ester/ether structure **44**. The chloromethyl groups of these compounds showed a characteristic absorption at 4.1–4.3 ppm in the ^1H NMR spectrum. Unfortunately the byproducts were not se-

(16) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow; F., Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1697.

(17) Alder, K.; Flock, F. H. *Chem. Ber.* **1956**, *89*, 1732.

Table I. Synthesis of Vinylic Chlorides Containing an Oxygen Substituent in the Allylic Position

substr	product	yield, %[a]	Z/E ratio
19	 38	64[b]	59/41
20	 39	64	
21	 40		
a, Ar = phenyl		74	57/43
b, Ar = 4-chlorophenyl		80	75/25
c, Ar = 4-nitrophenyl		63	58/42
d, Ar = 2,4-dinitrophenyl		66	61/39
22	 41		
a, Ar = phenyl		68	73/27
b, Ar = 3-methylphenyl		71	73/27
c, Ar = 4-chlorophenyl		67	72/28
23	 42	38	
24	 43	65	

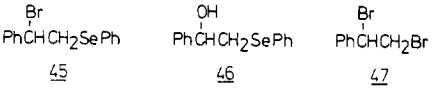
[a] Isolated yield after acid treatment. [b] No purification performed.

parable from the vinylic chlorides. However, they could be conveniently hydrolyzed by heating the crude reaction mixtures (before distillation) in acetic acid/water containing a small quantity of HCl. In the purification of compounds **40c** and **40d** (Table I) trifluoroacetic acid was used to effect hydrolysis. Products resulting from elimination *toward* an oxygen substituent have previously been isolated in the selenoxide elimination reaction, although in much smaller yields (0–3%[5]) than ours.

Phenylselenium Tribromide. Phenylselenium tribromide, $PhSeBr_3$, is conveniently obtained as an orange solid by treatment of diphenyl diselenide with bromine. This material has found very limited use in organic synthesis. We have studied, to some extent, the reactions of olefins with $PhSeBr_3$. When (*E*)- and (*Z*)-2-butene were bubbled at 0 °C into diethyl ether suspensions of $PhSeBr_3$, the insoluble selenium tribromide quickly disappeared and the adducts **6b** and **7b**, respectively, were isolated in good yields by precipitation with light petroleum. From the observed values of $^3J_{H-H}$ in deuteriochloroform (ϵ = 4.70) and methylene chloride-d_2 (ϵ = 8.9) we have assigned compound **6b** as an erythro isomer [$^3J_{H-H}$ = 7.6 ($CDCl_3$), 6.9 Hz (CD_2Cl_2)] and compound **7b** as a threo isomer [$^3J_{H-H}$ = 5.6 ($CDCl_3$), 5.9 Hz (CD_2Cl_2)]. It follows from these results that the addition of $PhSeBr_3$ is anti stereospecific. This stereospecificity was also observed for the addition of phenylselenium tribromide to (*E*)- and (*Z*)-1-phenylpropene, which yielded compounds **4b** and **5b**, respectively. Since the β-methyl group of compound **4b** resonated at 2.14 ppm and that of compound **5b** at 1.65 ppm, it was concluded that compound **4b** was an erythro isomer, while compound **5b** was a threo one.

Cyclohexene gave an adduct **9b** with $PhSeBr_3$ which has also been assigned a trans configuration ($^3J_{H-H\ methine}$ = 10.9 Hz).

Concerning the regiochemistry of addition, we have found that styrene regiospecifically yielded the Markovnikov adduct **15b** when treated with $PhSeBr_3$ in dry ether. This was shown by an independent synthesis of the compound from the known selenide **45** and bromine. Compounds **4b** and **5b** were assigned as Markovnikov adducts in analogy with this result.



45 46 47

The hydrolytic selenoxide elimination reaction was not useful for the adducts of $PhSeBr_3$. When compound **15b** was treated with $CH_2Cl_2/NaHCO_3$ (aqueous) in a separatory tunnel and left for 24 h, there was obtained an almost colorless organic phase (only a trace of PhSeSePh) containing the β-hydroxy selenide **46** and dibromostyrene (**47**) as the main products.

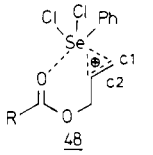
In general, the adducts of $PhSeBr_3$ with olefins are less stable than the corresponding adducts of $PhSeCl_3$. When the (β-bromoalkyl)phenylselenium dibromides **4b**, **5b**, **6b**, **7b**, and **15b** were dissolved in $CDCl_3$ and left for some time at ambient temperature they slowly turned deep brown/purple due to a decomposition reaction producing benzeneselenenyl bromide and the corresponding 1,2-dibromoalkane in analogy with eq 7. The progress of the reactions was conveniently followed by ^1H NMR.

The adduct of $PhSeBr_3$ with (*E*)-2-butene decomposed considerably more slowly than the one with (*Z*)-2-butene. However, in both cases the reaction occurred with retention of stereochemistry (retention/inversion = 97/3). Compound **4b** also decomposed with retention of configuration (93/7), whereas compound **5b** afforded mainly the inverted product (retention/inversion = 25/75).

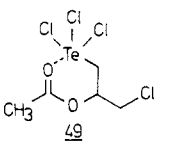
Discussion

The lack of regiospecificity imposes certain restrictions on the applicability of the mild and easy-to-perform sequence (addition–elimination) for the synthesis of vinylic or allylic chlorides. The methodology was most successfully applied to symmetrical olefins containing no allylic hydrogens or olefins containing an oxygen substitutent (acyloxy, aryloxy, or hydroxy group) in the allylic position.

The directing effect of the acyloxy group in the addition might be explained by assuming an initial weak coordination of the incoming electrophile, $PhSeCl_2^+$, to the carbonyl oxygen as depicted in structure **48**. The (acyl-



48



49

oxy)methyl group should also serve to reduce the relative charge density at carbon C2 relative to carbon C1. This electronic effect taken together with the steric effect (less hindrance at the terminal position) would direct the nucleophilic attack by chloride ion to occur preferentially at carbon C1. However, the carbonyl absorption in the IR spectrum of a typical addition compound [ν(C=O) = 1740 cm^{-1} for compound **19**] does not indicate any coordination of selenium to the carbonyl group. Such a coordination is known to lower the carbonyl absorption considerably as observed for the related tellurium compound **49** [ν(C=O) = 1630 cm^{-1}].[18] Similar reasoning can be used to account for the directing effect of an aryloxy/hydroxy group.

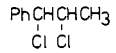
(18) Engman, L. *J. Am. Chem. Soc.* **1984**, *106*, 3977.

It was observed that the reaction rates as well as the product ratios of allylic/vinylic chloride varied dramatically with ring-size for the cyclic olefins (see eq 10). These effects can probably be attributed to conformational differences among the selenoxides. The selenoxide elimination reaction is known to require a syn orientation in the transition state between selenium and the hydrogen to be eliminated. A qualitative inspection of molecular models indicated that the five-, seven-, and eight-membered rings could attain such conformations considerably more easily than the six-membered ring.

The failure of the elimination process for adducts of $PhSeBr_3$ is not readily explained. The formation of the β-hydroxy selenide **46** and the dibromoalkane **47** from the attempted elimination of the selenium dibromide **15b** seems to involve disproportionation reactions of the substrate.

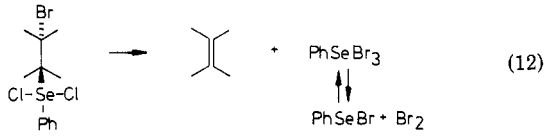
The olefin adducts of $PhSeCl_3$ and $PhSeBr_3$ decomposed in solution to produce 1,2-dihaloalkanes and the respective benzeneselenenyl halides. Several mechanisms are conceivable for these processes. Ward and Morella[19] have recently reported a method for cis chlorination of alkenes using a variation of this reaction. After trans addition of PhSeCl to the olefin, followed by chlorination, the resulting *trans*(β-chloroalkyl)phenylselenium dichloride was treated in boiling acetonitrile with tetrabutylammonium chloride to displace the benzeneselenenyl chloride with *inversion* of configuration.

If the decomposition is not induced by an external source of chloride ion, the benzeneselenenyl chloride is displaced with *retention* of configuration, as observed by Garratt and Schmid[4] and by us (compounds **4a** and **12**). It is likely that a mechanism involving a 1,2-shift of chlorine from selenium to carbon is operative in these reactions. When compound **4a** was decomposed in the presence of tetrabutylammonium chloride by using the Ward/Morella conditions,[19] the benzeneselenenyl chloride was displaced mainly with inversion of configuration to yield compound **50** (threo/erythro = 84/16; the spontaneous decomposition gave threo/erythro = 10/90).



50

There is also a third possible mechanism involving reversion of the addition process followed by disproportionation of the resulting phenylselenium trihalide and halogenation of the olefin (eq 12).[19]



(12)

The decomposition of the $PhSeCl_3$ adduct **4a** is not compatible with such a mechanism since chlorination of (*E*)-1-phenylpropene is known to occur with very poor stereoselectivity.[20]

The phenylselenium tribromide adducts **4b**, **6b**, and **7b** were all stereoselectively decomposed to 1,2-dibromoalkanes in $CDCl_3$ with retention of configuration. However, since the observed stereochemistries were very similar to those obtained by bromination of the respective olefins, no conclusive distinction can be made between a 1,2-bromine migration mechanism and the disproportionation/Br_2 addition mechanism.

Experimental Section

Melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus. NMR spectra were obtained at 200 MHz by using a Bruker WP 200 instrument. They were recorded in $CDCl_3$ solutions (unless otherwise stated) containing Me_4Si as internal standard and are reported in δ units. IR spectra were obtained by using a Perkin-Elmer 257 instrument. 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. (*E*)-3-Chloro-1-phenylpropene,[22] 3-chlorocyclopentene,[17] 2-cyclopenten-1-ol,[17] bis(2-cyclopenten-1-yl) ether,[17] 1-chlorocycloheptene (and analogously 1-chlorocyclooctene),[23] 2-bromo-2-phenylethyl phenyl selenide,[24] 1-phenyl-2-(phenylseleno)ethanol,[25] *erythro*- and *threo*-2,3-dibromobutane,[26] *erythro*- and *threo*-1,2-dichloro-1-phenylpropane,[20] and *erythro*- and *threo*-1,2-dibromo-1-phenylpropane[21] were prepared according to the literature methods. The different allyl alcohol benzoic acid esters were prepared from equivalent amounts of the allylic alcohol, pyridine, and the suitably substituted benzoyl chloride in dry ether in analogy with the literature methods.[27,28] The allylic acetates were prepared from the corresponding allylic alcohols by treatment in refluxing acetic anhydride containing some pyridine. The allyl phenyl ethers used were prepared in analogy with the preparation of allyl 4-chlorophenyl ether.[29] All other olefinic compounds used were commercially available. Diethyl ether was dried over sodium. Acetonitrile was dried over molecular sieves (4 Å). Chloroform was washed with water to remove ethanol and dried over $CaCl_2$.

Phenylselenium Trichloride (1a). $PhSeCl_3$ has been synthesized in several different ways in the literature.[30] We find the following procedure very convenient also for large-scale preparation of the material. Freshly distilled sulfuryl chloride was added dropwise to a stirred solution of diphenyl diselenide (10.0 g, 32.1 mmol) in dry $CHCl_3$ (40 mL) until the orange-brown color of benzeneselenenyl chloride (intermediately formed) had disappeared. The yellowish precipitate was then rapidly filtered, dried under pump–vacuum and stored in a freezer at −20 °C. This material (14.5 g, 86% yield) was not further purified due to the known[31] instability of the compound.

Phenylselenium tribromide was similarly prepared in 91% yield by treatment of diphenyl diselenide in chloroform with bromine.[32] This material was also stored in a freezer and used without further purification.

Addition Compounds of $PhSeCl_3$ and $PhSeBr_3$ with Various Olefinic Compounds. Typical Procedure. (2-Chloro-2-phenylethyl)phenylselenium Dichloride (15a). To a stirred suspension of $PhSeCl_3$ (1.0 g, 3.8 mmol) in dry ethyl ether (5 mL) was added styrene (0.45 g, 4.3 mmol) in dry ethyl ether (0.5 mL) dropwise at 0 °C. The solution became homogeneous and almost colorless within a few minutes, and after addition of light petroleum, bp 40–60 °C (30 mL), and cooling to −20 °C, 1.30 g (93%) white crystals of compound **15a** were isolated. Recrystallization from ether/light petroleum (bp 40–60 °C) afforded an analytical sample. The product was stored at −20 °C in a freezer.

The gaseous olefins were bubbled slowly through ether sus-

(19) Morella, A. M.; Ward, A. D. *Tetrahedron Lett.* **1984**, *25*, 1197. See also: Morella, A. M.; Ward, A. D. *Tetrahedron Lett.* **1985**, *26*, 2899.
(20) Fahey, R. C.; Schubert, C. *J. Am. Chem. Soc.* **1965**, *87*, 5172.
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(22) Caserio, F.F.; Dennis, G. E.; DeWolfe, R. H.; Young, W. G. *J. Am. Chem. Soc.* **1955**, *77*, 4182.
(23) Ball, W. J.; Landor, S. R. *J. Chem. Soc.* **1962**, 2298.
(24) Raucher, S.; Hansen, M. R.; Colter, M. A. *J. Org. Chem.* **1978**, *43*, 4885.
(25) Toshimitsu, A.; Aoai, T.; Owada, H.; Uemura, S.; Okano, M. *Tetrahedron* **1985**, *41*, 5301.
(26) Goering, H. L.; Larsen, D. W. *J. Am. Chem. Soc.* **1959**, *81*, 5937.
(27) Hauser, C. R.; Hudson, B. E.; Abramovitch, B.; Shivers, J. C. *Org. Synth.* **1944**, *24*, 19.
(28) Norris, J. F.; Rigby, G. W. *J. Am. Chem. Soc.* **1932**, *54*, 2088.
(29) White, W. N.; Gwynn, D.; Schlitt, R.; Girard, C.; Fife, W. *J. Am. Chem. Soc.* **1958**, *80*, 3271.
(30) Foster, D. G. *J. Am. Chem. Soc.* **1933**, *55*, 822. Behagel, O.; Seibert, H. *Ber. Dtsch. Chem. Ges.* **1933**, *66*, 708.
(31) Horn, V.; Paetzold, R. *Z. Anorg. Allg. Chem.* **1973**, *398*, 179.
(32) Horn, V.; Paetzold, R. *Z. Anorg. Allg. Chem.* **1973**, *398*, 173.

pensions of the phenylselenium trihalides until the solutions became homogeneous.

Melting points, yields, and analytical data can be found in the following (compound: mp °C; yield %. Analysis).

4a: 73–74 dec; 99. Anal. Calcd for $C_{15}H_{15}Cl_3Se$: C, 47.34; H, 3.97. Found: C, 47.84; H, 4.05.

5a: 115–120 dec; 99. Anal. Calcd for $C_{15}H_{15}Cl_3Se$: C, 47.34; H, 3.97. Found: C, 47.37; H, 4.09.

6a: 120–123 dec; 98. Anal. Calcd for $C_{10}H_{13}Cl_3Se$: C, 37.71; H, 4.11. Found: C, 37.91; H, 4.16.

7a: 103–105 dec; 97. Anal. Calcd for $C_{10}H_{13}Cl_3Se$: C, 37.71; H, 4.11. Found: C, 37.90; H, 4.16.

8: 45–50 dec; 90. Anal. Calcd for $C_{11}H_{13}Cl_3Se$: C, 39.97; H, 3.93. Found: C, 39.92; H, 4.03.

9a: 139–140 dec; 96. Anal. Calcd for $C_{12}H_{15}Cl_3Se$: C, 41.83; H, 4.39. Found: C, 42.15; H, 4.42.

10: 99–101 dec; 97. Anal. Calcd for $C_{13}H_{17}Cl_3Se$: C, 43.54; H, 4.78. Found: C, 43.73; H, 4.80.

11: 84–87 dec; 92. Anal. Calcd for $C_{14}H_{19}Cl_3Se$: C, 45.13; H, 5.14. Found: C, 44.35; H, 5.11.

12: 68–72 dec; 98. Anal. Calcd for $C_{18}H_{13}Cl_3Se$: C, 52.14; H, 3.16; C, 52.60; H, 3.48.

13: 70–73 dec; 96. Anal. Calcd for $C_{20}H_{17}Cl_3Se$: C, 54.27; H, 3.87. Found: C, 54.43; H, 4.21.

14: 75–78 dec; 93. Anal. Calcd for $C_{20}H_{17}Cl_3Se$: C, 54.27; H, 3.87. Found: C, 54.62; H, 4.29.

15a: 98–100 dec; 93. Anal. Calcd for $C_{14}H_{13}Cl_3Se$: C, 45.87; H, 3.57. Found: C, 45.55; H, 3.73.

18: 88–90 dec; 99. Anal. Calcd for $C_9H_{11}Cl_3OSe$: C, 33.73; H, 3.46. Found: C, 34.16; H, 3.50.

19: 62–65 dec; 94. Anal. Calcd for $C_{11}H_{13}Cl_3O_2Se$: C, 36.44; H, 3.61. Found: C, 36.65; H, 3.61.

21a: 105 dec; 99. Anal. Calcd for $C_{16}H_{15}Cl_3O_2Se$: C, 45.26; H, 3.56. Found: C, 45.49; H, 3.62.

21b: 108–110 dec; 92. Anal. Calcd for $C_{16}H_{14}Cl_4O_2Se$: C, 41.86; H, 3.07. Found: C, 42.19; H, 3.28.

21c: 115–117 dec, 98. Anal. Calcd for $C_{16}H_{14}Cl_3NO_4Se$: C, 40.92; H, 3.00. Found: C, 41.26; H, 3.02.

21d: 130–135 dec; 100. Anal. Calcd for $C_{16}H_{13}Cl_3N_2O_6Se$: C, 37.34; H, 2.55. Found: C, 37.57; H, 2.62.

22a: 88–90 dec; 96. Anal. Calcd for $C_{15}H_{15}Cl_3OSe$: C, 45.43; H, 3.81. Found: C, 45.57; H, 3.81.

22b: 78–80 dec; 92. Anal. Calcd for $C_{16}H_{17}Cl_3OSe$: C, 46.80; H, 4.17. Found: C, 47.16; H, 4.22.

22c: 104–105 dec; 95. Anal. Calcd for $C_{15}H_{14}Cl_4OSe$: C, 41.80; H, 3.27. Found: C, 42.06; H, 3.29.

23: 94–96 dec; 95. Anal. Calcd for $C_{12}H_{15}Cl_3O_2Se$: C, 38.28; H, 4.01. Found: C, 37.84; H, 4.35.

24: 119–121 dec; 94. Anal. Calcd for $C_{14}H_{17}Cl_3O_2Se$: C, 41.77; H, 4.27. Found: C, 42.02; H, 4.25.

4b: 48–52 dec; 92. Anal. Calcd for $C_{15}H_{15}Br_3Se$: C, 35.05; H, 2.94. Found: C, 34.95; H, 3.58.

5b: 62–67 dec; 92. Anal. Calcd for $C_{15}H_{15}Br_3Se$: C, 35.05; H, 2.94. Found: C, 34.66; H, 3.59.

6b: 75–80 dec; 86. Anal. Calcd for $C_{10}H_{13}Br_3Se$: C, 26.58; H, 2.90. Found: C, 25.50; H, 2.92.

7b: 58–63 dec; 88. Anal. Calcd for $C_{10}H_{13}Br_3Se$: C, 26.58; H, 2.90. Found: C, 25.19; H, 3.12.

9b: 96–98 dec; 95. Anal. Calcd for $C_{12}H_{15}Br_3Se$: C, 30.16; H, 3.16. Found: C, 30.35; H, 3.19.

15b: 70–77 dec; 99. Anal. Calcd for $C_{14}H_{13}Br_3Se$: C, 33.63; H, 2.62. Found: C, 33.40; H 2.27.

4a: ^1H NMR δ 1.90 (d, 3 H), 5.10 (m, 1 H), 5.88 (d, 1 H, J = 7.9 Hz), 7.43–7.50 (several peaks, 6 H), 7.68 (m, 2 H), 8.03 (m, 2 H).

5a: ^1H NMR δ 1.45 (d, 3 H), 5.28 (m, 1 H), 5.63 (d, 1 H, J = 10.4 Hz), 7.40–7.54 (several peaks, 8 H), 8.19 (m, 2 H).

$PhSeCl_3$ and 1-Butene. 1-Butene was bubbled at 0 °C into a suspension of $PhSeCl_3$ (1.0 g, 3.8 mmol) in dry ether (5 mL) until the solid material had all dissolved. Precipitation with light petroleum (bp 40–60 °C) and cooling to −20 °C yielded a white product, 1.11 g (92%), as a mixture of compounds **16** and **17** (**16**/**17** = 81/19 according to ^1H NMR).

PhSeCl and 1-Butene. 1-Butene was bubbled into a solution of PhSeCl (1.0 g, 5.2 mmol) in dry CH_2Cl_2 (8 mL) at −78 °C until the orange-brown colour faded away. SO_2Cl_2 (0.80 g, 5.9 mmol) in CH_2Cl_2 (2 mL) was then added and the solution kept at −78 °C for $^3/_4$ h. After warming to ambient temperature, the solvent was removed and the crude residue analyzed by ^1H NMR. The product was a mixture of compounds **16** and **17** (**16**/**17** = 87/13). Recrystallization from ether/light petroleum (bp 50–60 °C) afforded 1.60 g (96%) of the mixture as a white powder, which had turned slightly yellowish already by filtration in the air.

A similar experiment was also performed at ambient temperature by using chloroform as solvent. After the addition of 1-butene the reaction mixture was left overnight before the sulfuryl chloride was added. In this case there was formed a 7/93 mixture of compounds **16** and **17** (90% yield). Compound **17** was isolated in a pure form from this mixture by recrystallization from ether/light petroleum (bp 40–60 °C), mp 98–99 °C. Anal. Calcd for $C_{10}H_{13}Cl_3Se$: C, 37.71; H, 4.11. Found: C, 37.50; H, 4.36.

Conversion of 18 to 19. Compound **18** (0.30 g, 0.94 mmol) in a mixture of $CHCl_3$ (1 mL) and acetyl chloride (1.6 g) was heated to reflux for 15 min. The yellow solution was then evaporated and the residue crystallized from ether light petroleum (bp 40–60 °C). The product was identical in all respects with compound **19**. Yield: 0.25 g (71%).

(3-Acetoxy-2-chloropropyl)phenylselenium Dichloride (20). A solution of PhSeCl (5.0 g, 26.1 mmol) and allyl alcohol (1.55 g, 26.7 mmol) in dry $CHCl_3$ (20 mL) was stirred at ambient temperature for 3 days. At this point SO_2Cl_2 (3.6 g, 26.7 mmol) in $CHCl_3$ (5 mL) was added to the yellowish solution (exothermic reaction, gas evolution). After 2 h the solvent was evaporated and the resulting oil dissolved in a mixture of $CHCl_3$ (10 mL) and acetyl chloride (10 g) and refluxed for 30 min. After evaporation and crystallization from ether/light petroleum 8.64 g (91%) of compound **20** was isolated, mp 102–103 °C. Anal. Calcd for $C_{11}H_{13}Cl_3O_2Se$: C, 36.44; H, 3.61. Found: C, 36.63; H, 3.66.

(2-Chloro-3-butenyl)phenylselenium Dichloride (25). $PhSeCl_3$ (1.0 g, 3.8 mmol) was treated in dry ether with butadiene according to the typical procedure. After precipitation and cooling to −20 °C, a gummy white material was obtained. Upon trituration with a glass rod in the freezer, the material finally crystallized after several days. However, the compound melted below room temperature. Yield: 1.12 g (93%).

The product (0.15 g) in $CDCl_3$ (1 mL) was treated with 0.15 g of $NaHCO_3$ in H_2O (3 mL) in a separatory funnel. The yellow organic phase was separated after 2 h, dried, and Kugelrohr distilled. The NMR spectrum of the distillate was identical with that of chloroprene.

$PhSeCl_3$ and Isoprene. $PhSeCl_3$ (1.0 g, 3.8 mmol) and isoprene (0.30 g, 4.4 mmol) were reacted according to the typical procedure. After precipitation there was obtained a 1:1 mixture (according to ^1H NMR) of compounds **26** and **27** as a white unstable powder that turned yellow after a short exposure to the atmosphere. Yield: 1.14 g (90%).

$PhSeCl_3$ and Cyclopentadiene. $PhSeCl_3$ (2.0 g, 7.6 mmol) and freshly distilled cyclopentadiene (0.52 g, 7.9 mmol) were reacted according to the typical procedure. After precipitation there was obtained a white unstable material, 2.39 g (96%), mp 45–50 °C (crude material). The compound was assigned structure **28** in analogy with the results from the other dienes.

(4-Carboxy-2-chlorocyclohexyl)phenylselenium Dichloride (31). $PhSeCl_3$ (1.0 g, 3.8 mmol) and 3-cyclohexene-1-carboxylic acid (0.50 g, 4.0 mmol) were reacted according to the typical procedure. After precipitation there was isolated 1.44 g (97%) of compound **31**, mp 115–125 °C (ether/light petroleum bp 40–60 °C). Anal. Calcd for $C_{13}H_{15}Cl_3O_2Se$: C, 40.18; H, 3.89. Found: C, 40.70; H, 3.98. IR: 1685 and 2940 cm^{-1}.

4-(Phenylseleno)-6-oxabicyclo[3.2.1]octan-7-one (29). Compound **31** (1.0 g, 2.57 mmol) was added to a stirred solution of thiourea (0.40 g, 5.3 mmol) in acetone (25 mL). After 1 h the reaction mixture was poured into water/CH_2Cl_2 and the organic phase washed with water several times. Drying, evaporation of the solvent, and purification on silica (CH_2Cl_2) afforded 0.45 g (63%) of compound **29**, mp 87 °C (lit.[11] mp 91–92 °C).

Elimination Reactions. Typical Procedure. α-Chlorostyrene. (2-Chloro-2-phenylethyl)phenylselenium dichloride (**15a**) (2.0 g, 5.5 mmol) dissolved in CH_2Cl_2 (50 mL) was shaken with $NaHCO_3$ (2.6 g, 31 mmol in 50 mL of H_2O) in a separatory funnel until the initial gas evolution had ceased (≈5 min). The two-phase system was then left for 24 h to complete the elimination. During

this period the CH_2Cl_2 phase slowly turned yellow due to formation of diphenyl diselenide. After separation of the organic phase, drying, evaporation, and Kugelrohr distillation, 0.59 g (78%) of α-chlorostyrene was obtained. The ^1H NMR spectrum of the product was in excellent agreement with the literature data.[33]

Compounds **4a** and **5a** eliminated rather easily upon treatment with $NaHCO_3$ (aqueous). The organic phases were separated after 2 h and dried for 2 days over $CaCl_2$. After this period the intermediate allylic chloride 3-chloro-3-phenyl-1-propene had isomerized completely to (*E*)-3-chloro-1-phenylpropene. Compound **4a** afforded a 2:1 mixture of (*E*)-3-chloro-1-phenylpropene and (*Z*)-1-chloro-1-phenylpropene (**35**) according to GLC and ^1H NMR analysis. Yield: 88%. Compound **5a** similarly gave (*E*)-3-chloro-1-phenylpropene and (*E*)-1-chloro-1-phenylpropene (**36**) as a 7:1 mixture in 94% isolated yield. The ^1H NMR properties of compounds **35** and **36** showed good agreement with reported data.[34] When the eliminations were performed using ethyl ether as the organic solvent, the reactions were no longer regiospecific. Mixtures of compounds **35** and **36** were usually isolated from both compound **4a** and compound **5a**.

The eliminations of compounds **8**, **10**, and **11** were completed within 15 min according to TLC analysis. Compound **8** afforded a mixture of 3-chlorocyclopentene (4%), 2-cyclopenten-1-ol (31%), and di-2-cyclopenten-1-yl ether (21%) according to GLC and ^1H NMR analysis. All compounds were compared with authentic samples.

Compound **10** afforded a 9:1-mixture of 3-chlorocycloheptene and 1-chlorocycloheptene (87% combined yield). Compound **11** gave a 2:1 mixture of 3-chlorocyclooctene and 1-chlorocyclooctene (70% combined yield). Authentic samples of all compounds were prepared. The allylic chlorides were obtained by treatment of the corresponding allylic alcohols[35] (obtained from the respective allylic bromides) with thionyl chloride.

(*Z*)-1-Chloro-1,2-diphenylethylene. Compound **14** (1.0 g, 2.3 mmol) was eliminated according to the typical procedure for elimination reactions. In order to remove diphenyl diselenide (distillation could not be used) the crude reaction product was dissolved in EtOH (10 mL) and treated dropwise with $NaBH_4$ (5% aqueous) under N_2 until the yellow color had disappeared. Ethyl ether and water were then added, and the organic phase was separated by using a syringe through a septum. Drying and evaporation afforded 0.47 g (97%) of (*Z*)-1-chloro-1,2-diphenylethylene, mp 49–50 °C (lit.[36] mp 50–51 °C).

Compound **13** similarly afforded (*E*)-1-chloro-1,2-diphenylethylene[37] in 95% yield.

Compound **12** afforded 1-chloroacenaphthylene in 89% yield when submitted to the above reaction conditions, mp 20–22 °C (lit.[32] mp 19–20 °C).

The vinylic chlorides **38–43** (Table I) were all prepared according to the typical procedure with some modifications:

Compounds **21c** and **21d** were allowed to eliminate during 2 days. Compounds **23** and **24** eliminated slowly, and the two-phase system was left for 1 week before workup.

Compound **20** (8.5 g) was stirred in CH_2Cl_2 (100 mL) for 6 h at 50 °C with $NaHCO_3$ (6 g) in 75 mL H_2O (two-phase system).

The ^1H NMR spectra of the crude vinylic chlorides **38**, **40**, and **41** revealed the presence of a presumed vinyl ester/ether byproduct. [Compound (% vinyl ester/ether)]: **38** (10); **40a** (15); **40b** (0); **40c** (35); **40d** (27); **41a** (13); **41b** (15); **41c** (17). The impurity could be removed by treatment of the crude reaction product with acid as exemplified below: The reaction mixture from the elimination of 2.0 g of compound **22b** (the presumed vinyl ether appears as a doublet at 4.30 ppm) was dissolved in acetic acid (5 mL), water (0.5 mL), and concentrated HCl (1 drop) and heated to reflux for 30 min. After cooling, the product was poured into water/ethyl ether and extracted with 2 M NaOH. Kugelrohr distillation afforded the pure vinylic chloride **41b** as a *E*/*Z* mixture (71% yield).

All compounds **40** and **41** were purified as described above, except for compounds **40c** and **40d**, which were heated for 1 h in a refluxing mixture of trifluoroacetic acid (10 mL) and water (0.5 mL). Also, diphenyl diselenide was separated by chromatography before the purification of the nitro compounds (SiO_2; CH_2Cl_2/light petroleum = 1/1).

During Kugelrohr distillation small amounts of diphenyl diselenie usually codistilled with the products (compounds **40a**, **40b**, and **41**). This impurity could be conveniently removed by shaking of the product in methylene chloride with hydrogen peroxide (30% aqueous) in a separatory funnel until the yellow color of the diselenide suddenly faded away (5–15 min). The organic phase was then washed with 2 M NaOH and water.

Yields of purified products and *Z*/*E* ratios are shown in Table I.

An authentic sample of compound **38** (*E*/*Z* mixture) was prepared from commercially available 1,3-dichloropropene (*E*/*Z* mixture), which was hydrolyzed to 3-chloroallyl alcohol according to the literature method[39] and acetylated in acetic anhydride.

Decomposition Reactions. $CDCl_3$ solutions (0.05 M) of compounds **4a**, **4b**, **5a**, **5b**, **6b**, **7b**, and **15b** were prepared and their NMR spectra recorded at intervals over several weeks until the signals of the starting materials had disappeared. Compounds **4a** and **5a** required 11 and 23 days, respectively, for the decomposition. The reaction times for compounds **4b**, **5b**, **7b**, and **15b** were 24, 24, and 48 h and 7 days, respectively. The decomposition of compound **6b** was only completed to 85% after 16 days when GLC analysis was performed to establish the stereochemistry of the 2,3-dibromobutanes formed. All decomposition products were compared with authentic samples.

***trans*-1,2-Dichloroacenaphthene (33).** Compound **12** (1.53 g, 3.7 mmol) was dissolved in dry chloroform (30 mL) and left at ambient temperature for 2 weeks. During this time the solution turned orange-brown due to formation of benzeneselenenyl chloride. The $CHCl_3$ solution was then shaken in a separatory funnel with hydrogen peroxide (7 mL, 30%) until the orange-brown color faded away and treated successively with 2 M NaOH and water. The residue after drying and evaporation was recrystallized from aqueous ethanol to afford 0.51 g (62%) of compound **33**, mp 63–64 °C. After another recrystallization the material (0.41 g) melted at 66–67 °C (lit.[38] mp 66.5–68 °C).

Decomposition of Compound 4a in the Presence of Tetra-*n*-butylammonium Chloride. Compound **4a** was decomposed according to the literature procedure[19] to afford 1,2-dichloro-1-phenylpropane as a mixture (84/16) of threo and erythro isomers (93% yield).

Attempted Hydrolytic Selenoxide Elimination of Compound 15b. Compound **15b** (1.83 g, 3.7 mmol) dissolved in CH_2Cl_2 was treated with aqueous $NaHCO_3$ according to the typical procedure for selenoxide elimination. After 24 h the organic phase was almost colorless. Drying, evaporation, and chromatography (SiO_2/CH_2Cl_2) afforded dibromostyrene (**47**), 0.22 g (13%), mp 71–72 °C (lit.[40] 74–74.5 °C), and 1-phenyl-2-(phenylseleno)ethanol (**46**), 0.24 g (24%), as the only isolable products.

Independent Synthesis of Compounds 15b. Benzeneselenenyl bromide (0.75 g, 3.2 mmol) and styrene (0.33 g, 3.2 mmol) were stirred in dry CH_3CN (2 mL) for 30 min. The solvent was then evaporated and the product dissolved in light petroleum (bp 40–60 °C, 35 mL) and cooled to −20 °C (freezer). Bromine (0.51 g, 3.2 mmol) in CCl_4 (1 mL) was then added and the product allowed to crystallize in the freezer. The yield of compound **15b** (identical with the material obtained from $PhSeBr_3$ and styrene) was 1.16 g (75%).

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Registry No. **1a**, 42572-42-9; **4a**, 109391-76-6; **4b**, 109392-04-3; **5a**, 109391-77-7; **5b**, 109392-05-4; **6a**, 109391-78-8; **6b**, 109392-06-5; **7a**, 109391-79-9; **7b**, 109392-24-7; **8**, 109391-80-2; **9a**, 109391-81-3;

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9b, 109392-25-8; **10**, 109391-82-4; **11**, 109391-83-5; **12**, 109391-84-6; **13**, 109391-85-7; **14**, 109391-86-8; **15a**, 109391-87-9; **15b**, 109392-26-9; **16**, 109391-88-0; **17**, 109391-89-1; **18**, 109391-90-4; **19**, 109391-91-5; **20**, 109391-92-6; **21a**, 109391-93-7; **21b**, 109391-74-4; **21c**, 109391-75-5; **21d**, 109392-00-9; **22a**, 109391-94-8; **22b**, 109392-02-1; **22c**, 109392-03-2; **23**, 109391-95-9; **24**, 109432-28-2; **25**, 109391-96-0; **26**, 109391-97-1; **27**, 109391-98-2; **28**, 109391-99-3; **29**, 71404-67-6; **31**, 109392-01-0; **33**, 35468-33-8; **35**, 4541-85-9; **36**, 4541-86-0; (*Z*)-**38**, 109392-07-6; (*E*)-**38**, 109392-08-7; **39**, 692-72-8; (*Z*)-**40a**, 109392-09-8; (*E*)-**40a**, 109392-10-1; (*Z*)-**40b**, 109392-11-2; (*E*)-**40b**, 109392-12-3; (*Z*)-**40c**, 109392-13-4; (*E*)-**40c**, 109392-14-5; (*Z*)-**40d**, 109392-15-6; (*E*)-**40d**, 109392-16-7; (*Z*)-**41a**, 109392-17-8; (*E*)-**41a**, 109392-18-9; (*Z*)-**41b**, 109392-19-0; (*E*)-**41b**, 109392-20-3; (*Z*)-**41c**, 109392-21-4; (*E*)-**41c**, 109392-22-5; **42**, 10515-98-7; **43**, 109392-23-6; **46**, 51558-95-3; **47**, 93-52-7; *threo*-**50**, 21759-50-2; *erythro*-**50**, 21759-49-9; SO_2Cl_2, 7791-25-5; PhSeSePh, 1666-13-3; $PhSeBr_3$, 38927-01-4; $PhCH{=}CH_2$, 100-42-5; (*E*)-$PhCH{=}CHCH_3$, 624-64-6; (*Z*)-$PhCH{=}CHCH_3$, 766-90-5; (*E*)-$H_3CCH{=}CHCH_3$, 624-64-6; (*Z*)-$H_3CCH{=}CHCH_3$, 590-18-1; (*Z*)-PhCH=CHPh, 645-49-8; (*E*)-PhCH=CHPh, 103-30-0; $HOCH_2CH{=}CH_2$, 107-18-6; $AcOCH_2CH{=}CH_2$, 591-87-7; $PhCO_2CH_2CH{=}CH_2$, 583-04-0; 4-$ClC_6H_4CO_2CH_2CH{=}CH_2$, 15784-28-8; 4-$O_2NC_6H_4CO_2CH_2CH{=}CH_2$, 15727-80-7; 2,4-$(O_2N)_2C_6H_4CO_2CH_2CH{=}CH_2$, 109392-27-0; $PhOCH_2CH{=}CH_2$, 1746-13-0; 4-$H_3CC_6H_4OCH_2CH{=}CH_2$, 1758-10-7; 4-$ClC_6H_4OCH_2CH{=}CH_2$, 13997-70-1; $H_3CCH{=}CHCH_2OAc$, 628-08-0; $H_2C{=}CHCH_2CH_3$, 106-98-9; PhSeCl, 5707-04-0; $H_2C{=}C(CH{=}CH_2)_2$, 106-99-0; $H_2C{=}CHC(CH_3){=}CH_2$, 78-79-5; $PhC(Cl){=}CH_2$, 618-34-8; (*E*)-$PhCH{=}CHCH_2Cl$, 21087-29-6; (*Z*)-PhCH=C(Cl)Ph, 948-99-2; (*E*)-PhCH=C(Cl)Ph, 948-98-1; PhSeBr, 34837-55-3; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; acenaphthylene, 208-96-8; 2-cyclohexen-1-yl acetate, 14447-34-8; cyclopentadiene, 542-92-7; 3-cyclohexene-1-carboxylic acid, 4771-80-6; thiourea, 62-56-6; 3-chlorocyclopentene, 96-40-2; 2-cyclopenten-1-ol, 3212-60-0; di(2-cyclopenten-1-yl) ether, 15131-55-2; 3-chlorocycloheptene, 35021-99-9; 1-chlorocycloheptene, 13294-30-9; 3-chlorocyclooctene, 24618-80-2; 1-chlorocyclooctene, 1890-22-8; 1-chloroacenaphthylene, 65726-91-2.

Supplementary Material Available: ^1H NMR data for compounds **4b**, **5b**, **6–28**, **31**, (*Z*)-1-chloro-1,2-diphenylethylene, (*E*)-1-chloro-1,2-diphenylethylene, and **38–43** (6 pages). Ordering information is given on any current masthead page.

The Role of Neighboring Group Participation in the Acetolysis of α-(Phenylthio)-ω-[(*p*-tolylsulfonyl)oxy]alkanes

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In order to evaluate the relative importance of the neighboring group participation by the phenylthio group, the acetolysis of tosylates **1a–e** has been studied. The results obtained confirmed that the participation decreases with the increasing ring size of the intermediate cyclic sulfonium salts **2** in the order S-3 > S-5 > S-6. Among these salts only **2c** and **2d** were isolated, while the formation of **2b** and **2e** was indirectly demonstrated by the obtainment of mixtures of the isomeric acetates **4b,e** and **5b,e**, respectively. In the absence as well as in the presence of acetate, the acetolyses of **1a** and **1c** very probably proceed exclusively through the intermediacy of the corresponding cyclic sulfonium salt, while open-chain pathways predominate in the acetolyses of **1b** and **1e**. The acetolysis of **1d**, instead, follows a different pattern in the two media: in glacial AcOH only direct nucleophilic displacement of the leaving group occurs, along with cyclization to the stable salt **2d**, while in the presence of AcOK the latter undergoes solvolysis, presumably through counterion exchange, the reaction involving both open-chain and cyclic pathways.

Participation of thioether groups in solvolytic displacement reactions was studied by a number of authors to assess the effects of ring size on sulfur participation. In particular, in the hydrolysis and alcoholysis of a series of ω-(arylthio)alkyl halides, the anchimeric assistance was shown to decrease with the ring size in the order 3 > 5 > 6 > 4,[2-6] though Bordwell and Brannen[4] found no evidence of it in the methanolysis of 3-(phenylthio)propyl chloride. Indeed, sulfur participation involving four-membered ring intermediates is extremely rare[7,8] and seems to be restricted to substrates having the heteroatom rigidly placed so that formation of the strained thietanium cation might be facilitated.[9,10] However, it must be recognized that, in general, kinetic data cannot be taken by themselves as a proof that a reaction proceeds solely through a pathway involving neighboring group participation; indeed, there might be cases in which participation is involved after the transition state has been reached. In this case no rate acceleration can be observed, the neighboring group being able to capture the first formed intermediate following the rate-determining step.[11] On the other hand, the isolation

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