1.27 (3 H, d, J = 6.8 Hz), 3.45–3.85 (6 H, m), 4.26 (1 H, pentet, J = 6.8 hz), 4.4–4.9 (8 H, m), 7.25 (20 H, br s); ^{13}C NMR and ^{1}H NMR data were consistent with literature;[23] IR (neat) 3060, 2950, 1500, 1460, 1100 cm^{-1}.

α-2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-1-*C*-methyl-D-glucitol (7c). Reaction of **5c** with excess MeMgBr followed by reacetylation,[10n] gave a light yellow oil (68% crude yield), which was purified by chromatography on silica gel (60:40 ether–pentane) to afford **6c** (6% yield) and **7c** (6% yield): ^{13}C NMR (acetone-d_6) δ 13.1, 20.9, 63.5, 69.7, 70.0, 70.2, 70.9, 71.7, 170.4, 170.8; ^{1}H NMR ($CDCl_3$) δ 1.29 (3 H, d, J = 6.9 Hz), 2.02 (3 H, s), 2.04 (3 H, s), 2.08 (3 H, s), 2.10 (3 H, s), 3.9–4.3 (2 H, m), 4.37 (1 H, pentet, J = 6.5 Hz), 4.9–5.4 (3 H, m); ^{13}C NMR and ^{1}H NMR were consistent with literature;[23] IR (neat) 2950, 1750, 1500, 1460, 1230, 1070 cm^{-1}.

α-1,5-Anhydro-2,3,4,6-tetra-*O*-methyl-1-*C*-phenyl-D-glucitol (7e). PhMgBr (0.70 mL, 1.05 M, in ether, 0.734 mmol, 210 mol %) was added dropwise to a solution of **5a** (0.351 mmol) in ether (1.5 mL) at −60 °C. Stirring became impossible. After the reaction was stirred at 20 °C for 140 h, standard workup gave crude product (157 mg), which was purified by column chromatography on silica gel (50:50 ether–pentane), providing **6e** (23 mg, 22% yield) and **7a** (20 mg, 19% yield): $[\alpha]^{22}_D$ +66.6° (c 3.9, $CHCl_3$);[30a] ^{13}C NMR ($CDCl_3$) δ 58.7, 59.2, 60.1, 60.2, 71.6, 72.0, 73.2, 79.9, 83.0, 83.5, 127.5, 128.3, 128.3, 137.8; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.40 (3 H, s), 3.46 (3 H, s), 3.52 (3 H, s), 3.68 (3 H, s), 3.0–3.7 (6 H, m), 5.21 (1 H, d, J = 4.0 Hz), 7.3 (3 H, m), 7.68 (2 H, d); IR (neat) 2910, 1750, 1440, 1090 cm^{-1}; mass spectrum, m/e (relative intensity) 88 (46) 101 (100), 121 (19). Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 60.94; H, 7.70.

1,5-Anhydro-3,4,6-tri-*O*-methyl-2-deoxy-D-*arabino*-hex-1-enitol (8a) was purified by chromatography on silica gel (60:40 pentane–ether) followed by careful evaporation to prevent loss of volatile **8a**:[18] ^{13}C NMR ($CDCl_3$) δ 55.65, 59.08, 59.19, 70.63, 75.70, 76.07, 77.09, 99.38, 144.42; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 3.33 (3 H, s), 3.34 (3 H, s), 3.47 (3 H, s), 3.3–3.7 (5 H, m), 3.86 (1 H, dm), 4.75 (1 H, dd, J = 3, 6 Hz), 6.32 (1 H, dd, J = 1, 6 Hz); mass spectrum, m/e (relative intensity) 71 (100), 101 (100).

1,5-Anhydro-2,3,4,6-tetra-*O*-methyl-D-*arabino*-hex-1-enitol (9a). MeLi (0.75 mL, 1.6 M in ether, 1.20 mmol, 342 mol %) was added dropwise to a solution of **5a** (0.351 mmol) in ether at −35 °C. After 3.5 h at −35 °C, standard workup gave crude product (62 mg), a mixture of **5a** (30%) and **9a** (70%). The product was purified by column chromatography on silica gel (50:50 ether–pentane: ^{13}C NMR ($CDCl_3$) δ 55.79, 57.43, 58.48, 59.19, 70.56, 75.48, 76.66, 125.25, 139.75; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 3.36 (3 H, s), 3.46 (3 H, s), 3.50 (3 H, s), 3.6 (2 H, m), 3.9 (3 H, m), 6.13 (1 H, s);[17] mass spectrum, m/e (relative intensity) 71 (58), 86 (33), 101 (63), 116 (100), 218 (14).

2,3,4,6-Tetra-*O*-methyl-D-gluconic Acid δ-Lactone (10). Pyridinium chlorochromate (1.80 g, 8.35 mmol, 195 mol %) in dichloromethane (7.5 mL) was added to 2,3,4,6-tetra-*O*-methylglucopyranose (**4a**) (1.00 g, 4.27 mmol) dissolved in dichloromethane (7.5 mL), and the mixture was refluxed for 7.5 h. The cooled mixture was diluted with ether (75 mL), decanted, and filtered through magnesium silicate. Evaporation of the solvent followed by Kugelrohr distillation (90–120 °C, 0.2 mmHg) afforded **10** (855 mg, 86% yield) as an oil. The classical oxidation of **4a** to **10** with bromine affords a lower yield and requires a tedious isolation procedure:[28] ^{1}H NMR ($CDCl_3$) δ 3.41 (3 H, s), 3.51 (3 H, s), 3.53 (3 H, s), 3.57 (3 H, s), 3.1–3.9 (5 H, m), 4.5 (1 H, ddd).

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Methods for the Introduction of a Phenylselenium Dichloride Group into the α-Position of Carbonyl Compounds. Syntheses of Enones

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Phenylselenium trichloride, $PhSeCl_3$, directly introduced, in fair yield, a $PhSeCl_2$ group into the α-position of ketones with loss of HCl. To some extent, depending on the substrate, this reagent was also shown to act as a chlorinating agent toward ketones, yielding α-chloro ketones and α-phenylselenenyl ketones. The latter compounds were readily converted to selenium(IV) dichlorides by SO_2Cl_2 chlorination to significantly improve the overall yields of the selenation process. The consecutive treatment of ketones with PhSeCl and SO_2Cl_2 could also be used for the introduction of a $PhSeCl_2$ group, but this procedure was usually less efficient than the $PhSeCl_3$-based one. Unsymmetrical ketones were selenated with poor regiocontrol. Aldehydes were primarily chlorinated by treatment with $PhSeCl_3$, but consecutive treatment with $PhSeCl_3$ and SO_2Cl_2 introduced a $PhSeCl_2$ group into the α-position. Carboxylic acids and esters were unreactive toward $PhSeCl_3$ and PhSeCl. $PhSeCl_3$ underwent addition reactions with enones to introduce a $PhSeCl_2$ group α or β to the carbonyl group, depending on the substrate. The carbonyl compounds substituted in the α-position with a $PhSeCl_2$ group were easily converted to the corresponding α,β-unsaturated carbonyl compounds after hydrolysis/selenoxide elimination. Since the selenium(IV) intermediates involved were highly crystalline and easy to purify, the preparation of enones from symmetrical ketones via $PhSeCl_2$ introduction/hydrolytic elimination was especially convenient to perform from the operational point of view.

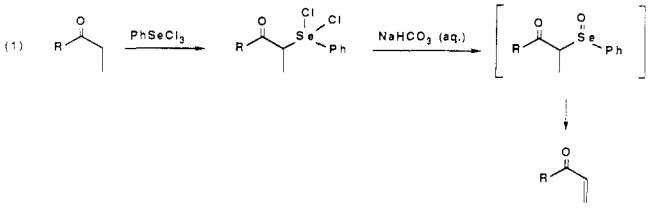
Introduction

The selenoxide syn-elimination reaction represents one of the most important methods for the introduction of unsaturation into organic molecules.[1] In order to make use of the reaction, selenium is commonly introduced in the *divalent* state into an organic molecule, starting from commercially available reagents like benzeneselenenyl halides or diphenyl diselenide. Oxidation of the resulting organyl phenyl selenide to a selenoxide is then usually accompanied by a rapid syn-elimination process to yield the desired olefinic product.

We recently reported a new variation of this reaction using phenylselenium trichloride for the introduction of *tetravalent* selenium into an organic molecule (eq 1).[2]

(1) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1986.

0022-3263/88/1953-4031$01.50/0



After isolation of a crystalline organylarylselenium dichloride, selenoxide formation/elimination was then induced by mild treatment with aqueous base.

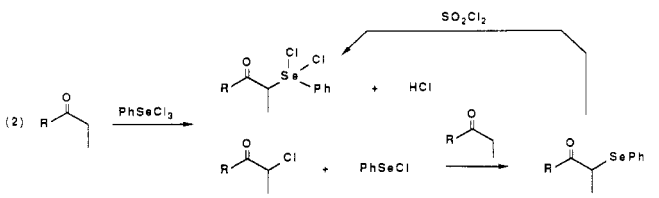
If this variation of the selenoxide elimination reaction is going to be of general interest, good methods for the introduction of a phenylselenium dichloride group into a large variety of organic compounds must be found. It is the intention of the present paper to define the scope and limitations of the new procedure as applied to the preparation of α,β-unsaturated carbonyl compounds.

Results

Phenylselenium trichloride has been found to readily introduce a $PhSeCl_2$ group into the α-position of various ketonic substrates. With aryl methyl ketones, the insoluble substitution products were slowly formed as white crystalline solids in good yields simply by stirring a suspension of $PhSeCl_3$ in dry ether with an excess of the ketone.[2] However, when the reaction was applied to other ketones possessing β-hydrogens and thus convertible to enones, some interesting color changes occurred. Furthermore, the yields were not always satisfying (Table I, method A). In a typical procedure, when a suspension of $PhSeCl_3$ in dry ether was stirred at 0 °C with 2 equiv of cyclohexanone, the colorless solution gradually turned orange-brown while the solid slowly disappeared. After some time, the dark color of the homogeneous solution started to fade away to give an almost colorless solution. The substitution product **1b** crystallized out from the reaction mixture in 65% yield after addition of hexane and cooling in a freezer. However, with butyrophenone and valerophenone we were unable to isolate any crystalline products by using this method.

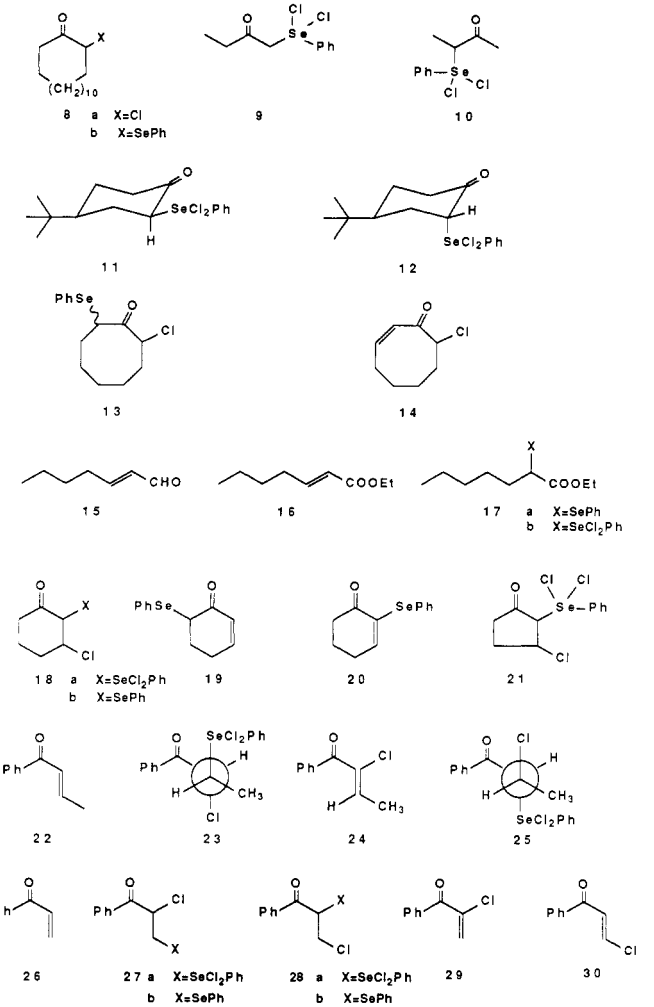
The appearance and disappearance of the orange-brown color during the experiments is suggesting that benzeneselenenyl chloride, PhSeCl, is formed and then consumed during the course of the reaction. This species is probably formed as a byproduct of a $PhSeCl_3$-induced chlorination of the ketone and consumed in an acid-catalyzed reaction with another molecule of the ketone. In support of this view, the mother liquor from an experiment with cyclopentadecanone (46% isolated yield of selenium(IV) product) was found to contain 2-chlorocyclopentadecanone (**8a**) (Chart I; 26% yield) and 2-(phenylselenenyl)cyclopentadecanone (**8b**), isolated as its *Se,Se*-dichloride **1f** (44% yield) by addition of sulfuryl chloride.

On the basis of these initial findings, another, more efficient, one-pot preparation of ketones containing a phenylselenium dichloride group in the α-position was developed (eq 2; Table I, method B). Phenyl selenium



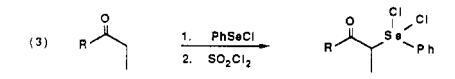
trichloride was stirred in dry ether with an excess of the

Chart I



appropriate ketone. After disappearance of the orange-brown color and precipitation with hexane, sulfuryl chloride was added and the crystalline selenium(IV) compound isolated in uniformly good yield (83–98%). Obviously, the $PhSeCl_3$-induced chlorination is highly substrate dependent, occurring only to a small extent with ketones like cyclopentanone and cycloheptanone but being the exclusive reaction with butyrophenone and valerophenone.

The above results, and others from the literature,[3,4] suggest that it should also be possible to prepare the desired selenium(IV) compounds via SO_2Cl_2 chlorination of α-phenylselenenyl ketones prepared from the reaction of benzeneselenenyl chloride with ketones (eq 3). However,



the yields obtained by using this strategy (Table I, method C) were generally inferior to those obtained by method B. Furthermore, the products were in several cases yellow-colored and less pure (according to ^1H NMR analysis) than those obtained by the other two methods.

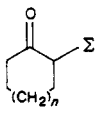
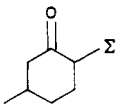
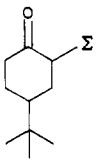
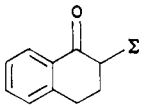
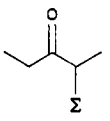
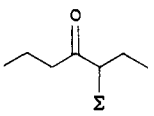
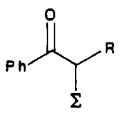
When $PhSeCl_3$ was allowed to react with 3-methylcyclohexanone (method A), the 3,6-disubstituted ketone **2** was isolated in 41% yield as the only selenium(IV)

(2) Engman, L. *Tetrahedron Lett.* **1985**, *26*, 6385.

(3) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137.

(4) Toshimitzu, A.; Owada, H.; Terao, K.; Uemura, S.; Okano, M. *J. Org. Chem.* **1984**, *49*, 3796.

Table I. Preparation of Ketones Substituted in the α-Position with a $PhSeCl_2$ Group. Conversion of the Products to Enones

ketone	α-substituted ketone (Σ = $SeCl_2Ph$)	yield, %, meth[a] A, B, C	mp, °C	enone (yield, %)
	 1			
cyclopentanone	**a**, n = 0	81, 86, –	70–72 dec	2-cyclopentenone (64)
cyclohexanone	**b**, n = 1	65, 92, 85	81–82 dec	2-cyclohexenone (47)
cycloheptanone	**c**, n = 2	81, 89, 90[d]	103–104 dec	2-cycloheptenone (74)
cyclooctanone	**d**, n = 3	56, 98, 85[d]	81–82 dec	2-cyclooctenone (80)
cyclododecanone	**e**, n = 7	60, 98, 96	111–112 dec	(*E*)-2-cyclododecenone (79)
cyclopentadecanone	**f**, n = 10	46, 90, 93	97–98 dec	(*E*)-2-cyclopentadecenone (92)
3-methylcyclohexanone	 2	41, –, –	87–89 dec	5-methyl-2-cyclohexenone (76)
4-*tert*-butylcyclohexanone	 3	49, 83, 77	*b*	4-*tert*-butyl-2-cyclohexenone (68)
α-tetralone	 4	40, 94, 80	83–84 dec	1-naphthol (52)[c]
diethyl ketone	 5	58, 90, 82[d]	87–88 dec	–
dipropyl ketone	 6	45, 95, –	84–85 dec	(*E*)-2-hepten-4-one (78)
	 7			
propiophenone	**a**, R = CH_3	62, 88, –	114–116 dec	1-phenyl-2-propen-1-one (97)
butyrophenone	**b**, R = C_2H_5	0, 98, 82[e]	86–89 dec	(*E*)-1-phenyl-2-buten-1-one (87)
valerophenone	**c**, R = C_3H_7	0, 89, –	78–81 dec	(*E*)-1-phenyl-2-penten-1-one (75)

[a] For details, see text. [b] Cis isomer mp 91–93 °C dec. Trans isomer mp 72 °C dec. [c] Product isolated as 1-naphthol. [d] Crude yield of yellowish impure product. [e] The selenide was purified by chromatography before addition of SO_2Cl_2.

product. In this case, additional chlorination to improve the yield resulted only in the separation of an unstable semisolid product that could not be further purified. An experiment according to method C, starting from PhSeCl, produced a similar gummy material. The regiocontrol of the substitution reaction can probably be attributed to steric factors, with the bulky $PhSeCl_2$ group avoiding the sterically more hindered position next to the methyl group in favor of the other α-carbon. Unfortunately, phenylselenium trichloride did not generally show much regioselectivity in its reactions with unsymmetrical ketones. For example, ethyl methyl ketone produced a 57:43 mixture of methyl- and methylene-substituted products **9** and **10** when reacted with $PhSeCl_3$ according to method A. No substitution product was obtained from 2-methylcyclohexanone.

The 4-*tert*-butylcyclohexanone-derived compound **3** was obtained in two isomeric forms, the isomer distribution being dependent on the mode of preparation. A synthesis according to method A afforded predominantly (9:1) one isomer, assigned by ^1H NMR spectroscopy as the 2,4-cis-disubstituted ketone **11**. The other isomer, assigned as the 2,4-trans-disubstituted compound **12**, was obtained upon addition of SO_2Cl_2 to the mother liquor from the above preparation. Both compounds were independently converted to 4-*tert*-butyl-2-cyclohexenone by using the hydrolytic variation of the selenoxide elimination reaction (vide infra). When 4-*tert*-butylcyclohexanone was reacted

with PhSeCl in ether and the resulting α-phenylselenenyl ketone chlorinated (after column chromatography), a 4:6 mixture of isomers **11** and **12** was obtained.

The organylphenylselenium dichlorides shown in Table I are rather unstable solids melting with decomposition. All compounds were obtained as white glittering prisms after recrystallization from CH_2Cl_2/hexane. However, most of them had turned light yellow by the time they were filtered off. Some of the materials decomposed to yellow liquids after less than 24 h exposure to the ordinary laboratory atmosphere. Due to this lability, elemental analyses could not be obtained for the new compounds. However, satisfactory ^1H NMR spectra were recorded by using freshly prepared solutions in $CDCl_3$. If kept in a freezer, recrystallized samples of the Se(IV) compounds could be stored for several weeks without any visible decomposition.

When compound **1d** was allowed to decompose under controlled conditions in chloroform solution at ambient temperature, 2-chloro-8-(phenylselenenyl)cyclooctanone (**13**) was isolated as the major product, together with 2-chlorocyclooctanone. The decomposition reaction can be explained by assuming a 1,2-shift of chlorine from selenium to carbon,[5] with formation of benzeneselenenyl chloride and 2-chlorocyclooctanone. The ketone **13** is then formed in a secondary process from PhSeCl and the α-chloro ketone. In support of the suggested mechanism, when 2-chlorocyclooctanone and benzeneselenenyl chloride were stirred in chloroform, compound **13** was obtained as the only observed substitution product (54% yield). SO_2Cl_2 chlorination of this selenide, followed by hydrolytic selenoxide elimination, yielded the enone **14** in 60% yield.

The ketones **1–7** (Table I), substituted in the α-position with a $PhSeCl_2$ group, were all converted to the corresponding enones in fair to good yields under mild conditions after hydrolysis/selenoxide elimination. The reaction was most conveniently performed by shaking of a CH_2Cl_2 solution of the organoselenium compound in a separatory funnel with an aqueous solution of sodium hydrogen carbonate. After the initial gas evolution had ceased, the organic phase rapidly turned yellow as the elimination reaction proceeded (due to formation of diphenyl diselenide). The diselenide is a well-known disproportionation product of benzeneselenenic acid, the primary product of the elimination reaction. In addition, small amounts of α-phenylselenenyl ketones were usually formed as byproducts in the elimination. The enones were isolated in pure form after Kugelrohr distillation (low-boiling compounds) or flash chromatography (for yields, see Table I).

Like ketones, aldehydes are easily enolizable and known to react with selenium electrophiles in an acid-catalyzed reaction. In an attempt to extend the scope of the hydrolytic variation of the selenoxide elimination reaction, $PhSeCl_3$ was reacted with heptanal and with hydrocinnamic aldehyde, by employing two of the procedures used for ketones (methods A and B). However, we were unable to isolate crystalline selenium(IV) compounds with either of the substrates. As observed with butyrophenone and valerophenone, chlorination seemed to be the primary reaction, followed by PhSeCl selenation of unreacted carbonyl compound. When heptanal was treated consecutively with $PhSeCl_3$ and SO_2Cl_2 (0.5 equiv of each) and the product, without isolation, treated with aqueous $NaHCO_3$, (*E*)-2-heptenal (**15**) was isolated in 84% yield after careful flash chromatography. Hydrocinnamic aldehyde was similarly converted to cinnamic aldehyde in 84% yield, but in this case the enal could not be separated from the α-chlorohydrocinnamic aldehyde present. When crystalline selenium(IV) dichlorides cannot be obtained, the hydrolytic variation of the selenoxide elimination reaction does not offer any advantages over existing methods for the preparation of α,β-unsaturated carbonyl compounds.

Carboxylic acids and esters, nitriles, nitroalkanes, and sulfones did not react at all with $PhSeCl_3$ when stirred in dry ether for many hours. Since ester enolates are known to be readily phenylselenenated by treatment with PhSeCl,[3,6] an attempt was made to introduce a $PhSeCl_2$ group into the α-position of ethyl heptanoate by treatment of the corresponding lithium enolate with $PhSeCl_3$ in dry ether at −78 °C. However, after warming to 0 °C and treatment with aqueous $NaHCO_3$, the α,β-unsaturated ester **16** was detected only as a minor component among many other (unidentified) products. The successful conversion (76% yield) of ethyl 2-(phenylselenenyl)heptanoate (**17a**) to ethyl (*E*)-2-heptenoate (**16**), via the *Se,Se*-dichloride **17b**, shows that the hydrolytic variation of the selenoxide elimination is well suited also for the preparation of α,β-unsaturated esters if the required selenium(IV) compounds can only be prepared.

When phenylselenium trichloride was treated in dry ether with 2-cyclohexenone, a white crystalline compound **18a** separated out in 69% yield. According to ^1H NMR analysis, an addition to the doule bond had occurred rather than a substitution reaction. Similar additions to enones are known with PhSeCl,[7] but there is also a report[8] describing the formation of a substitution product, 6-(phenylselenenyl)-2-cyclohexenone (**19**), from the reaction of PhSeCl with 2-cyclohexenone. When we carried out this reaction in ether, a highly crystalline but unstable addition product **18b** was isolated in 83% yield. Upon treatment with SO_2Cl_2, this material afforded a selenium(IV) dichloride identical with the product **18a** obtained from $PhSeCl_3$ and 2-cyclohexenone. The regiochemistry of addition was deduced from an elimination experiment with compound **18b**: treatment in chloroform with pyridine afforded 2-(phenylselenenyl)-2-cyclohexenone (**20**) in 94% yield. This seems to indicate that selenium is bonded to the 2-position in adducts **18a** and **18b**. However, an attempt to obtain a chloro enone from compound **18a** via hydrolysis/selenoxide elimination was unsuccessful. 2-Cyclopentenone also afforded an addition compound with $PhSeCl_3$ (tentatively assigned structure **21**), which could also not be eliminated to give a chloro enone. (*E*)-1-Phenyl-2-buten-1-one (**22**) afforded the addition product **23** in 81% yield when treated with $PhSeCl_3$ in ether. This was concluded from an elimination experiment which yielded the chloro enone **24** as the only product in 89% yield. The anti stereospecificity of the addition follows from the geometry of the chloro enone (as determined by a NOE experiment), assuming that the selenoxide elimination reaction occurs exclusively in a syn fashion. Surprisingly, PhSeCl with enone **22** in ether afforded, after chlorination of the primary adduct, a material that was different from product **23**. Furthermore, the compound did not undergo a clean selenoxide elimination reaction.

(5) Engman, L. *J. Org. Chem.* **1987**, *52*, 4086.

(6) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

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(8) Zima, G.; Liotta, D. *Synth. Commun.* **1979**, *9*, 697. Compound **19** has also been prepared from 2-cyclohexenone via LDA deprotonation/phenylselenenylation,[8a] but no spectroscopic data were given. (a) Al-Hassan, M. I. *Gazz. Chim. Ital.* **1987**, *117*, 187.

We therefore tentatively assign it as the other possible regioisomer **25**. A similar difference in addition regiochemistries between $PhSeCl_3$ and PhSeCl was observed with 1-phenyl-2-propen-1-one (**26**). Thus, when ether was used as solvent, $PhSeCl_3$ afforded a 75:25 mixture of compounds **27a** and **28a** whereas PhSeCl gave a 17:83 mixture of compounds **27b** and **28b**. However, when the latter addition was carried out in $CDCl_3$, equal amounts of the two isomers were formed. Since the isomer distribution of the ether-prepared mixture of compounds **27b/28b** did not change after 25 h in $CDCl_3$ solution, we conclude that the addition is irreversible. The isomeric mixture obtained from $PhSeCl_3$ and ketone **26** was subjected to the usual elimination conditions to give a 4:1 mixture of chloro enones **29** and **30**, respectively (81% total yield).

Discussion

A strategy of introducing tetravalent selenium into the α-position of carbonyl compounds, followed by selenoxide elimination to create a double bond, has previously been used with reagents like benzeneseleninic anhydride[9,10] and benzeneseleninyl chloride.[6] However, due to the lability of the selenoxide function, the organoselenium intermediates were never isolated. The indirect synthesis of selenoxides described in the present paper involves the isolation of readily prepared, unstable but isolable and often recrystallizable selenium(IV) dichlorides. This is a definite advantage from the operational point of view when it comes to purification of the product. The conventional selenoxide protocol[6] for olefin syntheses usually involves the low-temperature preparation of an α-organylselenenyl carbonyl compound that has to be purified from unreacted starting material and byproducts by chromatographic methods before it can be oxidized/eliminated.

The halogenation/hydrolysis concept for indirect oxidation of selenides to selenoxides has some precedence in the literature,[11] but to the best of our knowledge, it has never been used with substrates that can undergo a selenoxide elimination reaction. Our elimination results indicate that this procedure should be a useful addition to the direct oxidation methods available (involving H_2O_2, $NaIO_4$, peracids, ozone, etc.).

Our method to synthesize α,β-unsaturated compounds (via introduction of a $PhSeCl_2$ group/hydrolytic elimination) was most successful with easily enolizable substrates like ketones and aldehydes. As compared with other methods, the preparation of enones from the corresponding symmetrical ketones was particularly competitive, involving only two operationally very simple steps. The overall yields of enones were usually equal to or slightly better than those obtained by using conventional phenylselenenylation/oxidation methodology (see ref 6). Unfortunately, we could not find direct methods to introduce the $PhSeCl_2$ group into the α-position of carboxylic acids, esters, and aldehydes. Unsymmetrical ketones were selenated with poor regiocontrol.

Early observations[12] showed that $PhSeCl_3$ and PhSeCl are interrelated by the reaction shown in eq 4. Since the

(4) $PhSeCl_3 \rightleftharpoons PhSeCl + Cl_2$

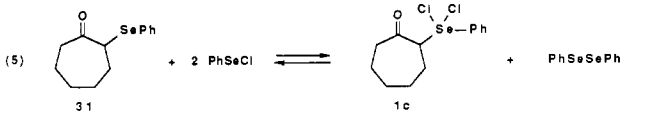
supernatant of a $PhSeCl_3$ suspension in ether stays practically colorless after prolonged stirring at 0 °C, the equilibrium must be strongly shifted to the left. However, we cannot say if the chlorinating properties of $PhSeCl_3$ are due to a reaction with the reagent itself or a secondary reaction with Cl_2.

Similarly, the formation of selenium(IV) dichlorides from the reaction of ketones with $PhSeCl_3$ could occur either in a direct fashion or via a reaction with PhSeCl followed by chlorination. The results with 4-*tert*-butylcyclohexanone (predominant formation of one isomer **11** with $PhSeCl_3$ and an isomeric mixture **11/12** with PhSeCl, after chlorination) show that different mechanisms are operative with the two reagents. This suggests that $PhSeCl_3$ can undergo a direct reaction with the enol form of a ketone. Furthermore, the isolation by chlorination of essentially pure trans-isomer **12** from the mother liquor of the $PhSeCl_3$ reaction indicates that PhSeCl generated in situ (produced in the chlorination reaction) behaves differently from the commercially available material. At present we have no explanation for this observation.

The different addition behavior of PhSeCl and $PhSeCl_3$ toward certain enones also shows that $PhSeCl_3$ can undergo a direct reaction which does not involve the formation of PhSeCl.

The addition regiochemistry of $PhSeCl_3$ was highly substrate dependent, affording α-selenated products with cyclic enones and predominantly β-selenated ones with phenyl alkenyl ketones. However, only the ketones carrying a $PhSeCl_2$ group in the β-position were successfully eliminated to give olefins. As observed with other β-selenated ketones,[13] the elimination occurred exclusively toward the carbonyl group to give a chloro enone.

As shown in Table I, the consecutive treatment of ketones with PhSeCl and SO_2Cl_2 (method C) could sometimes effectively replace $PhSeCl_3$ (or $PhSeCl_3/SO_2Cl_2$) for the introduction of a $PhSeCl_2$ group into the α-position of ketones. However, with some substrates, impure products were obtained. These problems can probably be attributed to the chlorinating properties of PhSeCl. Reich reported that alkyl phenyl selenides were chlorinated by treatment with PhSeCl in a reversible reaction to give diorganylselenium dichlorides and diphenyl diselenide.[14] A similar equilibrium can also be set up with phenylselenenylated ketones. In fact, when cycloheptanone was treated with PhSeCl in dry ether, compound **1c** precipitated out as the major product, isolated in 67% yield in addition to 2-(phenylselenenyl)cycloheptanone (**31**) (26% yield) and diphenyl diselenide. In dilute $CDCl_3$ solution, where no solubility effects could interfere, the equilibrium mixture contained 40% of selenium(IV) dichloride **1c** and 60% of selenide **31** as determined by ^1H NMR spectroscopy starting from appropriate mixtures of either **31**/PhSeCl or **1c**/PhSeSePh (eq 5). The formation of impure

(5) 

31 1c

products with some ketones by using method C can probably be attributed to coprecipitation of $PhSeCl_3$ in the chlorination step (from SO_2Cl_2 and PhSeSePh).

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 containing Me_4Si as internal standard and are reported in δ units. IR spectra were obtained by using a Per-

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kin-Elmer 1710 FT infrared spectrometer. Elemental analyses were performed by Novo Microanalytical Laboratory, Bagsvaerd, Denmark. Diethyl ether was dried over sodium. Chloroform was washed with water to remove ethanol and dried over $CaCl_2$. Sulfuryl chloride was freshly distilled. Phenylselenium trichloride[5] and 2-chlorocyclooctanone[15] were prepared according to literature methods. All ketonic starting materials were obtained from commercial suppliers. The ^1H NMR properties of all enones prepared showed good agreement with reported data: 2-cyclopentenone,[16] 2-cyclohexenone,[16] 2-cycloheptenone,[6] 2-cyclooctenone,[6] 2-cyclododecenone,[6] 2-cyclopentadecenone,[17] 5-methyl-2-cyclohexenone,[18] 4-*tert*-butyl-2-cyclohexenone,[19] (*E*)-2-hepten-4-one,[6] 1-phenyl-2-propen-1-one,[6] (*E*)-1-phenyl-2-buten-1-one,[6] (*E*)-1-phenyl-2-penten-1-one,[20] 8-chloro-2-cyclooctenone,[21] and 2-chloro-1-phenyl-2-propen-1-one.[22]

Preparation of Ketones Substituted in the α-Position with a $PhSeCl_2$ Group. Typical Procedure. (1-Oxo-2-cyclohexyl)phenylselenium Dichloride (1b). Method A. To a stirred suspension of $PhSeCl_3$ (1.0 g, 3.8 mmol) in dry ether (5 mL) at 0 °C was added cyclohexanone (0.75 g, 7.6 mmol) in one portion. The colorless ether solution gradually turned orange and then orange-brown while the solid material slowly disappeared. After about 10 min, the dark reaction mixture was homogeneous whereupon the color faded away during the next 10 min to give an almost colorless solution. At this point, hexane (40 mL) was added to cause precipitation of compound **1b**. After final crystallization in a freezer (−20 °C), 0.80 g (65% yield) of white crystals was isolated. The other ketones behaved similarly. The reactions with butyrophenone (24 h), valerophenone (24 h), dipropyl ketone (1.5 h), and propiophenone (2 h) required significantly longer reaction times at ambient temperature to go to completion.

Method B. To the heterogeneous reaction mixture obtained from the above preparation after addition of hexane was added sulfuryl chloride (0.21 g, 1.6 mmol). This caused additional precipitation of compound **1b**, which was isolated in 92% yield (1.17 g) after cooling/filtration.

Typical Procedure, (1-Oxo-2-cyclopentadecyl)phenylselenium Dichloride (1f). Method C. To a stirred solution of PhSeCl (1.0 g, 5.2 mmol) in dry ether (5 mL) was added cyclopentadecanone (1.35 g, 6.0 mmol) in one portion. After 2 h at ambient temperature, a yellowish solution resulted, which was then diluted with hexane (40 mL) and cooled in an ice bath. Dropwise addition of sulfuryl chloride (0.77 g, 5.7 mmol) caused precipitation of compound **1f** (2.19 g, 93% yield). Other ketones behaved similarly. The reaction with butyrophenone required 24 h to go to completion. The reactions with cyclopentanone, cyclohexanones, cycloheptanone, and cyclooctanone were run at 0 °C. No crystalline product was obtained from cyclopentanone, and the products from cycloheptanone, cyclooctanone, and diethyl ketone were yellowish and less pure (according to ^1H NMR analysis) than the materials obtained by using method B.

All selenium(IV) dichlorides were obtained as glittering prisms after recrystallization from CH_2Cl_2/hexane. The melting points are shown in Table I. Many of the compounds were sent for analysis, but due to their instability, unsatisfactory results were always obtained. The following ^1H NMR data for compounds **1**, **2**, and **4**–**7** were obtained by using freshly prepared solutions in $CDCl_3$.

1a: 2.06 (m, 1 H), 2.28–2.51 (several peaks, 3 H), 2.69–2.84 (several peaks, 2 H), 5.11 (t, 1 H, J = 8.8 Hz), 7.49–7.58 (several peaks, 3 H), 8.09 (m, 2 H).

1b: 1.75–2.80 (several peaks, 8 H), 5.47 (dd, 1 H, J = 6.5 and 13.0 Hz), 7.50–7.54 (several peaks, 3 H), 8.07 (m, 2 H).

1c: 1.25–2.97 (several peaks, 10 H), 5.56 (dd, 1 H, J = 2.9 and 11.1 Hz), 7.52–7.58 (several peaks, 3 H), 8.01 (m, 2 H).

1d: 1.20–2.99 (several peaks, 12 H), 5.40 (dd, 1 H, J = 4.8 and 11.1 Hz), 7.50–7.55 (several peaks, 3 H), 7.98 (m, 2 H).

1e: 1.33–2.70 (several peaks, 18 H), 2.82 (m, 2 H), 5.24 (dd, 1 H, J = 3.2 and 11.4 Hz), 7.53–7.56 (several peaks, 3 H), 8.05 (m, 2 H).

1f: 1.13–2.37 (several peaks, 24 H), 2.79 (m, 2 H), 5.23 (dd, 1 H, J = 3.3 and 10.0 Hz), 7.52–7.57 (several peaks, 3 H), 8.00 (m, 2 H).

2: 1.08 (d, 3 H), 1.60–2.84 (several peaks, 7 H), 5.48 (dd, 1 H, J = 6.4 and 12.9 Hz), 7.50–7.55 (several peaks, 3 H), 8.06 (m, 2 H).

4: 2.52 (m, 1 H), 3.00–3.25 (several peaks, 3 H), 5.76 (dd, 1 H, J = 4.4 and 12.5 Hz), 7.28–7.62 (several peaks, 6 H), 8.15–8.20 (several peaks, 3 H).

5: 1.20 (t, 3 H), 1.94 (d, 3 H), 2.72 (q, 2 H), 5.48 (q, 1 H), 7.51–7.56 (several peaks, 3 H), 8.05 (m, 2 H).

6: 0.97 (t, 3 H), 1.11 (t, 3 H), 1.73 (m, 2 H), 2.32 (m, 2 H), 2.73 (q, 2 H), 5.14 (dd, 1 H, J = 5.0 and 8.4 Hz), 7.52–7.55 (several peaks, 3 H), 8.06 (m, 2 H).

7a: 2.04 (d, 3 H), 6.36 (q, 1 H), 7.50–7.67 (several peaks, 6 H), 8.02–8.15 (several peaks, 4 H).

7b: 0.98 (t, 3 H), 2.49 (m, 2 H), 6.13 (t, 1 H), 7.47–7.68 (several peaks, 6 H), 8.04–8.14 (several peaks, 4 H).

7c: 0.89 (t, 3 H), 1.33 (m, 2 H), 2.40 (m, 2 H), 6.19 (t, 1 H), 7.46–7.64 (several peaks, 6 H), 8.03–8.13 (several peaks, 4 H).

Compound **3** was obtained as an isomeric mixture (**11**/**12**, 9:1) in 49% yield when prepared according to method A. The major isomer **11** was obtained in pure form by recrystallization from CH_2Cl_2/hexane: IR 1711 cm^{-1}; ^1H NMR 0.89 (s, 9 H), 1.50–2.86 (several peaks, 7 H), 5.55 (dd, 1 H, J = 6.5 and 12.6 Hz), 7.50–7.56 (several peaks, 3 H), 8.04 (m, 2 H).

Addition of sulfuryl chloride (0.5 equiv) to the mother liquor of the above preparation caused precipitation of pure compound **12** (34% yield): IR 1733 cm^{-1}; ^1H NMR 0.90 (s, 9 H), 1.64–3.00 (several peaks, 7 H), 5.45 (dd, 1 H, J = 7.0 and 8.6 Hz), 7.49–7.55 (several peaks, 3 H), 8.06 (m, 2 H).

The preparation of compound **3** according to method C afforded a 4:6 mixture of isomers **11** and **12**, respectively.

The mother liquor from the preparation of compound **1f** (method B) was evaporated and subjected to column chromatography (CH_2Cl_2/hexane, 1:1) to yield 2-chlorocyclopentadecanone (**8a**) in 26% yield as an oil: ^1H NMR 1.17–1.39 (several peaks, 20 H), 1.67 (m, 2 H), 1.97 (m, 2 H), 2.64 (m, 2 H), 4.26 (dd, 1 H, J = 5.8 and 7.7 Hz). Anal. Calcd for $C_{15}H_{27}ClO$: C, 69.61; H, 10.51. Found: C, 69.34; H, 10.80.

When $PhSeCl_3$ and ethyl methyl ketone were reacted at ambient temperature according to method B, compounds **9** and **10** were obtained in 71% yield as a 57:43 mixture. **9**: ^1H NMR 1.22 (t, 3 H), 2.70 (q, 2 H), 5.24 (s, 2 H), 7.54–7.59 (several peaks, 3 H), 7.96 (m, 2 H). **10**: ^1H NMR 1.94 (d, 3 H), 2.43 (s, 3 H), 5.49 (m, 1 H), 7.54–7.59 (several peaks, 3 H), 8.06 (m, 2 H).

Decomposition of Compound 1d. (1-Oxo-2-cyclooctanyl)phenylselenium dichloride (0.85 g, 2.4 mmol) was dissolved in $CHCl_3$ (20 mL) and allowed to decompose for 6 days. Evaporation and chromatography (CH_2Cl_2/hexane, 1:1) afforded 0.41 g (54%) of 2-chloro-8-(phenylselenenyl)cyclooctanone (**13**) and 0.05 g (13%) of 2-chlorocyclooctanone as a mixture, from which the organoselenium compound crystallized after treatment with hexane: mp 68–69 °C; ^1H NMR 1.10–2.30 (several peaks, 10 H), 3.82 (dd, 1 H, J = 4.4 and 12.1 Hz), 4.80 (dd, 1 H, J = 4.2 and 11.8 Hz), 7.29–7.35 (several peaks, 3 H), 7.59 (m, 2 H). Anal. Calcd for $C_{14}H_{17}ClOSe$: C, 53.26; H, 5.43. Found: C, 53.43; H, 5.45.

2-Chloro-8-(phenylselenenyl)cyclooctanone (13). PhSeCl (0.50 g, 2.6 mmol) and 2-chlorocyclooctanone (0.42 g, 2.6 mmol) were stirred in $CHCl_3$ (5 mL) at ambient temperature for 24 h. Evaporation, chromatography (CH_2Cl_2/hexane, 1:1), and crystallization from hexane afforded 0.44 g (54%) of compound **13**.

Typical Elimination Procedure. (*E*)-1-Phenyl-2-buten-1-one. Compound **7b** (4.0 g, 10.7 mmol) was dissolved in CH_2Cl_2 (50 mL) and shaken in a separatory funnel with water (50 mL) containing $NaHCO_3$ (3.6 g, 42.9 mmol). After the initial gas evolution had ceased, the two-phase system was left for 4 h to complete the elimination. The yellow organic phase was then separated, dried ($CaCl_2$), and evaporated and the residue Ku-

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gelrohr-distilled to give 1.35 g (87%) of (*E*)-1-phenyl-2-buten-1-one.[6]

The elimination product from compound **4** was isolated as 1-naphthol and compared with an authentic sample. The following compounds were isolated by column chromatography: 4-*tert*-butyl-2-cyclohexenone, 2-cycloheptenone, 2-cyclooctenone, 2-cyclododecenone, 2-cyclopentadecenone, and 1-naphthol. For yields of enones, see Table I.

(*E*)-2-Heptenal (15). $PhSeCl_3$ (1.0 g, 3.8 mmol) and heptanal (0.87 g, 7.6 mmol) were stirred in dry ether (5 mL) at ambient temperature for 1.5 h. After dilution of the resulting pale yellow solution with $CHCl_3$ (20 mL) and addition of SO_2Cl_2 (0.51 g, 3.8 mmol), the reaction mixture was transferred to a separatory funnel containing $NaHCO_3$ (1.28 g, 15.2 mmol) dissolved in water (20 mL). Workup according to the typical elimination procedure and column chromatography afforded 0.36 g (84%) of (*E*)-2-heptenal.[23]

Hydrocinnamic aldehyde was similarly converted to cinnamic aldehyde (84% yield), but in this case, the enal could never be isolated in pure form.

Ethyl (*E*)-2-Heptenoate (16). To a solution of ethyl 2-(phenylselenenyl)heptanoate (**17a**)[24] (0.50 g, 1.6 mmol) in 20 mL of $CHCl_3$ was added SO_2Cl_2 (0.22 g, 1.6 mmol). The reaction mixture was then transferred to a separatory funnel and shaken with aqueous $NaHCO_3$ (4 equiv) according to the typical elimination procedure. Usual workup including Kugelrohr distillation yielded ethyl (*E*)-2-heptenoate (0.19 g, 76%).[25]

(3-Chloro-1-oxo-2-cyclohexyl)phenylselenium Dichloride (18a). $PhSeCl_3$ (1.0 g, 3.8 mmol) and 2-cyclohexenone (0.55 g, 5.7 mmol) were stirred in dry ether (5 mL) at 0 °C for 0.5 h. At this point, hexane (35 mL) was added to the light yellow homogeneous solution to cause precipitation of compound **18a** (0.94 g, 69%). Addition of SO_2Cl_2 (0.15 g, 1.1 mmol) to the mother liquor caused precipitation of an additional amount (0.29 g, 21%) of compound **18a**: mp 72–74 °C dec; ^1H NMR 1.80–2.85 (several peaks, 6 H), 5.11 (m, 1 H), 5.49 (d, 1 H, J = 7.5 Hz), 7.47–7.57 (several peaks, 3 H), 8.28 (m, 2 H). No satisfactory elemental analysis could be obtained due to the instability of the material.

3-Chloro-2-(phenylselenenyl)cyclohexanone (18b). PhSeCl (1.0 g, 5.2 mmol) and 2-cyclohexenone (0.50 g, 5.2 mmol) were stirred in dry ether (10 mL) at 0 °C for 2 h. Toward the end of this period, a white precipitate had separated out. After addition of hexane (30 mL) and final precipitation in a freezer, 1.25 g (83%) of compound **18b** was isolated as a very unstable material. Recrystallization from CH_2Cl_2/hexane yielded glittering prisms, mp 71–73 °C dec. However, the material decomposed to an oil within 12 h. IR: 1701 cm^{-1}. ^1H NMR: 1.98 (m, 1 H), 2.07 (m, 1 H), 2.26–2.41 (several peaks, 3 H), 2.92 (m, 1 H), 3.88 (ddd, 1 H, J = 1.9, 1.9, and 2.6 Hz), 4.84 (m, 1 H), 7.29–7.34 (several peaks, 3 H), 7.56 (m, 2 H). Compound **18b** was quantitatively (by NMR) converted to compound **18a** by treatment with a stoichiometric amount of SO_2Cl_2.

2-(Phenylselenenyl)-2-cyclohexenone (20). Compound **18b** (0.2 g, 0.73 mmol) was stirred in $CHCl_3$ (5 mL) with pyridine (0.12 g, 1.5 mmol) for 48 h. After chromatography, 0.17 g (93%) of compound **20** was isolated. The material was compared with an authentic sample.[8]

(3-Chloro-1-oxo-2-cyclopentyl)phenylselenium dichloride (21) was obtained in 73% yield by a procedure analogous with the preparation of compound **18a**: ^1H NMR 2.43–3.00 (several peaks, 4 H), 5.08 (m, 1 H), 5.23 (m, 1 H), 7.54–7.60 (several peaks, 3 H), 8.17 (m, 2 H).

***erythro*-(3-Chloro-4-oxo-4-phenyl-2-butyl)phenylselenium Dichloride (23).** $PhSeCl_3$ (1.0 g, 3.8 mmol) and (*E*)-1-phenyl-2-buten-1-one (0.60 g, 4.1 mmol) were stirred at 0 °C in dry ether (5 mL) for 2.5 h. During this period, the insoluble selenium compound gradually disappeared and a white precipitate was formed. After addition of 0.20 g of enone to remove the last traces of $PhSeCl_3$, hexane was added after 30 min to give, after final crystallization in the freezer, 1.26 g (81%) of compound **23**: mp 74–75 °C; ^1H NMR 1.90 (d, 3 H), 5.11 (m, 1 H), 6.28 (d, 1 H, J = 7.0 Hz), 7.49–7.58 (several peaks, 6 H), 8.09–8.18 (several peaks, 4 H).

(*Z*)-2-Chloro-1-phenyl-2-buten-1-one (24) was obtained in 89% yield from compound **23** after hydrolytic selenoxide elimination according to the typical procedure: mp 70 °C; ^1H NMR 2.05 (d, 3 H), 6.77 (q, 1 H), 7.41–7.56 (several peaks, 3 H), 7.69 (m, 2 H). The assigned stereochemistry was confirmed by a NOE experiment. Upon saturation of the methine proton at 6.77 ppm, the intensity of the aromatic ortho protons was increased by 3.8%. On the other hand, saturation of the methyl group at 2.05 ppm did not cause any intensity increase in the aromatic region. Compound **24** has previously been reported with undefined stereochemistry (mp 64 °C)[26] and with nonconfirmed *E* stereochemistry (mp 70 °C).[27]

***erythro*-(3-Chloro-1-oxo-1-phenyl-2-butyl)phenylselenium Dichloride (25).** PhSeCl (0.13 g, 0.68 mmol) and (*E*)-1-phenyl-2-buten-1-one (0.10 g, 0.68 mmol) were stirred in dry ether (5 mL) overnight. After dilution of the yellowish solution with hexane and addition of SO_2Cl_2 (0.10 g, 0.74 mmol), 0.20 g (72%) of compound **25** was isolated: mp 71–73 °C dec; ^1H NMR 1.84 (d, 3 H), 5.27 (m, 1 H), 6.28 (d, 1 H, J = 10.2 Hz), 7.29–7.59 (several peaks, 6 H), 7.97 (m, 2 H), 8.18 (m, 2 H).

$PhSeCl_3$ and 1-phenyl-2-propen-1-one were allowed to react by following the procedure for compound **23** (no extra enone was added) to give a 75:25 mixture of (2-chloro-3-oxo-3-phenylpropyl)phenylselenium dichloride (**27a**) and (3-chloro-1-oxo-1-phenyl-2-propyl)phenylselenium dichloride (**28a**), in 76% total yield. **27a**: ^1H NMR 4.79 (m, 2 H), 6.28 (m, 1 H), 7.50–7.67 (several peaks, 6 H), 8.00–8.16 (several peaks, 4 H). **28a**: ^1H NMR 4.34 (d, 2 H), 6.26 (t, 1 H), 7.50–7.60 (several peaks, 6 H), 8.08–8.19 (several peaks, 4 H).

Hydrolytic selenoxide elimination of the mixture **27a**/**28a** according to the typical procedure afforded a 4:1 mixture (81% yield) of 2-chloro-1-phenyl-2-propen-1-one (**29**) and (*E*)-3-chloro-1-phenyl-2-propen-1-one (**30**). Compound **30** was compared with an authentic sample.[28]

PhSeCl and 1-phenyl-2-propen-1-one were allowed to react (equimolar amounts) in an NMR tube ($CDCl_3$). After 18 h, a 1:1 mixture of 2-chloro-1-phenyl-3-(phenylselenenyl)-1-propanone (**27b**) and 3-chloro-1-phenyl-2-(phenylselenenyl)-1-propanone (**28b**) was present according to ^1H NMR analysis (SO_2Cl_2 chlorination yielded compounds **27a** and **28a**, respectively). **27b**: ^1H NMR 3.32 (dd, 1 H, J = 4.6 and 12.5 Hz), 3.71 (dd, 1 H, J = 10.4 and 12.4 Hz), 5.25 (dd, 1 H), 7.25–7.61 (several peaks, 8 H), 7.95 (m, 2 H). **28b**: ^1H NMR 3.93 (dd, 1 H, J = 4.5 and 10.7 Hz), 4.21 (dd, 1 H, J = 10.6 and 10.7 Hz), 4.79 (dd, 1 H), 7.26–7.60 (several peaks, 8 H), 7.95 (m, 2 H).

When the addition reaction was performed in dry ether, a 17:83 mixture of compounds **27b** and **28b** was obtained. This isomeric ratio remained unchanged after 24 h in $CDCl_3$ solution.

PhSeCl as a Chlorinating Agent. PhSeCl (2.0 g, 10.4 mmol) and cycloheptanone (1.3 g, 11.6 mmol) were stirred in ether (15 mL) at 0 °C for 1.5 h. After addition of hexane (10 mL) and cooling, 0.79 g (67%) of compound **1c** was isolated. Evaporation of the mother liquor and chromatography yielded 0.72 g (26%) of 2-(phenylselenenyl)cycloheptanone (**31**).[6]

Treatment of selenide **31** with a 2-fold excess of PhSeCl in ether at 0 °C caused separation of compound **1c** (79% yield).

The equilibrium concentrations according to eq 5 were determined by ^1H NMR spectroscopy in $CDCl_3$. Appropriate mixtures of either **31**/PhSeCl or **1c**/PhSeSePh contained 40% of compound **1c** and 60% of selenide **31** after 1 h at ambient temperature.

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